1982

Chemistry of 19-electron dinitrosyl complexes of tungsten and secondary carbene derivatives of iron

Siu-Yeung Yu
Iowa State University

Recommended Citation

Yu, Siu-Yeung, "Chemistry of 19-electron dinitrosyl complexes of tungsten and secondary carbene derivatives of iron " (1982). *Retrospective Theses and Dissertations*. 8400.
https://lib.dr.iastate.edu/rtd/8400

INFORMATION TO USERS

This reproduction was made from a copy of a document sent to us for microfilming. While the most advanced technology has been used to photograph and reproduce this document, the quality of the reproduction is heavily dependent upon the quality of the material submitted.

The following explanation of techniques is provided to help clarify markings or notations which may appear on this reproduction.

1. The sign or "target" for pages apparently lacking from the document photographed is "Missing Page(s)". If it was possible to obtain the missing page(s) or section, they are spliced into the film along with adjacent pages. This may have necessitated cutting through an image and duplicating adjacent pages to assure complete continuity.
2. When an image on the film is obliterated with a round black mark, it is an indication of either blurred copy because of movement during exposure, duplicate copy, or copyrighted materials that should not have been filmed. For blurred pages, a good image of the page can be found in the adjacent frame. If copyrighted materials were deleted, a target note will appear listing the pages in the adjacent frame.
3. When a map, drawing or chart, etc., is part of the material being photographed, a definite method of "sectioning" the material has been followed. It is customary to begin filming at the upper left hand corner of a large sheet and to continue from left to right in equal sections with small overlaps. If necessary, sectioning is continued again—beginning below the first row and continuing on until complete.
4. For illustrations that cannot be satisfactorily reproduced by xerographic means, photographic prints can be purchased at additional cost and inserted into your xerographic copy. These prints are available upon request from the Dissertations Customer Services Department.
5. Some pages in any document may have indistinct print. In all cases the best available copy has been filmed.

University
Microfilms
International

300 N. Zeeb Road
Ann Arbor, MI 48106

8307803

Yu, Siu-Yeung

CHEMISTRY OF 19-ELECTRON DINITROSYL COMPLEXES OF TUNGSTEN AND SECONDARY CARBENE DERIVATIVES OF IRON

Iowa State University PH.D. 1982

University
Microfilms
International 300 N. Zeeb Road, Ann Arbor, MI 48106

Chemistry of 19-electron dinitrosyl complexes of tungsten and secondary carbene derivatives of iron

by

Siu-Yeung Yu

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of the
Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Department: Chemistry
Major: Chemistry
(Inorganic-Organic)

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

For the Major Department

Signature was redacted for privacy.

For the Graduate College

Iowa State University
Ames, Iowa

1982

TABLE OF CONTENTS

Page

DEDICATION iv

SYMBOLS AND ABBREVIATIONS v

GENERAL INTRODUCTION 1

SECTION I. SYNTHESIS, STRUCTURE AND REACTIONS OF 19-ELECTRON $(\eta^5\text{-}C_5H_5)W(NO)_2(PR_3)$ RADICALS 7

INTRODUCTION 8

EXPERIMENTAL 10

RESULTS AND DISCUSSION 17

REFERENCES 33

APPENDIX 1. FINAL POSITIONAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS FOR $Cp(NO)_2WP(OPh)_3$ 35

APPENDIX 2. FINAL THERMAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS FOR $Cp(NO)_2WP(OPh)_3$ 38

APPENDIX 3. STRUCTURAL FACTORS FOR $Cp(NO)_2WP(OPh)_3$ 40

SECTION II. THE CHEMISTRY OF THIOMETHOXYL AND AMINO SECONDARY CARBENE COMPLEXES OF IRON 48

INTRODUCTION 49

EXPERIMENTAL 67

RESULTS AND DISCUSSION 104

REFERENCES 199

Page

APPENDIX 1. FINAL POSITIONAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS FOR $\{Cp(CO)_2Fe[CH(SMe)P(OCH_2)_3CMe]\}PF_6$ 207

APPENDIX 2. THERMAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS FOR $\{Cp(CO)_2Fe[CH(SMe)P(OCH_2)_3CMe]\}PF_6$ 210

APPENDIX 3. STRUCTURAL FACTORS FOR $\{Cp(CO)_2Fe[CH(SMe)P(OCH_2)_3CMe]\}PF_6$ 212

SUMMARY 219

ADDITIONAL LITERATURE CITED 224

ACKNOWLEDGMENTS 226

DEDICATION

To my mother and father

SYMBOLS AND ABBREVIATIONS

acac	acetylacetonato ligand
Bu	butyl
br	broad
Cp	η^5-cyclopentadienyl
Cy	cyclohexyl
d	doublet
Dabco	1,4 diazabicyclo [2,2,2] octane
dppe	1,2 bis(diphenylphosphino) ethane
Eqn.	equation or reaction
eqv.	equivalent
Et	ethyl
h	heptet
L	donor ligand
M	metal atom or complex
m	multiplet
Me	methyl
Ph	phenyl
PPN^+	$[(Ph_3P)_2N]^+$
Pr	propyl
q	quartet
Pyr	pyridine
R	organic substituent
t	triplet

THF	tetrahydrofuran
TMS	tetramethylsilane
TPP	meso-tetraphenylporphyrin
ν	infrared stretching mode

GENERAL INTRODUCTION

Nitrosyl Complexes

Transition metal nitrosyl complexes have been known for years[1], although they have attracted less attention than metal carbonyl complexes. Nevertheless, hundreds of publications concerning nitrosyl compounds have been cited.

The bonding of an NO ligand to a metal is similar to that of CO; the sp hybridized lone electron pair on the nitrogen is bound to a metal in a σ fashion while the π^* orbitals of the NO accept electron density from the metal d orbitals via a π interaction. The π-bonding effect strengthens the M-N bond and weakens the N-O bond; the extent of this effect depends upon the metal and its auxiliary ligands. By and large, the NO ligand is regarded as being a better π acid than CO.

The bonding modes for metal coordinated terminal NO ligands are believed to be diverse, including those in which the NO is a one or three electron donor ligand. As a single electron donor ligand, the unpaired electron on nitrogen is bonded to the metal forming a bent M-N-O angle (Figure 1-A). The M-N-O angle in these complexes is found to be in the range of 120-140° by X-ray crystallographic studies.[2] The ν(NO) frequencies for bent NO complexes fall in the 1525-1690 cm^{-1} range. As a three-electron donor ligand, the lone pair and unpaired electrons are all involved in bonding with the metal (Figure 1-B). This type of bonding often gives M-N-O angles which are close to linear

(170-175)[2].

In recent years, the chemistry of the coordinated NO ligand has been explored[3]. Based on studies of reactions between NO complexes and nucleophiles, it was suggested that mononitrosyl metal complexes having ν(NO) values greater than 1886 cm^{-1} or f(NO) higher than 13.8 mdyn Å^{-1} are susceptible to nucleophilic attack at the NO nitrogen atom. Though less predictable, low ν(NO) wavenumber complexes, below 1806 but as high as 1852 cm^{-1}, are liable to attack by electrophiles at the nitrogen.

A B

Figure 1. Nitrosyl bonding modes

Carbene Complex

One of the most intriguing developments in transition-metal chemistry is the discovery of metal carbene complexes. In 1964, Fischer and Massböl[4] successfully synthesized a stable carbene complex of tungsten, $(CO)_5W[C(OCH_3)Ph]$. Since that initial discovery, hundreds of carbene complexes have been characterized, and their chemistry has proven to be rich and varied.[5-6] The popularity of transition-metal carbene chemistry was partially sparked by interest in a number of metal-catalyzed organic reactions, olefin metathesis,[7-8] Fischer-Tropsch synthesis[9-11] and cyclopropanation,[12-13] in which a metal carbene is postulated as a key intermediate. Potential industrial applications of these catalytic reactions have stimulated in recent years much interest in the roles which metal carbenes play in these reactions.

An isolated carbene group is frequently depicted as :CXY. When it is incorporated into an organometallic compound by bonding to the metal, the resulting complex is written as LnM(:CXY), where M is the metal and Ln represents the auxiliary ligands bonded to the metal. In general, the structure of a transition-metal carbene complex is planar where X, Y and M are approximately coplanar about the carbene carbon, C_{carb} (Figure 2). However, the geometry of the carbene ligand relative to Ln varies considerably; for example, in $Cp(CO)_2FeCH_2^+$, the carbene can be in an axial (A), equatorial (B) or somewhere between the two positions with respect to Ln (Figure 3).

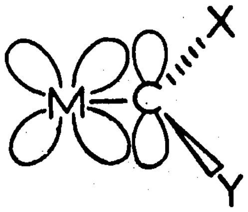


Figure 2. Bonding scheme for carbene ligand

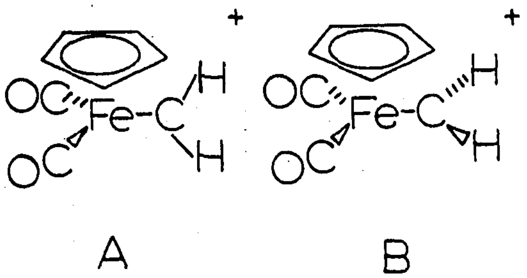


Figure 3. The possible configurations for $Cp(CO)_2FeCH_2^+$

A theoretical calculation[14] suggests A is more favorable than B due to better orbital overlap. The same conclusion is also reached for $Cp(PH_3)_2FeCH_2^+$.[15] However, in the case of $Cp(CO)NOFeCH_2^{2+}$,[16] the carbene ligand adopts a geometry almost coincident with the metal-nitrosyl bond (Figure 4).

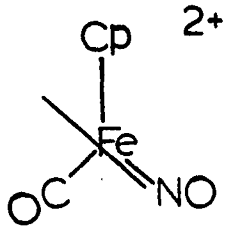


Figure 4. The predicted geometry for $Cp(CO)(NO)FeCH_2^{2+}$

The bonding of a carbene ligand in organometallic compounds may be represented by the three canonical forms illustrated in Figure 5.

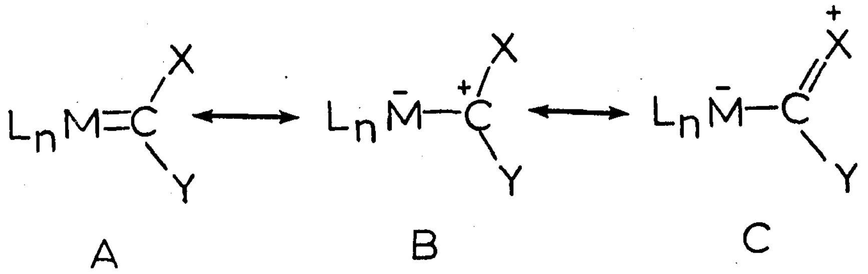


Figure 5. Resonance structures for carbene complexes

The C_{carb} is bonded to the metal by donating a pair of electrons localized in an sp^2 hybridized orbital into a vacant metal orbital; at the same time the empty C_{carb} Pz orbital which is perpendicular to the M-X-Y plane accepts d-electron density from the metal and from the lone pair P-electrons of the adjacent X and Y groups. The extent of d-P and p-p π bonding is primarily dependent upon the nature of the X and Y groups. When either X or Y is a heteroatom (N, O or S) with lone pairs available for π backbonding to the C_{carb}, some double-bond character between C_{carb} and X, Y is expected as represented by resonance structure C. When X and Y are hydrogen atoms or alkyl groups, only d-P π backbonding from the metal is possible and is best represented by resonance structure A. Finally, when X and Y are either aryl or alkene groups, carbene bonding is most accurately described by a combination of A and C.

Empirically, carbene complexes with structures more closely resembling C are more stable than those with structure A. Indeed, most well-characterized and stable carbene complexes reported are p-π-electron stabilized by X or Y groups containing N, O or S. In contrast, few methylene complexes, MCH_2, have been cited in the literature and they tend to be very unstable.[17-21] In general, the stability of a series of homologous complexes decreases in the order: $NR_2 > SR \geq SeR > OR > aryl > alkyl > H$.[5,22]

With few exceptions, the carbene ligand reacts as an electrophilic center and is most accurately represented by resonance form B. That is, an incoming nucelophile preferably attacks the empty Pz of the C_{carb}; then, the C_{carb} rehybridizes to an sp^3 geometry affording the metal σ-alkyl complex.

Explanation of Dissertation Format

The material in this dissertation is organized in two sections. The numbering of literature references, figures, equations, tables, schemes and appendices are applicable only to those contained within that section, and the references are listed at the end of the text of each section. Those literature references cited in General Introduction are summarized in Additional Literature Cited.

SECTION I. SYNTHESIS, STRUCTURE AND REACTIONS OF 19-ELECTRON $(\eta^5-C_5H_5)W(NO)_2(PR_3)$ RADICALS

INTRODUCTION

There has been much interest in the reactions of metal carbonyl ligands with nucleophiles such as amines and alkoxides,[1] e.g.,

$$M\text{-}C\equiv O^{+} + OR^{-} \longrightarrow M\text{-}C\begin{matrix}{/\!\!/}O \\ \diagdown OR\end{matrix} \qquad (1)$$

to give carbamoyl and alkoxycarbonyl complexes. While much is known about transition metal nitrosyl complexes,[2-6] there are in contrast to the metal carbonyl situation, still relatively few examples of alkoxide attack at nitrosyl ligands to yield alkyl nitrite complexes,[7-9]

$$M\text{-}N\equiv O^{+} + OR^{-} \longrightarrow M\text{-}N\begin{matrix}{/\!\!/}O \\ \diagdown OR\end{matrix} \qquad (2)$$

Such reactions appear to occur only in electron-poor complexes in which the $\nu(NO)$ frequency is greater than $1850cm^{-1}$.[8]

Although the $\nu(CO)$ frequency $(2116cm^{-1})$[10] of $CpW(NO)_2(CO)^+$ indicates that this complex is sufficiently electron-poor to promote nucleophilic attack at the carbonyl group, its reactions with alkoxides and amines only yielded products resulting from the displacement of the CO group. This result, together with others,[11] suggests that high $\nu(CO)$ values not only indicate enhanced CO susceptibility to nucleophilic attack but also weakened CO bonding to the metal which makes CO displacement more likely.

To probe the possibility that nucleophiles would attack the NO groups in this electron-poor system, we examined the reactions of the phosphite-substituted complexes, $CpW(NO)_2[P(OR)_3]^+$,[10] where Cp = η^5-C_5H_5. In reactions with alkoxides, the surprising result was that no products resulting from nucleophilic attack on the NO were identified, but instead only one-electron reduction products $CpW(NO)_2[P(OR)_3]$ were isolated.

EXPERIMENTAL

General Procedure

The complexes $[CpW(NO)_2(P(OR)_3]PF_6$, and $[CpW(NO)_2(PPh_3)]PF_6$ were prepared as described in the literature.[10] The supporting electrolyte $[(\underline{n}\text{-Bu})_4N]BF_4$ for the electrochemical studies was prepared by mixing $[(\underline{n}\text{-Bu})_4N]Br$ and 48% aqueous HBF_4 in water, collecting the precipitate by filtration, recrystallizing it twice from acetone-diethyl ether, and drying it in vacuum. Reagent-grade CH_2Cl_2 was stored over molecular sieves. Other chemicals were purchased from commercial sources.

ESR spectra of solutions were obtained on a Varian E-3 spectrometer operating at 9.52 GHz. The solutions, prepared with acetone deaerated by freeze-thawing, were studied in flat quartz cells at -28°C under argon. ESR spectra of solids were measured on a Bruker ER 220D SR at about 9.5 GHz at ambient temperature. Infrared spectra were recorded on a Perkin-Elmer Model 281 spectrophotometer.

Hydrocarbon products were analyzed on a Varian 3700 FID gas chromatograph equipped with a 1/8" x 6' 5% OV 101 column. Other organic products were analyzed on a Varian 1700 TCD gas chromatograph using a 1/4" x 15' 10% DC550 column. Electrochemical experiments were carried out on a Princeton Applied Research model 173 potentiostat and model 175 universal programmer. Cyclic voltammograms were obtained using a platinum disc working electrode, a platinum wire counter electrode, and a saturated (NaCl) calomel (SSCE) reference electrode. The solutions contained approximately 1 x 10^{-3}M complex and 0.1 M $[(\underline{n}\text{-Bu})_4N]BF_4$ supporting electrolyte; the scan rate was 20 mV/s.

Synthesis and Reactions

Reduction and oxidization

Synthesis of $CpW(NO)_2(L)$ by NaOR reduction A 0.035 g (0.66 mmol) sample of NaOMe was suspended in 5 mL of CH_2Cl_2 under an N_2 atmosphere. Subsequently, 0.10 g (0.13 mmol) of $[CpW(NO)_2(P(OPh)_3)]PF_6$ was added to the solution. The green mixture was stirred for 30 min. at room temperature. The solution had then become red-brown and was evaporated at 25°C under vacuum; the residue was extracted twice with 15 mL of diethyl ether. The solution was filtered through Celite under nitrogen pressure. Pentane (10 mL) was added to the purple ether solution which was then chilled to -20°C in a CCl_4-dry ice bath overnight. Analytically pure purple crystals of $CpW(NO)_2(P(OPh)_3)$ were obtained (0.025 g, 31%). Anal. Calcd: C, 44.62; H, 3.23; N, 4.52. Found: C, 44.57; H, 3.29; N, 4.58.

The other complexes $CpW(NO)_2(PR_3)$ were prepared by the same method in similar yields, and were characterized by their IR spectra (Table 2). The $CpW(NO)_2(PR_3)$ complexes are very sensitive to air and should be stored under argon at -20°C.

A procedure similar to that used in the NaOMe reaction was also used for the other alkoxide ($NaOCH_2Ph$, NaOEt, $NaOCMe_3$ and $NaOCH(CH_3)_2$) reduction reactions.

Reduction of $[CpW(NO)_2(L)]PF_6$ with $N_2H_4 \cdot H_2O$ A 0.10 g (0.13 mmol) sample of $[CpW(NO)_2(P(OPh)_3)]PF_6$ was dissolved in 5 mL of CH_2Cl_2 under an N_2 atmosphere. Subsequently, 17.5 μL(0.66 mmol) of $N_2H_4 \cdot H_2O$ (64% in H_2O) was injected through a rubber septum into the CH_2Cl_2 solution. The greenish solution turned red within 1 min., and the solvent was removed under vacuum. Using the same work-up employed in the previous synthesis, 0.053 g (65%) of IIa was obtained. Complexes IIb and IIc were also obtained in good yields utilizing this method (50-60%).

Reduction of $[CpW(NO)_2(P(OPh)_3)]PF_6$ with NaOH To a suspension of crushed NaOH (0.40 g, 10 mmol) in 5 mL of CH_2Cl_2 under an N_2 atmosphere was added 0.20 g (0.26 mmol) of $[CpW(NO)_2(P(OPh)_3)]PF_6$ and 0.1 mL of degassed water. The mixture was allowed to react at room temperature for 30 min. Following the work-up procedure described for the NaOR reduction, 0.042 g (26%) of $CpW(NO)_2(P(OPh)_3)$ was isolated.

Reduction of $[CpW(NO)_2(P(OPh)_3)]PF_6$ with Zn Zinc dust (0.20 g, 3.1 mmol) was added to a solution of $[CpW(NO)_2(P(OPh)_3)]PF_6$ (0.05 g, 0.07 mmol) in 5 mL of THF. After stirring the mixture at room temperature for 30 min, $CpW(NO)_2(P(OPh)_3)$ was isolated as given in the NaOR reduction procedure in 24% (0.01 g) yield.

Reduction of $[Cp(NO)_2W(P(OPh)_3)]PF_6$ with $PPN[Co(CO)_4]$ $PPN[Co(CO)_4]$(0.05g,0.07 mmol) was added to a solution of $[Cp(NO)_2W(P(OPh)_3]PF_6$ (0.05g,0.07 mmol) in 5 ml THF. A purple solution was obtained instantly. The solvent was distilled into a liquid-N_2 trap and found to contain $Co(CO)_3NO$ (vide infra). The remaining purple solid was extracted with Et_2O to give a mixture of $Cp(NO)_2W(P(OPh)_3)$ and an orange product. The orange product, which could not be separated from the radical was identified by its ^{31}P NMR and IR spectra to be $Cp(NO)(CO)W(P(OPh)_3)$, which was synthesized independently in refluxing toluene solution of $Cp(NO)W(CO)_2$ and $P(OPh)_3$.[12]

IR(CH_2Cl_2) of $Cp(NO)(CO)W(P(OPh)_3)$: 1926(s,ν(CO)),1623(s,ν(NO))

$^{31}P(CDCl_3)$: 154.82(JwP = 716.9)

Reaction of $CpW(NO)_2(P(OPh)_3)$, IIa, with $[Ph_3C]BF_4$ A 0.027 g (0.044 mmol) sample of $CpW(NO)_2(P(OPh)_3)$ was dissolved in 2 mL of CH_2Cl_2 under an N_2 atmosphere, and 0.015 g (0.046 mmol) of $[Ph_3C]BF_4$ was added. The purple solution turned green immediately. The solvent was removed under vacuum, and the green residue was extracted with 6 mL of diethyl ether. The extract was filtered through a glass fiber filter, and the solvent was slowly evaporated from the filtrate in air; a white precipitate was obtained. The solid was washed with acetone and dried under vacuum, leaving 0.002 g (13%) of $Ph_3COOCPh_3$ which was identified by its melting point[13] and mass spectrum. The green residue was redissolved in CH_2Cl_2 and was identified as Ia (88%) by the positions and intensities of its ν(NO) IR absorptions.

Reaction of IIa with HSO_3CF_3 A 0.03 g (0.05 mmol) sample of IIa was dissolved in 2 mL of CH_2Cl_2 under N_2, and 4.4 μL (0.071 mmol) of HSO_3CF_3 was injected into the solution. A green solution was obtained immediately. It was diluted further with an additional 4 mL of CH_2Cl_2; Ia (75%) was identified in the infrared spectrum of the solution. The same procedure was employed in the reaction of $CpW(NO)_2(P(OPh)_3)$ with CH_3SO_3F. The CH_3SO_3F reaction was complete within 1 min., and Ia (70%) was identified in solution by IR; the gas phase analyzed by GC contained ethane.

Reaction of IIa with $AgBF_4$ A 0.03 g (0.05 mmol) sample of IIa was dissolved in 2 mL of CH_2Cl_2 under N_2, and 0.01 g (0.05 mmol) of $AgBF_4$ was added to the solution. The purple solution became green within 1 min. The resulting solution was analyzed by IR and contained Ia(80%).

Reaction of IIa with I_2 A 0.03 g (0.05 mmol) sample of IIa was dissolved in 2 mL of CH_2Cl_2 under N_2, and a small crystal of I_2 was added to the solution. The purple solution gradually turned green in a period of 15 min. Ia and $CpW(NO)_2I$ were identified in the reaction mixture by their infrared spectra. Stirring the solution for an additional 15 min resulted in the disappearance of 1a and the increase of $CpW(NO)_2I$ to about 75%.

X-Ray Data

Collection and refinement

Crystal data $CpW(NO)_2(P(OPh)_3)$, MW 618.58, monoclinic, $P2_1/n$, a = 9.810(4), b = 14.450(7), c = 15.45(1) Å, $\beta = 91.04(5)^\circ$, V = 2189.7 $Å^3$, ρ_{calcd} = 1.876 g/cm^3, Z = 4 and μ = 56.9 cm^{-1}.

Data acquisition Automated Syntex $P2_1$ four-circle diffractometer; Mo K_α (λ = 0.71069 Å); ω-scan; 4170 reflections measured in almost 4 octants; $2\Theta \leq 50^\circ$; Lorentz-polarization, absorption[14] and decomposition corrections applied; 2581 reflections with $I \geq 3\sigma_I$ after averaging; agreement between equivalent reflections is 4%.

The title compound yielded purple plate-like crystals which were readily indexed using 12 independent reflections and an automatic indexing procedure[15]. Appreciable (approximately 10%) and accelerating decay was noted approximately midway through data collection; therefore, a second crystal was mounted and used for the latter part of data collection and the two data sets scaled to a common basis. The standard heavy atom technique was used for structural solution, and a combination of block matrix-full matrix least-squares refinement[16] of all non-hydrogen atoms converged to conventional and weighted residuals of R = 0.061 and R_w = 0.067, respectively. The scattering factors[17] were modified for anomalous dispersion effects[18] and hydrogens were included but not refined. The bond distances, angles (Table 1); atom positions (Appendix 1); thermal parameters (Appendix 2) and structural factors (Appendix 3) are listed.

RESULTS AND DISCUSSION

Synthesis

Radical

Reduction of $CpW(NO)_2(L)^+$ If the NO groups are each considered 3-electron donors, the $CpW(NO)_2(L)^+$ complexes are 18-electron systems. They react with a variety of reducing agents to give (Eqn. 3) the 19-electron complexes $CpW(NO)_2(L)$.

$$\underset{\text{Ia-c}}{CpW(NO)_2(L)^+} \xrightarrow[\text{agent}]{\text{reducing}} \underset{\text{IIa-c}}{CpW(NO)_2(L)} \qquad (3)$$

L = $P(OPh)_3$(Ia), PPh_3(Ib), $P(OMe)_3$(Ic)

reducing agents = OR^-, OH^-, $N_2H_4 \cdot H_2O$, Zn

$$CpW(NO)_2(P(OPh)_3)^+ + Co(CO)_4^- \longrightarrow CpW(NO)_2(P(OPh)_3) + CpW(NO)CO(P(OPh)_3) + Co(NO)(CO)_3 \qquad (4)$$

The reaction of $CpW(NO)_2(P(OPh)_3)^+$, Ia, with excess NaOMe in CH_2Cl_2 produces a purple solution from which an air- and heat-sensitive purple compound (IIa) is isolated in 31% yield. In air, IIa decomposes in solution within 30 minutes. Even in the solid state under argon at -20°C, it shows evidence of decomposition within

15 days

The same purple compound is isolated from reactions of Ia with $PhCH_2O^-$, i-PrO$^-$, t-BuO$^-$, EtO$^-$, and OH$^-$. The mechanism of these reductions is not known, but the alkoxide may act as a one-electron donor giving RO· as the initial product. Subsequently, the β-H or alkyl group of RO· could be lost or abstracted by another RO· to give the corresponding aldehyde or ketone and alcohol[19]. In support of this possibility is the GC detection of PhCHO and $PhCH_2OH$ as products of the reaction of Ia with $PhCH_2O^-$, The complexes, $CpW(NO)_2(PPh_3)^+$, Ib, and $CpW(NO)_2(P(OMe)_3)^+$, Ic, are also reduced to give similar yields of IIb and IIc, but these products are much less stable thermally and to air than IIa. Due to their instability, they were only characterized by their spectra and electrochemistry.

A still better reducing agent is hydrazine hydrate, $N_2H_4 \cdot H_2O$, which converts Ia to IIa in 65% yield. This is also the more effective reducing agent for the preparations of IIb and IIc. Powdered Zn reduces Ia, but the reaction is much slower (∿ 30 min.) and decomposition of the product IIa greatly reduces the yield. Finally, $PPN(Co(CO)_4)$ also reduces Ia to IIa; though, $Co(CO)_3NO$ and $CpW(NO)(CO)(P(OPh)_3)$ are also produced (Eqn. 4).

Structure of $CpW(NO)_2(P(OPh)_3)$ Although the spectroscopic properties of the $CpW(NO)_2(L)$ compounds are consistent with a mononuclear complex, there was some question whether these 19-electron compounds might be dimers, especially in the solid state.

To examine this possibility, as well as to determine whether the added electron causes the expected linear NO in $CpW(NO)_2(L)^+$ to bend in the neutral complex, an X-ray structural investigation of $CpW(NO)_2(P(OPh)_3)$, IIa, was performed.

As shown in the ORTEP drawing (Fig. 1) of IIa, the complex is clearly mononuclear with a 3-legged piano-stool structure. There are no unusually short distances between molecules which would suggest intermolecular interactions. Bond distances and angles are given in Table 1. Within experimental error, the W-C cyclopentadienyl distances are equal, and the C-C distances in the ring are equal within approximately 3 standard deviations, yet the C_{23}-C_{19} distance (1.46Å) is somewhat longer than the average (1.40Å). Both the W-C and C-C distances of the Cp ring in IIa are comparable to those in the 18-electron complex $CpW(NO)_2Cl$.[20]

If one assumes that the 18-electron $CpW(NO)_2(P(OPh)_3)^+$ complex has a structure very similar to that of structurally characterized $CpW(NO)_2Cl$, then any deviation in the structure of IIa from $CpW(NO)_2Cl$ might be attributed to effects of the extra electron in IIa. The major differences between IIa and $CpW(NO)_2Cl$ occur in the distances and angles associated with the NO ligands; these are shown in Fig. 2. There is much discussion in the literature[2-7,21] about the influence of electron density on M-N-O bond angles in metal nitrosyl complexes. In some systems, additional electron-density provided to the complex causes a linear M-N-O bond to

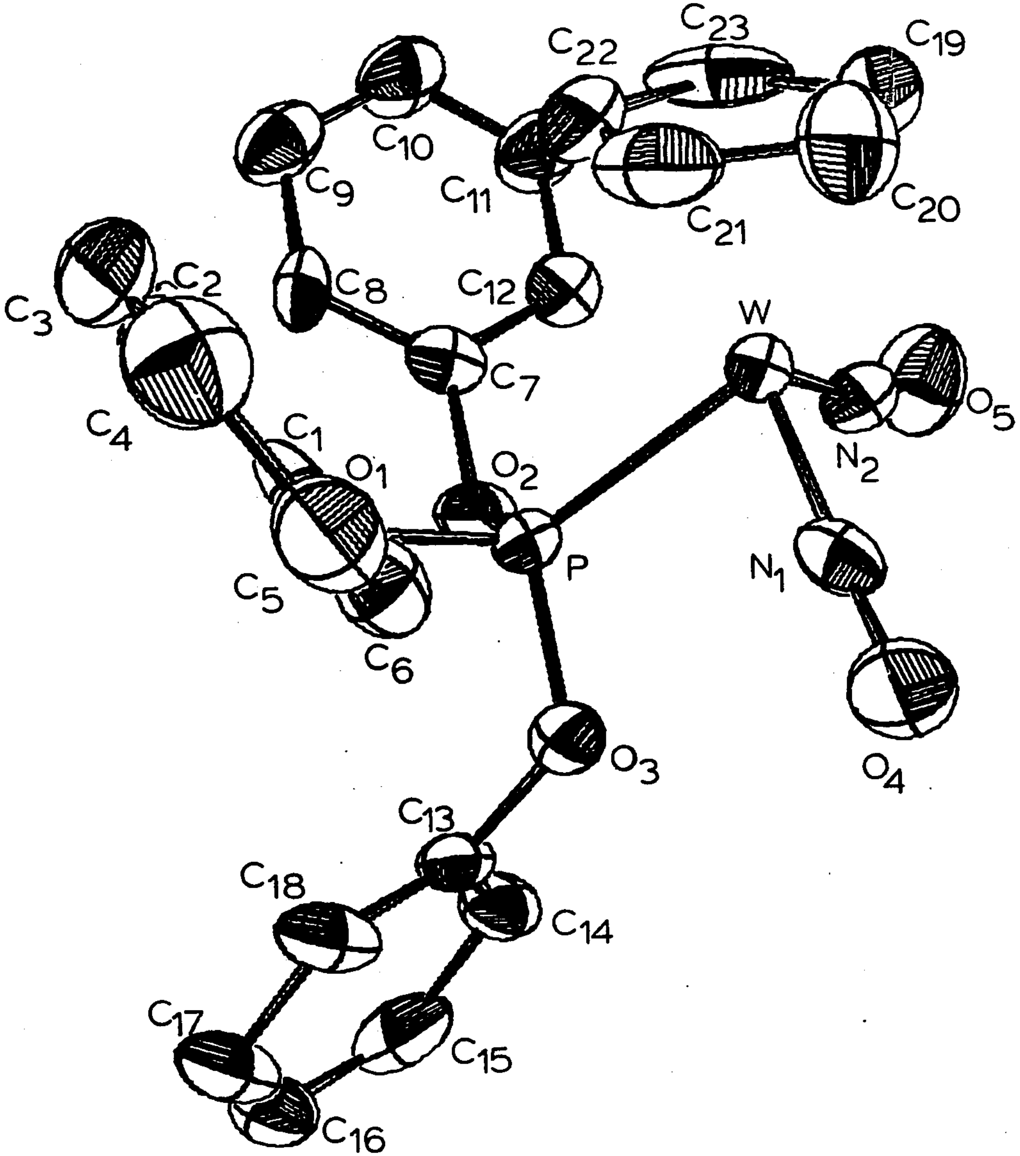


Figure 1. ORTEP Drawing of CpW(NO)$_2$(P(OPh)$_3$), IIa

Table 1. Interatomic distances (Å) and bond angles and their estimated standard deviations (in parentheses) for CpW(NO)$_2$P(OPh)$_3$

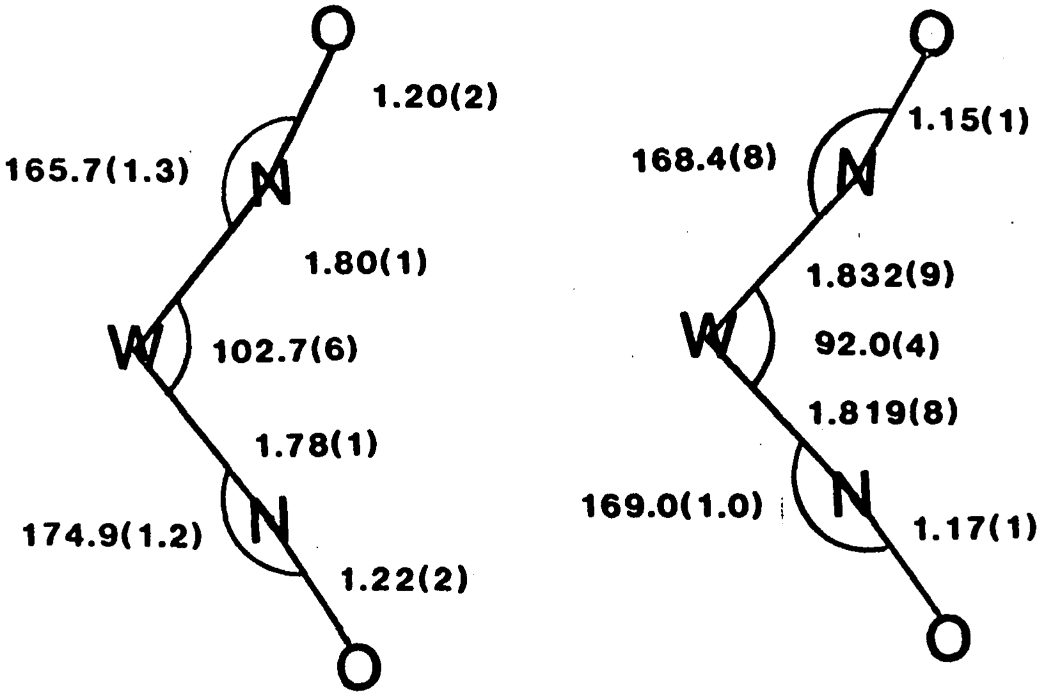
A. Bond distances

W-P	2.386(4)	O2-O7	1.41(1)
W-N1	1.78(1)	O3-C13	1.39(1)
W-N2	1.80(1)	C1-C2	1.39(2)
W-C19	2.30(2)	C2-C3	1.37(3)
W-C20	2.32(2)	C3-C4	1.37(3)
W-C21	2.33(2)	C4-C5	1.39(3)
W-C22	2.34(1)	C5-C6	1.37(2)
W-C23	2.32(2)	C6-C1	1.37(2)
N1-O4	1.22(2)	C7-C8	1.36(2)
N2-O5	1.20(2)	C8-C9	1.39(2)
P-O1	1.58(1)	C9-C10	1.36(2)
P-O2	1.59(1)	C10-C11	1.41(2)
P-O3	1.58(1)	C11-C12	1.41(2)
C19-C20	1.35(3)	C12-C7	1.35(2)
C20-C21	1.38(3)	C13-C14	1.41(2)
C21-C22	1.39(3)	C14-C15	1.46(2)
C22-C23	1.41(2)	C15-C16	1.40(3)
C23-C19	1.46(3)	C16-C17	1.33(3)
O1-C1	1.43(2)	C17-C18	1.43(2)
		C18-C13	1.33(2)

Table 1. continued

B. Bond angles

W-N1-O4	174.9(1.2)	O2-C7-C12	117(1)
W-N2-O5	165.7(1.3)	C7-C8-C9	119(1)
N1-W-N2	102.7(6)	C8-C9-C10	119(1)
P-W-N1	89.0(4)	C9-C10-C11	121(1)
P-W-N2	91.0(5)	C10-C11-C12	117(1)
W-P-O1	119.0(4)	C11-C12-C7	119(1)
W-P-O2	119.4(4)	C12-C7-C8	123(1)
W-P-O3	113.7(4)	O3-C13-C14	114(1)
O1-P-O3	104.0(6)	O3-C13-C18	120(1)
O1-P-O2	98.2(6)	C13-C14-C15	116(1)
O2-P-O3	99.2(6)	C14-C15-C16	117(1)
O1-C1-C6	120(1)	C15-C16-C17	121(1)
O1-C1-C2	117(1)	C16-C17-C18	122(1)
C1-C2-C3	118(1)	C17-C18-C13	116(1)
C2-C3-C4	120(1)	C18-C13-C14	124(1)
C3-C4-C5	118(1)	C19-C20-C21	111(2)
C4-C5-C6	121(1)	C20-C21-C22	105(1)
C5-C6-C1	118(1)	C21-C22-C23	111(1)
C6-C1-C2	121(1)	C22-C23-C19	103(1)
O2-C7-C8	119(1)	C23-C19-C20	108(1)



$CpW(NO)_2(P(OPh)_3)$ $CpW(NO)_2Cl$

Figure 2. Bond distances and angles associated with the NO groups in $CpW(NO)_2(P(OPh)_3)$ and $CpW(NO)_2Cl$

become bent, even up to 120°. As seen in Figure 2, there is little difference in the average W-N-O bond angles between $CpW(NO)_2Cl$ (168.7° average) and $CpW(NO)_2(P(OPh)_3)$ (170.3° average), although there is a greater variation between the two angles in IIa than in $CpW(NO)_2Cl$. Differences appear more evident in the W-N-O distances, although standard deviations are too large to prevent their unequivocal interpretation. In the 19-electron IIa, the W-N distances (1.79 Å average) are shorter than those in $CpW(NO)_2Cl$ (1.825 Å average), while the N-O distances in IIa (1.21 Å average) are longer than in $CpW(NO)_2Cl$ (1.16 Å average). The major difference in structure is the substantially larger N-W-N angle in IIa (102.7°) as compared to that in $CpW(NO)_2Cl$ (92.0°).

These structural differences in the 18- and 19-electron complexes may be readily understood in terms of a recent molecular orbital calculation[22] for complexes of the type, $CpM(NO)_2X$, where M=Cr, W and X=Cl, Br, I. The lowest unoccupied MO (13a'' in Fig. 2 of reference 22) of $CpCr(NO)_2Cl$, which is separated from higher energy MOs and would accept the 19th electron, has 89% NO 2π character and is antibonding between the two NO ligands and antibonding between the N and O atoms of each NO ligand[23]. Thus, occupation of this level would lead to an increase in the N-W-N bond angle and an increase in the N-O bond distances, which are the observed major structural differences between IIa and $CpW(NO)_2Cl$. Although 13a'' is 89% NO 2π character[23], the lengthening of the NO bond distance lowers the energy of the 2π orbital, thereby increasing the W-N π-bonding. This effect is reflected in the shorter W-N bond distance.

Infrared and ESR spectra and electrochemistry of the CpW(NO)$_2$(L) complexes The ν(NO) frequencies in the infrared region of Ia (1788,1712cm^{-1}) are 160-175 cm^{-1} higher than those (1613,1553cm^{-1}) in the 19-electron reduced complex IIa. Similar changes in ν(NO) values in complexes Ib and Ic are also observed (Table 2). These decreases of ν(NO) values upon one-electron reduction are substantially larger than those observed (50cm^{-1}) in the pair Fe(NO)(das)$_2^{+2}$(1760cm^{-1}) and Fe(NO)(das)$_2^{+}$(1710cm^{-1}), which are 17- and 18-electron species, respectively (das=o-phenylenebis dimethylarsine)[24]. Much larger decreases ($\sim$300 cm^{-1}) in ν(NO) are observed upon reduction of 18-electron complexes such as Ru(bipy)$_2$(NO)Cl^{2+} (1940cm^{-1}) to 19-electron Ru(bipy)$_2$(NO)Cl^{+} (1640cm^{-1}).[25,26] These IR and other studies were interpreted to indicate that the additional electron in the 19-electron ruthenium complex is primarily localized on the NO group. In the present CpW(NO)$_2$(L) complexes, the 160-175cm^{-1} shift in ν(NO) suggests that the additional electron is substantially on the two NO ligands, as was also inferred from the X-ray structural results.

ESR spectra of IIa and IIb in acetone solution at -28°C show a ten-line pattern with approximate peak intensities of 1:1:2:2:3:3:2:2:1:1: (Fig. 3). This pattern results from hyperfine

Table 2. IR and ESR data for I and II

Complex	$\nu(NO)^a$, CM^{-1}	EPR data^b
$[CpW(NO)_2(P(OPh)_3)]PF_6$	1788(s), 1712(vs)	
$CpW(NO)_2(P(OPh)_3)$	1613(s), 1553(s)	a_N = 7.0 g, a_P = 5.0 g^c
$[CpW(NO)_2(P(Ph)_3)]PF_6$	1770(vs), 1690(s)	
$CpW(NO)_2(P(Ph)_3)$	1595(s), 1526(vs)	a_N = 7.0 g, a_P = 4.4 g^c
$[CpW(NO)_2(P(OCH_3)_3)]PF_6$	1777(s), 1702(vs)	
$CpW(NO)_2P(OCH_3)_3$	1605(s), 1533(vs)	-^{d}

[a] Solvent is CH_2Cl_2.

[b] Solvent is acetone, temperature is -28°C.

[c] The g value is 2.02, obtained at room temperature in the solid state with DPPH as the internal reference.

[d] Decomposed too rapidly for ESR measurement.

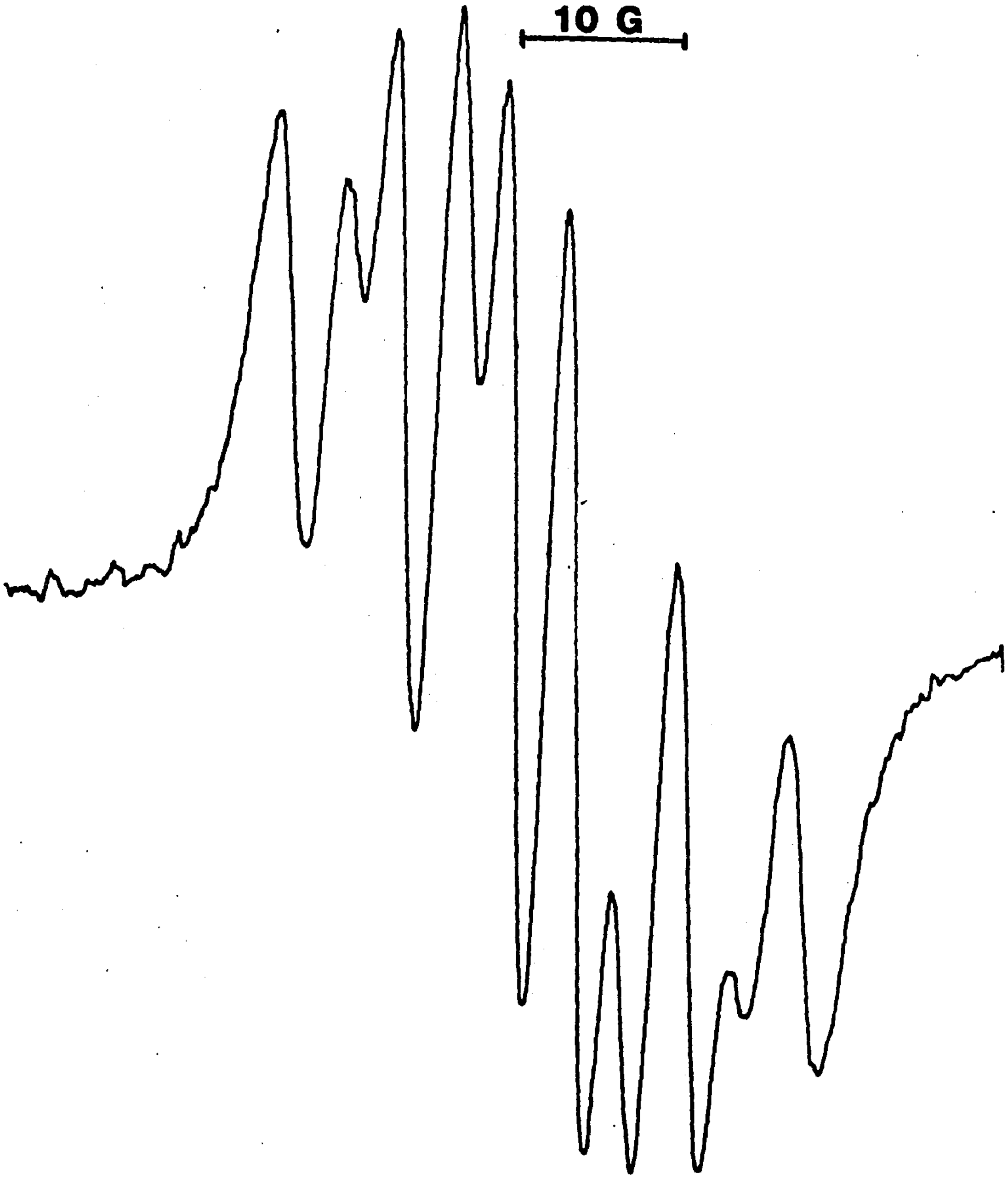


Figure 3. ESR Spectrum of $CpW(NO)_2(PPh_3)$ in acetone at -28°C

Table 3. Reduction potentials for the $[CpW(NO)_2L]PF_6$ complexes[a]

Complexes[b]	$E_{1/2}(1)$,V	$E_{1/2}(2)$,V
$[CpW(NO)_2(P(OPh)_3)]PF_6$	-0.09	-1.58
$[CpW(NO)_2(P(OCH_3)_3)]PF_6$	-0.16	-1.60
$[CpW(NO)_2(P(Ph)_3)]PF_6$	-0.18	-1.68

[a] Carried out in CH_2Cl_2 (0.1 M $[Bu_4N]BF_4$) solution using a scan rate of 20 mV/s. The potentials are measured against a SSCE reference electrode.

[b] Concentrations of the complexes are 1 x 10^{-3}M.

coupling of the unpaired electron with the two equivalent $^{14}N(I=1)$ and $^{31}P(I=1/2)$ nuclei. Coupling constants to ^{14}N are 7.0 g in both IIa and IIb; the coupling constant to ^{31}P is 5.0 g in IIa and 4.4 g in IIb. Both compounds in the solid state have g values of 2.02 (Table 2).

ESR spectra of two other 19-electron dinitrosyl species, $Fe(CO)_2(NO)_2^-$ and $Co(NO)_2(CO)_2$,[27,28] generated in situ by irradiation, were interpreted to indicate that the unpaired electron is largely confined to the NO ligands. It appears therefore that the addition of another electron to an 18-electron dinitrosyl complex occurs predominantly into the NO ligands.

Reduction potentials of the $CpW(NO)_2(L)^+$ complexes in CH_2Cl_2 solution were determined by cyclic voltammetry (Table 3). All complexes undergo reduction in two steps. The first wave is quasi-reversible and occurs at -0.09 to -0.18V. The small potentials for these reductions account for the easy chemical reductions of I to II. The second wave is non-reversible showing no corresponding oxidation peak on the reverse scan (Figure 4). Although the product of the second reduction step is not clear, a possible species is the 20-electron anion $CpW(NO)_2(L)^-$. An attempt to prepare this anion of IIa in THF solution was made by reduction of IIa with 3% sodium-amalgam. This reaction yielded only a clear solution which showed no $\nu(NO)$ absorptions. Both the first and second reduction

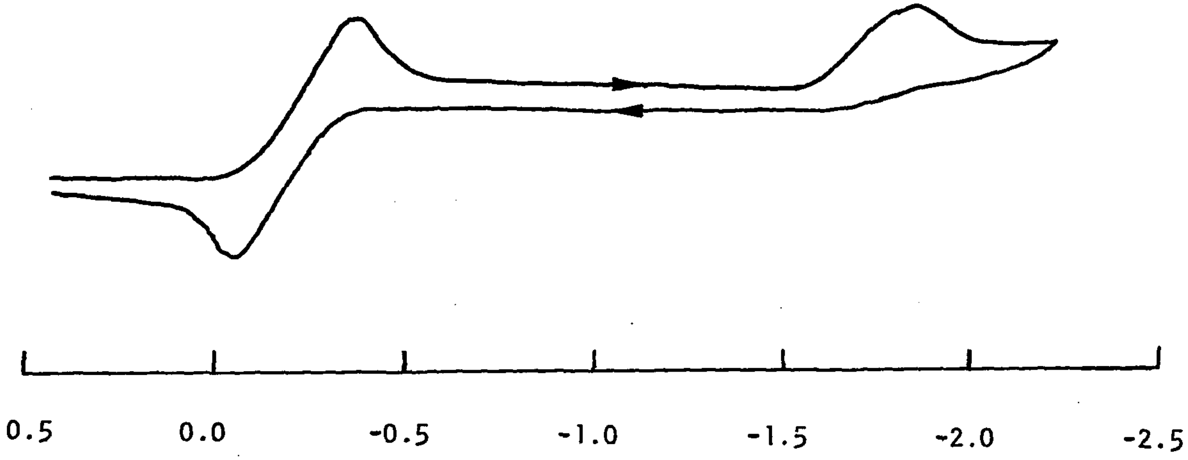
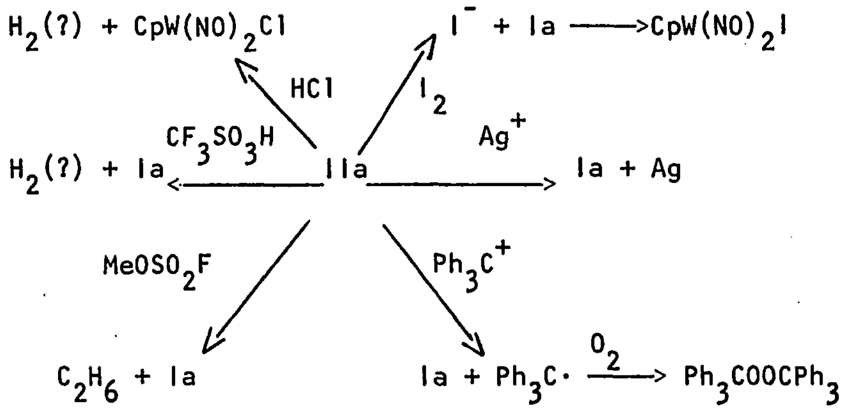


Figure 4. Cyclic voltammogram of $CpW(NO)_2(PPh_3)$ in CH_2Cl_2

potentials become more negative with changes in L in the order: $P(OPh)_3 > P(OMe)_3 > PPh_3$. This is also the order of decreasing Π-acceptor/σ-donor ratios for these ligands, which is consistent with the most strongly electron-withdrawing phosphorus ligands giving the most easily reduced species.

Reactions of $CpW(NO)_2(P(OPh)_3)$ The $CpW(NO)_2(P(OPh)_3)$ complex (IIa) is easily oxidized to the cation $CpW(NO)_2(P(OPh)_3)^+$ (Ia) by a variety of oxidizing agents:



The purple CH_2Cl_2 solution of IIa becomes the characteristic green of Ia within one minute upon treatment with $AgBF_4$. Oxidation of IIa by $Ph_3C^+BF_4^-$ occurs immediately; the organic product, $Ph_3COOCPh_3$, is isolated in 13% yield, presumably formed from $Ph_3C\cdot$ during work up of the reaction mixture in air[13].

The reaction of IIa with CH_3OSO_2F is complete within one minute and yields Ia and the reduction product ethane, which was detected by gas chromatography. An immediate reaction occurs between IIa and CF_3SO_3H to give 75% Ia; the other product is presumably H_2. When HCl gas is slowly bubbled into a CH_2Cl_2 solution of IIa, $CpW(NO)_2Cl$ is the only NO-containing product identified by IR in the reaction solution. The formation of $CpW(NO)_2Cl$ presumably occurs by Cl^- substitution of $P(OPh)_3$ in Ia generated by acid oxidation. When I_2 is added to a CH_2Cl_2 solution of IIa, the purple solution gradually turns green over a 15 minute period; at this stage both Ia and $CpW(NO)_2I$ are present. On standing 15 additional minutes, only $CpW(NO)_2I$ is present in 75% yield; presumably Ia is converted to the iodo complex by substitution of the $P(OPh)_3$ in Ia.

To examine the possibility that the $CpW(NO)_2(P(OPh)_3)$ radical initiates the polymerization of styrene, IIa was added to a CH_2Cl_2 solution of styrene; no reaction occurred.

REFERENCES

1. Angelici, R. J. *Acc. Chem. Res.* 1972, *5*, 335.
2. Connelly, N. G. *Inorg. Chim. Acta Rev.* 1972, *6*, 47.
3. Griffith, W. P. *Adv. Organometal. Chem.* 1968, *7*, 211.
4. Enemark, J. H.; Feltham, R. D. *Coord. Chem. Rev.* 1974, *13*, 339.
5. Bottomley, F. *Coord. Chem. Rev.* 1978, *26*, 7.
6. Johnson, B. F. G.; McCleverty, J. A. *Prog. Inorg. Chem.* 1966, *7*, 277.
7. McCleverty, J. A. *Chem. Rev.* 1979, *79*, 53.
8. Bottomley, F. *Acc. Chem. Res.* 1978, *11*, 158.
9. Walsh, J. L.; Bullock, R. M.; Meyer, T. J. *Inorg. Chem.* 1980, *19*, 865 and references therein.
10. Stewart, R. P.; Moore, G. T. *Inorg. Chem.* 1975, *14*, 2699.
11. Hershberger, S.; Angelici, R. J. Unpublished results, Dept. of Chem., Iowa State University, Ames, IA.
12. Burnner, H. *J. Organomet. Chem.* 1969, *16*, 119.
13. Bachmann, W. E. *J. Am. Chem. Soc.* 1931, *53*, 2758.
14. An empirical absorption correction was made using the method described by B. A. Karcher, Ph.D. Dissertation, Iowa State University, 1981.
15. Jacobson, R. A. *J. Appl. Crystallogr.* 1976, *9*, 115.
16. Lapp, R. L.; Jacobson, R. A. "ALLS, A Generalized Crystallographic Least Squares Program," U.S.D.O.E. Report; Iowa State University and Ames Laboratory; Ames Laboratory; Ames, Iowa, 1979.
17. Gromer, D. T.; Waber, J. T. "International Tables for X-Ray Crystallography," Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2A, pp. 71-97.
18. Templeton, D. H. "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham, England: 1962; Vol. III, Table 3.3.2c, pp. 215-6.

19. Kochi, J. K. in "Free Radicals," J. K. Kochi, Ed.; John Wiley & Sons: New York, 1973, Vol. II, pp. 677-692.

20. Greenhough, T. J.; Kolthammer, B. W. S; Legzdins, P.; Trotter, J. *Acta Crystallogr*. 1980, *B36*, 795.

21. Eisenberg, R.; Hendricksen, D. E. *Advances in Catalysis* 1979, *28*, 79.

22. Morris-Sherwood, B. J.; Kolthammer, B. W. S; Hall, M. B. *Inorg. Chem*. 1981, *20*, 2771.

23. Hall, M. B. personal communication, Dept. of Chem., Texas A & M University, College Station,TX.

24. Nappier, T. E.; Feltham, R. D.; Enemark, J. H.; Kruse, A.; Cooke, M. *Inorg. Chem*. 1975, *14*, 806.

25. Callahan, R. W.; Brown, G. M.; Meyer, T. J. *J. Am. Chem. Soc*. 1975, *97*, 894.

26. Callahan, R. W.; Meyer, T. J. *Inorg. Chem*. 1977, *16*, 574.

27. Couture, C.; Morton, J. R.; Preston, K. F.; Strach, S. J. *J. Magn. Reson*. 1980, *41*, 88.

28. Morton, J. R.; Preston, K. F.; Strach, S. J. *J. Phys. Chem*. 1980, *84*, 2478.

APPENDIX 1. FINAL POSITIONAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS (IN PARENTHESES)[a] FOR $Cp(NO)_2WP(OPh)_3$

Atom	X	Y	Z
W	0.5938(0)	0.3837(0)	0.5978(0)
P	0.2921(4)	0.7621(2)	0.3960(2)
O1	0.3164(11)	0.8282(7)	0.3157(6)
O2	0.1291(11)	0.7650(7)	0.3953(6)
O3	0.3220(12)	0.8259(7)	0.4775(7)
O4	0.6328(14)	0.7000(8)	0.5099(9)
O5	0.2052(15)	0.5200(10)	0.5199(9)
N1	0.5362(14)	0.6679(8)	0.4685(9)
N2	0.2875(18)	0.5739(10)	0.4803(9)
C1	0.4383(17)	0.8242(9)	0.2662(11)
C2	0.4243(21)	0.8155(12)	0.1765(11)
C3	0.5399(25)	0.8104(13)	0.1275(11)
C4	0.6675(22)	0.8174(14)	0.1657(14)
C5	0.6779(21)	0.8291(13)	0.2555(14)
C6	0.5642(19)	0.8314(11)	0.3064(12)
C7	0.0543(14)	0.7092(10)	0.3363(10)
C8	0.0393(19)	0.7370(12)	0.2526(11)
C9	-0.0287(20)	0.6794(14)	0.1938(12)

---

[a] Positional parameters are listed in fractional unit cell coordinates.

Atom	X	Y	Z
C10	-0.0801(20)	0.5967(14)	0.2214(12)
C11	-0.0697(21)	0.5700(14)	0.3091(12)
C12	0.0067(16)	0.6276(12)	0.3659(10)
C13	0.2731(17)	0.9155(10)	0.4898(10)
C14	0.1688(19)	0.9229(11)	0.5513(12)
C15	0.1206(24)	1.0162(16)	0.5711(12)
C16	0.1832(25)	1.0907(12)	0.5298(14)
C17	0.2806(25)	1.0774(12)	0.4716(14)
C18	0.3333(21)	0.9873(12)	0.4515(12)
C19	0.4420(29)	0.4713(14)	0.3443(12)
C20	0.5555(25)	0.5213(17)	0.3283(15)
C21	0.5261(26)	0.5952(14)	0.2741(14)
C22	0.3876(23)	0.5877(13)	0.2528(10)
C23	0.3275(22)	0.5132(15)	0.2972(14)

Atom	X	Y	Z
H_2	0.3260	0.8107	0.1458
H_3	0.5303	0.8024	0.0596
H_4	0.7565	0.8139	0.1272
H_5	0.7751	0.8354	0.2865
H_6	0.5735	0.8406	0.3758
H_8	0.0789	0.8002	0.2309
H_9	-0.0402	0.6995	0.1287
H_{10}	-0.1329	0.5535	0.1777
H_{11}	-0.1094	0.5068	0.3308
H_{12}	0.0182	0.6075	0.4309
H_{14}	0.1242	0.8657	0.5816
H_{15}	0.0427	1.103	0.6160
H_{16}	0.1477	1.116	0.5446
H_{17}	0.3252	1.113	0.4413
H_{18}	0.4111	0.9780	0.4065
H_{19}	0.4350	0.4152	0.3863
H_{20}	0.6544	0.5061	0.3514
H_{21}	0.5971	0.6437	0.2519
H_{22}	0.3335	0.6356	0.2113
H_{23}	0.2248	0.4899	0.2944

APPENDIX 2. FINAL THERMAL PARAMETERS (x 10^{-4}) AND THEIR ESTIMATED STANDARD DEVIATIONS (IN PARENTHESES) FOR $Cp(NO)_2WP(OPh)_3$

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
W	99(0)	25(0)	23(0)	0(0)	- 6(0)	0(0)
P	89(5)	26(2)	22(1)	- 3(2)	- 9(2)	- 1(1)
O1	97(15)	34(6)	34(5)	17(7)	-12(7)	6(4)
O2	109(15)	36(5)	29(4)	- 3(8)	1(7)	-11(4)
O3	121(17)	31(6)	35(5)	10(8)	-20(8)	- 3(4)
O4	139(20)	46(7)	76(9)	-16(10)	-49(11)	- 4(6)
O5	149(21)	75(10)	55(7)	-19(12)	6(10)	14(7)
N1	105(19)	22(6)	44(7)	- 8(9)	- 4(9)	1(5)
N2	157(23)	38(8)	28(6)	6(12)	- 5(10)	- 4(6)
C1	83(22)	16(7)	41(8)	5(10)	21(11)	7(6)
C2	150(30)	35(9)	32(8)	6(13)	-14(13)	3(7)
C3	196(36)	51(11)	28(8)	3(16)	24(15)	5(8)
C4	119(28)	51(12)	60(12)	17(15)	14(15)	0(9)
C5	112(28)	47(10)	53(11)	- 8(14)	0(14)	6(8)
C6	82(23)	30(9)	45(9)	- 1(11)	0(12)	3(7)
C7	37(17)	30(8)	44(8)	17(10)	3(9)	-12(6)
C8	136(27)	46(9)	31(8)	23(13)	-21(12)	6(7)
C9	103(26)	68(14)	35(9)	12(15)	- 9(12)	0(9)
C10	99(26)	80(15)	41(9)	- 2(15)	-23(12)	- 1(9)

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C11	140(30)	60(12)	46(10)	-24(16)	-22(14)	2(9)
C_{12}[a]						
C13	63(21)	30(8)	34(7)	4(10)	-15(10)	-11(6)
C14	101(25)	28(8)	50(9)	19(11)	-18(13)	-11(7)
C15	193(38)	70(15)	35(9)	3(20)	-19(15)	-12(9)
C16	169(33)	28(10)	55(11)	8(14)	-29(16)	- 8(8)
C17	196(36)	34(9)	52(11)	-27(15)	- 3(17)	-11(8)
C18	159(30)	32(9)	51(10)	-11(14)	- 5(14)	-15(8)
C19	212(41)	48(12)	36(9)	34(20)	4(16)	- 2(8)
C20	127(32)	63(15)	59(13)	35(18)	-19(17)	- 5(12)
C21	188(37)	53(14)	51(11)	- 7(17)	7(16)	-24(10)
C22	158(32)	52(11)	24(7)	6(15)	2(12)	- 7(7)
C23	158(35)	71(14)	61(12)	-64(19)	32(17)	-37(11)

---

[a] Did not refine anisotropically.

APPENDIX 3. STRUCTURAL FACTORS FOR $Cp(NO)_2W(P(OPh)_3)$

L =-20

H	K	FO	FC
0	0	552	596

L =-19

H	K	FO	FC
3	0	533	-493
1	1	495	-475
4	1	512	-415
0	2	493	-545
2	2	559	-538
3	4	368	382
0	6	348	395

L =-18

H	K	FO	FC
2	0	674	-634
4	0	419	-403
0	1	513	-543
3	1	474	-409
1	2	553	-528
5	2	402	458
0	3	393	-395
3	3	376	371
4	3	331	284
2	4	469	481
4	4	504	442
1	5	370	311
3	5	498	450
1	6	588	601
0	7	580	624
2	8	512	-538

L =-17

H	K	FO	FC
0	-1	415	-357
1	0	810	-851
3	0	566	-546
2	1	443	-482
0	2	674	-701
4	2	683	597
6	2	380	310
2	3	435	410
5	3	529	491
1	4	528	453
3	4	517	497
0	5	347	327
2	5	624	597
5	5	366	-284
0	6	563	615
4	6	528	-511
1	7	358	342
2	7	336	-315
3	7	460	-406
1	8	632	-634
2	9	432	-490

L =-16

H	K	FO	FC
0	0	856	-855
2	0	479	-449
4	0	394	271
6	0	593	494
1	1	705	-689
2	1	459	444
4	1	441	370
5	1	406	319
3	2	644	616
5	2	431	344
1	3	583	576
2	3	333	303
4	3	624	569
0	4	661	694
2	4	636	629
6	4	593	-545
1	5	715	718
4	5	427	-361
5	5	394	-396
3	6	622	-616
0	7	395	365
1	7	340	-326
2	7	624	-559
4	7	533	-502
0	8	655	-672
2	8	385	-429
0	9	345	-226
1	9	355	-472
5	9	429	311
3	10	477	420
2	11	393	341

L =-15

H	K	FO	FC
1	0	843	-865
3	0	323	296
5	0	731	619
0	1	803	-776
1	1	613	619
3	1	586	558
4	1	431	434
6	1	500	439
2	2	885	867
4	2	524	429
6	2	448	-361
0	3	524	508
1	3	346	335
3	3	646	680
4	3	427	-364
1	4	621	594
5	4	694	-680
0	5	786	804
3	5	432	-382
4	5	467	-535
6	5	367	-369
2	6	841	-828
0	7	419	-398
1	7	630	-674
3	7	636	-649
1	8	671	-657
5	8	473	384
0	9	625	-627
4	9	457	488
6	9	459	418
2	10	483	486
5	10	447	326
3	11	426	460

L =-14

H	K	FO	FC
2	-8	406	318
0	-6	368	346
0	0	1183	-1228
2	0	662	636
4	0	853	786
6	0	349	288
0	1	780	745
2	1	752	714
3	1	559	593
5	1	502	486
6	1	349	-314
1	2	1161	1120
3	2	475	445
5	2	437	-417
8	2	334	-102
0	3	619	594
2	3	670	672
3	3	347	-326
6	3	623	-594
0	4	555	555
1	4	564	533
2	4	348	-377
4	4	987	-915
2	5	539	-505
3	5	706	-752
5	5	408	-423
6	5	383	356
1	6	1092	-1131
3	6	491	-515
5	6	436	364
7	6	440	454
0	7	716	-712
2	7	647	-633
6	7	418	402
0	8	565	-566
1	8	398	-433
4	8	582	623
3	9	607	679
5	9	493	503
1	10	463	505
3	10	415	421
0	11	388	407
2	11	647	650
4	12	397	-381

L =-13

H	K	FO	FC
1	-8	406	320
2	-6	416	285
1	0	948	922
3	0	1209	1218
5	0	298	218
1	1	983	946
2	1	765	768
3	1	313	-346
4	1	480	519
5	1	492	-453
0	2	1083	1066
2	2	761	711
4	2	481	-462
6	2	846	-783
1	3	841	809
2	3	360	-368
4	3	404	-386
5	3	743	-749
0	4	401	425
1	4	479	-477
5	4	389	-295
9	4	435	313
0	5	298	252
1	5	516	-503
2	5	950	-939
4	5	722	-679
5	5	461	434
8	5	454	347
0	6	1082	-1073
1	6	553	-550
4	6	631	608
6	6	521	543
1	7	816	-779
2	7	354	361
5	7	621	521
7	7	424	328
0	8	419	-410
3	8	754	792
4	8	324	226
1	9	395	391
2	9	762	745
4	9	605	615
0	10	685	701
2	10	400	394
3	10	460	479
4	10	388	-381
6	10	515	-448
1	11	638	655
5	11	556	-524
0	12	433	437
3	12	522	-508
2	13	565	-562
4	13	380	-348
0	14	494	-499

L =-12

H	K	FO	FC
0	-12	350	-294
1	-12	332	-272
0	0	727	737
2	0	1442	1385
6	0	497	-482
8	0	443	-654
0	1	1218	1223
1	1	865	861
2	1	376	-382
3	1	732	770
4	1	711	-748
6	1	326	-322
1	2	682	647
3	2	607	-701
4	2	292	265
5	2	803	-763
0	3	813	822
1	3	544	-494
3	3	660	-756
4	3	863	-827
6	3	516	-482
0	4	475	-455
2	4	1058	-1045
3	4	433	-506
4	4	330	-317
6	4	675	682
8	4	359	365
0	5	387	-334
1	5	1130	-1107
3	5	515	-590
4	5	609	649
7	5	338	492
1	6	518	-512
2	6	518	-525
5	6	776	695
9	6	445	-375
0	7	1113	-1124
1	7	525	570
3	7	351	332
4	7	684	670
6	7	442	414
0	8	439	450
2	8	950	951
3	8	427	454
4	8	329	338
5	8	407	392
6	8	328	-361
8	8	372	-363
0	9	351	318
1	9	819	828
3	9	503	578
0	10	340	254
1	10	357	392
2	10	435	457
3	10	425	-410
5	10	698	-617
0	11	485	510
4	11	700	-652
6	11	353	-296
2	12	574	-577
6	12	390	340
1	13	647	-767
3	13	400	-482
1	14	332	-250
2	14	370	-379
0	15	544	-523

L =-11

H	K	FO	FC
1	-6	528	-480
1	0	1895	1853
5	0	908	-818
0	1	1103	1074
1	1	285	-261
2	1	811	803
3	1	528	-573
4	1	389	-368
6	1	713	-643
0	2	607	629
2	2	831	-854
3	2	288	274
4	2	1319	-1294
8	2	480	493
10	2	389	284
0	3	542	-537
2	3	495	-488
5	3	626	-617
6	3	663	616
9	3	386	339
0	4	318	305
1	4	1197	-1189
5	4	712	689
7	4	352	435
0	5	1070	-1097
2	5	647	-669
3	5	426	494
4	5	419	440
5	5	471	383
6	5	710	669
8	5	372	257
0	6	694	-696
2	6	845	819
4	6	843	800
8	6	461	-412
0	7	417	414
1	7	410	359
2	7	317	266
5	7	572	492
9	7	467	-398
2	8	353	305
3	8	378	450
4	8	357	332
5	8	530	-443
7	8	586	-488
0	9	879	905
2	9	839	849
3	9	414	-455
6	9	679	-649
1	10	377	393
2	10	442	-448
4	10	576	-588
3	11	667	-792
5	11	517	-479
0	12	359	338
1	12	518	-561
2	12	376	-369
3	12	365	-384
4	12	375	-412
5	12	471	400
7	12	359	276
0	13	697	-722
2	13	498	-524
4	13	323	219
6	13	522	422
0	14	387	-351
1	14	362	-454
4	14	343	327
3	15	501	536

L =-10

H	K	FO	FC
0	-11	347	274
1	-4	330	312
0	-2	257	-216
0	0	1956	1913
4	0	1062	-1033
6	0	685	-643
10	0	536	454
1	1	716	699
2	1	1201	-1157
3	1	376	-409
4	1	309	-260
5	1	817	-851
8	1	442	452
1	2	768	-766
4	2	296	-261
1	3	745	-748
2	3	1139	-1120
3	3	422	419
4	3	621	-599
5	3	909	921
6	3	623	589
8	3	420	476
0	4	1279	-1259
2	4	547	-577
3	4	417	-399
4	4	916	929
6	4	995	940
1	5	1024	-1012
2	5	470	479
4	5	374	353
5	5	739	645
6	5	360	-430
9	5	425	-315
0	6	654	-656

```
 1  6 1005 1005
 4  6  452  469
 7  6  497 -561
 9  6  442 -285
 1  7  353  380
 2  7 1116 1165
 3  7  354 -322
 4  7  445  427
 8  7  579 -626
 0  8 1274 1241
 3  8  319  362
 4  8  800 -823
 6  8  593 -612
 7  8  321 -231
 1  9  905  912
 5  9  787 -760
 0 10  427  407
 1 10  549 -620
 3 10  692 -806
 4 10  343 -295
 7 10  443  371
 2 11  781 -816
 4 11  621 -647
 6 11  425  393
 8 11  439  400
 0 12  590 -608
 1 12  489 -504
 3 12  423 -420
 4 12  494  484
 6 12  413  351
 1 13  624 -654
 3 13  324  326
 5 13  598  512
 0 14  542 -576
 1 14  495  519
 2 15  504  583
 0 16  443  434

   L = -9
 H  K   FO   FC
 2-13  395  317
 0 -4  285  259
 1  0  707  633
 5  0  701 -705
 0  1 1050 1047
 1  1 1436-1359
 2  1  579 -580
 4  1 1125-1103
 8  1  320  320
10  1  439  349
 0  2 1198-1169
 1  2  474   86
 2  2 1363-1385
 6  2  958  957
 8  2  488  524
 0  3  399 -460
 1  3 1093-1105
 2  3  253  236
 4  3  866  921
 5  3  453  434
 6  3  390  358
 8  3  448 -322
 1  4  713 -699
 2  4  425 -419
 5  4 1126 1079
 9  4  545 -412
 0  5 1290-1240
 1  5  346  323
 2  5  366  377
 3  5  469  486
 4  5  938  943
 5  5  322 -317
 6  5  424  360
 8  5  409 -350
 0  6  845  839
 1  6  312 -317
 2  6 1061 1075
 3  6  370  481
 6  6  722 -784
 8  6  447 -489
 0  7  588  595
 2  7  335 -339
 3  7  422  467
 4  7  440 -436
 5  7  428 -371
 7  7  539 -655
 2  8  451  459
 5  8  761 -662
 6  8  393 -430
 9  8  563  488
 0  9  785  782
 1  9  657 -672
 4  9  872 -861
 8  9  411  331
 0 10  620 -652
 1 10  374  316
 3 10  366 -404
 5 10  534 -500
 6 10  622  628
 8 10  357  281
 3 11  552 -578
 5 11  522  429
 7 11  573  488
 0 12  582 -607
 2 12  469 -459
 3 12  458  494
 5 12  615  599
 0 13  720 -723
 4 13  467  604
 0 14  478  458
 2 14  469  512
 3 14  328  345
 1 15  633  709
 2 16  332  374

   L = -8
 H  K   FO   FC
 3-11  327  230
 0  0  719  710
 2  0 1299-1346
 4  0 1353-1355
 8  0  786  891
10  0  418  325
 0  1 1650-1608
 2  1  274 -317
 4  1  696  745
 5  1  394 -458
 6  1  698  694
10  1  360 -272
 0  2  417 -410
 1  2 1945-1934
 5  2 1222 1261
 6  2  384  330
11  2  367 -408
 0  3 1173-1094
 2  3 1244-1238
 4  3  545  566
 5  3  361  342
 6  3  902  941
 9  3  323 -256
 0  4  393 -359
 1  4  671 -665
 2  4 1087 1122
 3  4  258 -272
 4  4 1297 1347
 5  4  325  358
 6  4  384 -421
 8  4  669 -642
 1  5  457  434
 2  5  563  583
 4  5  279 -240
 5  5  516  567
 6  5  697 -692
 7  5  331 -568
 9  5  572 -453
 0  6  649 -593
 1  6 1447 1447
 2  6  419  455
 5  6  985 -950
 7  6  555 -634
11  6  408  326
 0  7 1517 1520
 1  7  676 -660
 2  7  797  848
 3  7  436 -569
 4  7  726 -753
 6  7  714 -663
 0  8  353  383
 1  8  530  554
 2  8 1001-1054
 3  8  281  320
 4  8  491 -445
 5  8  561 -533
 8  8  582  570
10  8  354  230
 0  9  663 -630
 1  9  362 -340
 5  9  451 -423
 7  9  616  582
 1 10  892 -950
 2 10  389 -405
 4 10  420 -518
 5 10  674  690
 7 10  417  374
 0 11 1066-1015
 2 11  546 -532
 4 11  451  413
 6 11  675  679
 2 12  522  610
 4 12  421  526
 8 12  433 -316
 1 13  422  464
 3 13  686  778
 7 13  401 -306
 1 14  545  622
 2 14  432  450
 4 14  325  343
 0 15  835  854
 2 15  345  352
 4 15  355 -372
 6 15  521 -516

   L = -7
 H  K   FO   FC
 2-12  420 -288
 2 -6  291 -233
 0 -3  262  198
 1 -2  277  302
 1  0 2263-2168
 1  1  642 -638
 4  1  374 -390
 5  1  710  731
 6  1  693  691
 8  1  490  455
 0  2 2129-2033
 2  2  328  338
 4  2 1507 1548
 6  2  712  750
 8  2  305 -294
10  2  643 -536
 1  3 1197-1170
 2  3 1076 1083
 5  3 1246 1366
 6  3  425 -444
 8  3  412 -352
 9  3  388 -419
 0  4  408 -418
 2  4  355 -319
 5  4  414 -408
 7  4  318 -804
 0  5 1162 1147
 1  5  447  445
 4  5  418  378
 5  5  898 -834
 6  5  760 -756
 8  5  688 -702
 0  6 1821 1731
 1  6  909  936
 3  6  424  444
 4  6  996-1038
 5  6  477 -508
 6  6  662 -637
10  6  445  362
 1  7  851  857
 2  7  446 -510
 5  7  667 -687
 8  7  380  310
 9  7  425  459
 0  8  335  322
 2  8  285  301
 3  8  539 -659
 4  8  437 -468
 7  8  717  635
 0  9  572 -552
 5  9  382  256
 6  9  707  717
 8  9  555  545
 0 10  948 -932
 1 10  438 -447
 3 10  448 -531
 4 10  733  763
 6 10  517  506
 7 10  444  405
 1 11  619 -698
 3 11  433  497
 6 11  378 -265
 9 11  382 -287
 0 12  968 -958
 1 12  601  673
 3 12  443  457
 4 12  418  460
 6 12  377  307
 7 12  519 -450
 2 13  811  823
 8 13  513 -468
 0 14  699  688
 1 14  664  649
 4 14  406 -491
 6 14  378 -282
 7 14  386 -350
 1 15  339  396
 3 15  377 -402
 5 15  624 -558
 0 16  457  443
 4 16  440 -393
 2 17  536 -551

   L = -6
 H  K   FO   FC
 2-16  352 -341
 3-11  301  276
 0  0 1346-1344
 6  0 1048 1068
 8  0  381  341
10  0  499 -448
 0  1  774 -757
 1  1 1857-1842
 3  1  231 -266
 4  1 1229 1281
 5  1  568  638
 6  1  305  213
 8  1  681 -689
10  1  475 -377
 1  2  469  457
 5  2  976 1019
 6  2  398  387
 0  3  495 -500
 2  3  756  801
 3  3  331  331
 4  3 1519 1542
 5  3  711 -702
 8  3  565 -517
 0  4 1513 1428
 2  4 1767 1955
 4  4  289 -269
 5  4  480  442
 6  4 1347-1372
 8  4  357 -343
 3  5  698  709
 4  5  950 -986
 5  5  738 -735
 7  5  646 -783
 8  5  311  356
11  5  343  322
 0  6 1210 1177
 1  6  260 -287
 2  6  556  558
 4  6  412 -437
 5  6  719 -740
 9  6  670  585
 0  7 1539 1461
 2  7  798 -849
 4  7  889 -951
 8  7  508  538
 0  8 1974-1899
 1  8  331  160
 2  8  934-1011
 3  8  427 -427
 4  8  505  539
 5  8  419 -400
 6  8  679  706
 7  8  357  373
 8  8  490  499
 0  9  489 -472
 2  9  367  397
 3  9  466 -597
 5  9  893  849
 7  9  626  643
 0 10  418 -393
 2 10  516 -565
 3 10  825  971
 5 10  814  739
 6 10  508  489
 7 10  430 -353
 9 10  382 -375
 0 11  701 -674
 2 11  688  728
 0 12  652  672
 2 12  650  688
 3 12  585  612
 6 12  560 -587
 9 12  353 -289
 1 13 1125 1176
 5 13  475 -450
 7 13  508 -492
 0 14  579  622
 2 14  523  568
 3 14  460 -514
 6 14  370 -381
 0 15  492  499
 2 15  420 -460
 4 15  454 -559
 0 16  442 -443
 3 16  479 -454
 5 16  417 -288
 1 17  539 -578
 0 18  426 -430

   L = -5
 H  K   FO   FC
 1  0  804 -864
 3  0  465  439
 5  0 1456 1467
 7  0  289  669
 0  1 1519-1490
 1  1 1598 1587
 4  1  890  940
 5  1  257  243
 6  1  821  830
10  1  463 -363
 0  2  555  516
 1  2  410 -361
 4  2  880  935
 5  2  346  378
 6  2  599 -606
 8  2  782 -775
 0  3 2229 2131
 2  3  259  266
 4  3  415 -499
 5  3  354  353
 6  3  439 -446
 7  3  334 -609
 9  3  388 -310
 0  4  268  209
 1  4 1455 1507
 3  4  329 -417
 4  4  367  333
 5  4 1776-1844
 8  4  334 -346
11  4  402  379
 0  5 2446 2291
 1  5  274 -373
 4  5 1200-1304
```

```
 6  5  893 -894
 7  5  417  433
10  5  437  400
 2  6 1335-1492
 4  6  771 -816
 5  6  311 -313
 6  6  342  461
 8  6  913  878
 0  7 1011-1054
 2  7  311 -312
 4  7  355  373
 6  7  439  388
 7  7  461  447
 9  7  424  412
 0  8  319 -321
 2  8  479 -519
 4  8  488 -487
 5  8  696  709
 7  8  628  643
 0  9 1072-1059
 1  9  458  440
 2  9  502 -558
 6  9  930  947
10  9  532 -387
 1 10  408 -436
 2 10 1012 1056
 5 10  554  589
 6 10  503 -507
 8 10  618 -542
 1 11  638  662
 3 11 1083 1185
 7 11  657 -609
 9 11  374 -291
 1 12  873  925
 2 12  827  882
 5 12  595 -549
 8 12  398 -330
 0 13 1270 1255
 4 13  475 -580
 6 13  604 -597
 1 14  483  475
 2 14  547 -519
 5 14  358 -408
 7 14  361 -211
 8 14  461  388
 1 15  514 -543
 3 15  683 -758
 7 15  442  413
 1 16  379 -353
 2 16  566 -621
 4 16  424 -360
 5 16  388  380
 0 17  630 -616
 2 17  406 -354
 4 17  405  365
 1 18  362 -367

     L = -4
 H  K   FO   FC
 1 -3  289 -232
 0  0  910 -908
 4  0 1621 1813
 6  0  977  981
 8  0  791 -761
10  0  663 -580
 0  1 1523 1361
 1  1  553 -506
 5  1  956  969
 6  1  412 -587
 8  1  522 -488
 9  1  314 -487
 0  2  590  589
 1  2 2307 2306
 2  2  447 -450
 5  2  431 -513
 7  2  527-1119
 0  3  793  754
 3  3  506 -580
 4  3  291  292
 5  3  478 -521
 6  3 1233-1273
 8  3  371 -370
 9  3  376  374
 0  4  917  989
 2  4  213 -247
 4  4 1589-1710
 6  4  326 -346
 7  4  313 -343
 8  4  567  578
10  4  496  516
 0  5  618 -656
 4  5  285 -336
 5  5 1282-1314
 6  5  699  772
 9  5  657  564
 0  6  561  566
 2  6  408 -470
 5  6  478  429
 6  6  294 -255
 7  6  835  862
11  6  473 -391
 0  7 1277-1249
 1  7  415 -424
 2  7 1163-1292
 5  7  363  487
 6  7  716  725
 8  7  679  644
 0  8 1941-1885
 1  8  436 -465
 2  8  658  716
 3  8  352 -425
 4  8 1097 1115
 6  8  455  427
 7  8  359  350
 8  8  442 -439
10  8  519 -476

 0  9  425  461
 1  9  546 -561
 2  9  522  527
 5  9 1175 1196
 9  9  458 -439
 0 10  369 -338
 1 10  887  962
 3 10  653  730
 7 10  655 -609
 0 11  883  837
 1 11  289  266
 2 11 1155 1205
 5 11  347 -373
 6 11  845 -879
 8 11  507 -466
 0 12 1025 1042
 1 12  790  843
 3 12  324  379
 7 12  482 -389
 3 13  759 -793
 5 13  639 -622
 0 14  581  547
 1 14  819 -843
 2 14  320 -295
 3 14  402 -370
 4 14  558 -602
 7 14  439  350
 0 15  654 -659
 2 15  820 -876
 6 15  454  452
 0 16  505 -511
 1 16  538 -537
 3 16  399 -379
 4 16  334  347
 5 16  372  209
 3 17  531  465
 5 17  627  563
 0 18  459 -388

     L = -3
 H  K   FO   FC
 1  0 1586 1521
 5  0  636  679
 7  0  313 -624
 9  0  663 -746
 0  1 1798-1548
 1  1 2070 2024
 2  1  450  578
 3  1  368  398
 4  1 1361 1540
 5  1  684 -665
 7  1  421 -640
 8  1  717 -680
11  1  332  321
 0  2 2511 2203
 1  2 1518-1544
 3  2  628  635
 4  2  711 -784
 5  2  654  607

 6  2 1372-1424
 8  2  363 -372
10  2  507  431
12  2  403  288
 0  3  246 -240
 1  3  829  912
 4  3  921 -932
 5  3 1613-1707
 7  3  507 -652
 8  3  523  539
10  3  343  279
11  3  398  360
 1  4  488 -575
 2  4  214 -181
 5  4 1061-1127
 7  4  669  787
 9  4  511  492
 0  5  725  714
 1  5  970-1040
 3  5  228 -255
 4  5  828 -915
 5  5  843  838
 8  5  844  845
 0  6 2459-2384
 1  6  520 -573
 2  6  962-1030
 3  6  620 -615
 4  6  559  550
 5  6  359 -392
 6  6  852  877
 7  6  410  399
10  6  484 -396
 1  7 1757-1925
 2  7  487  593
 4  7  521  518
 5  7  901  974
 7  7  930  979
 8  7  490 -538
11  7  377 -330
 0  8  299 -313
 1  8  435  486
 2  8  283 -244
 4  8  341  314
 5  8  433  469
 6  8  537  547
 7  8  315 -353
 9  8  570 -521
 0  9  584 -623
 1  9  421  436
 2  9  923  979
 7  9  346 -420
 8  9  520 -484
 0 10  815  776
 2 10  906  936
 3 10  624  654
 6 10  868 -881
 7 10  382 -343
10 10  379  280
 1 11 1168 1231

 5 11  967-1025
 7 11  553 -494
 0 12  791  827
 1 12  311 -280
 2 12  400  448
 3 12 1002-1084
 4 12  487 -481
 6 12  456 -487
 9 12  392  337
 0 13  377  375
 2 13  852 -917
 4 13  598 -651
 8 13  566  495
 0 14  963 -956
 1 14  298 -198
 2 14  351 -322
 3 14  585 -587
 4 14  354  287
 6 14  361  456
 1 15  873 -924
 5 15  495  543
 0 16  529 -545
 2 16  451 -485
 3 16  424  396
 6 16  407  384
 2 17  574  541
 4 17  697  659
 3 18  489  494

     L = -2
 H  K   FO   FC
 4-14  315 -172
 2-13  325  245
 0  0  980  821
 6  0  365 -475
 8  0  896 -895
12  0  341  298
 0  1 3217 2723
 1  1 1886 1895
 4  1  747 -767
 5  1  401 -411
 6  1  905 -891
 7  1  750 -920
 9  1  462 -432
10  1  537  512
11  1  329  212
 0  2  862  766
 1  2 1540 1640
 2  2  361  316
 4  2  725  709
 5  2 1977-2087
 6  2  363 -335
 9  2  697  696
11  2  422  341
 0  3 1598 1548
 1  3 1876-1936
 4  3 1160-1256
 5  3  292 -256
 6  3  697 -719

 7  3  825  826
 9  3  376  390
10  3  375  373
12  3  367  223
 0  4  523 -426
 1  4  647 -645
 3  4  537 -529
 4  4 1149-1194
 5  4  279 -222
 6  4 1096 1135
 7  4  306 -364
 8  4  779  760
 0  5  662 -684
 1  5 1371-1529
 2  5  228 -293
 4  5  419  432
 6  5  291  225
 7  5  852  856
 9  5  389  420
10  5  376 -322
 0  6  663 -652
 1  6  894-1011
 4  6  404 -429
 5  6 1186 1209
 7  6  510  479
 8  6  483  523
 9  6  511 -427
11  6  422 -280
 0  7 2177-2178
 1  7  507  547
 4  7 1160 1216
 6  7 1020 1044
 7  7  441 -478
 8  7  370 -316
10  7  552 -468
 0  8  534  531
 1  8  520 -540
 2  8 1626 1681
 3  8  281  301
 4  8  473  483
 5  8  599  609
 6  8  591 -642
 8  8  838 -820
 0  9  910  929
 1  9  916  989
 2  9  286 -278
 3  9 1237 1278
 5  9  384 -306
 7  9  720 -656
 1 10  685  722
 2 10  627  656
 3 10  669 -728
 4 10  305  264
 5 10  972-1020
 6 10  504 -487
 7 10  309 -116
 9 10  370  266
 0 11 1116 1095
 3 11  331 -297

 4 11 1112-1197
 6 11  516 -607
 0 12  321 -281
 1 12  565  579
 2 12 1020-1024
 3 12  433 -476
 4 12  387 -444
 5 12  504 -562
 6 12  607  573
 8 12  466  418
 1 13 1012-1064
 3 13  790 -817
 7 13  629  603
 1 14  373 -385
 2 14  720 -727
 3 14  408  459
 5 14  426  473
 6 14  356  195
 7 14  349  225
 8 14  357  265
 0 15  856 -863
 4 15  590  580
 6 15  412  357
 1 16  379 -419
 2 16  573  553
 5 16  537  507
 1 17  519  504
 3 17  636  678
 2 18  601  559

     L = -1
 H  K   FO   FC
 3 -6  242 -254
 3  0  318  375
 5  0  914 -957
 7  0 1388-1457
11  0  501  424
 0  1 1914 1538
 1  1  627 -558
 5  1  457 -505
 6  1 1223-1255
 8  1  482 -474
 9  1  606  567
 0  2 1864 1696
 4  2 1759-1952
 5  2  616 -638
 8  2 1079 1082
10  2  591  597
 0  3 1486-1425
 1  3  374  358
 4  3  244  304
 5  3 1036-1036
 6  3  932  933
 7  3  634  611
 9  3  558  498
12  3  360 -218
 0  4 1933 1820
 1  4 1721-1978
 4  4  396 -419
```

5	4	1408	1454
7	4	1089	1152
0	5	1274	-1289
1	5	1117	-1019
2	5	1710	-1790
5	5	698	684
6	5	953	978
8	5	585	585
0	6	1709	-1700
1	6	491	-565
2	6	1406	1473
4	6	1538	1582
7	6	553	601
8	6	763	-727
10	6	539	-508
0	7	762	785
1	7	405	480
2	7	330	384
3	7	1477	1569
5	7	1053	1040
7	7	534	-506
9	7	769	-726
0	8	965	-934
1	8	1725	1835
2	8	324	396
3	8	533	599
4	8	645	654
5	8	795	-804
7	8	794	-795
0	9	1209	1187
1	9	325	-379
2	9	1349	1381
3	9	348	-393
4	9	341	-311
6	9	1048	-1097
8	9	490	-420
0	10	957	988
1	10	665	676
2	10	492	-505
3	10	288	333
4	10	1144	-1114
5	10	523	-518
3	11	1093	-1159
5	11	915	-942
7	11	341	307
9	11	556	472
0	12	352	409
1	12	799	-781
2	12	354	-296
3	12	537	-493
4	12	600	-647
5	12	661	686
7	12	342	350
8	12	424	420
0	13	1332	-1358
2	13	815	-779
6	13	580	569
8	13	406	310
0	14	554	-551
1	14	837	-852
2	14	627	563
4	14	503	471
7	14	457	386
3	15	798	790
5	15	523	495
1	16	531	536
4	16	597	631
0	17	503	500
2	17	611	607
1	18	582	591

L = 0

H	K	FO	FC
4	-13	315	-258
4	0	1403	-1452
6	0	1107	-1154
8	0	452	-462
10	0	631	595
1	1	1847	1717
3	1	346	-325
4	1	292	-299
5	1	1540	-1589
8	1	1008	1041
9	1	320	318
11	1	346	316
0	2	262	-179
1	2	1451	-1398
2	2	316	-325
3	2	1542	-1751
7	2	1089	1113
9	2	685	652
1	3	335	380
2	3	2366	-2354
3	3	238	205
4	3	1534	-1496
5	3	1240	1214
6	3	788	775
8	3	737	725
9	3	386	-456
1	4	1069	-1082
2	4	1188	-1304
4	4	1074	1174
6	4	1227	1249
10	4	620	-540
12	4	455	-379
1	5	2098	-2161
2	5	1088	1132
3	5	661	655
4	5	797	810
5	5	846	881
6	5	385	-408
7	5	692	745
11	5	461	-406
12	5	339	104
0	6	308	-413
1	6	1367	1419
2	6	236	241
3	6	1910	2009
4	6	231	243
6	6	601	633
7	6	922	-888
9	6	591	-555
1	7	690	702
2	7	1689	1770
3	7	265	205
4	7	987	974
5	7	513	-527
7	7	474	-507
8	7	991	-933
0	8	1186	1222
1	8	323	296
2	8	563	561
3	8	873	916
4	8	955	-926
6	8	921	-914
10	8	505	521
1	9	1629	1651
2	9	347	-373
3	9	502	-543
5	9	1272	-1257
6	9	304	142
7	9	352	-391
11	9	481	369
0	10	1007	1021
1	10	666	-696
2	10	429	423
3	10	1305	-1349
4	10	571	-589
6	10	459	-467
7	10	536	454
9	10	350	362
1	11	331	-293
2	11	1121	-1128
4	11	867	-865
6	11	523	514
8	11	621	550
0	12	365	-345
1	12	618	-567
2	12	624	-652
3	12	553	-537
4	12	663	631
6	12	671	675
7	12	375	382
1	13	931	-895
5	13	853	770
7	13	439	489
0	14	969	-996
1	14	587	582
2	14	331	-309
3	14	594	636
4	14	414	406
6	14	462	417
2	15	849	855
4	15	618	609
0	16	582	578
3	16	654	619
4	16	383	-298
1	17	498	443
5	17	709	-646
0	18	545	497
2	18	338	283
3	18	333	-323

L = 1

H	K	FO	FC
1	-13	311	351
0	-11	279	-269
3	-1	223	-180
1	0	784	665
3	0	1810	-1863
5	0	1032	-1092
7	0	299	-229
9	0	984	880
1	1	3272	-2872
4	1	1317	-1320
6	1	642	-652
7	1	904	899
8	1	475	497
10	1	431	507
1	2	560	461
3	2	585	575
4	2	615	-601
5	2	236	-246
6	2	1451	1528
8	2	762	736
12	2	423	-346
1	3	2084	-1859
2	3	331	-282
3	3	1205	-1240
4	3	1350	1322
5	3	733	757
6	3	325	293
7	3	842	857
8	3	371	-429
1	4	1485	-1426
2	4	791	-831
3	4	1352	1430
4	4	376	401
5	4	1621	1590
6	4	390	123
9	4	657	-616
11	4	341	-253
1	5	1148	1073
2	5	691	722
3	5	865	861
4	5	1791	1823
5	5	678	-626
6	5	614	625
7	5	540	-589
8	5	640	-629
9	5	323	-291
10	5	675	-645
1	6	283	313
2	6	2189	2234
3	6	380	376
5	6	358	370
6	6	893	-904
8	6	693	-629
9	6	395	-409
1	7	1303	1315
2	7	304	-271
3	7	1454	1503
4	7	309	-289
5	7	439	-347
6	7	447	-390
7	7	1023	-1000
8	7	307	193
1	8	250	271
2	8	1192	1165
3	8	982	-1056
5	8	1059	-1052
6	8	473	-479
9	8	399	430
1	9	425	-461
2	9	303	-241
4	9	1302	-1310
6	9	345	-316
7	9	399	397
8	9	456	409
10	9	425	454
1	10	310	334
2	10	1247	-1297
3	10	629	-619
5	10	665	-631
6	10	805	759
8	10	494	500
1	11	998	-978
3	11	1005	-1026
5	11	400	380
7	11	697	667
1	12	409	-320
2	12	446	-435
3	12	740	763
5	12	1018	1015
9	12	401	-288
2	13	438	429
4	13	857	850
6	13	483	458
1	14	349	-279
2	14	687	693
3	14	500	457
5	14	527	468
8	14	366	-360
1	15	1004	978
3	15	507	547
7	15	604	-585
2	16	623	632
3	16	475	-462
5	16	439	-333
6	16	463	-482
4	17	664	-598
2	18	427	-379
3	18	429	-346

L = 2

H	K	FO	FC
2	0	4920	-4470
4	0	721	-807
8	0	1281	1303
10	0	558	536
1	1	216	-167
2	1	600	-627
3	1	1767	-1816
4	1	831	823
5	1	839	-862
6	1	678	723
7	1	632	615
8	1	343	353
9	1	494	465
10	1	409	-383
1	2	2799	-2392
3	2	401	-358
4	2	342	-325
5	2	1261	1302
6	2	332	296
7	2	943	988
11	2	460	-436
1	3	1369	-1262
2	3	1624	-1696
3	3	1598	1541
4	3	681	696
5	3	637	617
6	3	1209	1230
7	3	343	-370
9	3	314	-276
10	3	473	-425
12	3	388	-338
1	4	1087	-1088
2	4	1500	1517
4	4	1591	1589
6	4	346	-358
8	4	761	-736
10	4	387	-370
1	5	1348	1289
2	5	997	1035
3	5	1753	1781
4	5	631	-589
5	5	403	396
6	5	785	-763
7	5	386	-416
9	5	664	-606
1	6	1875	1907
2	6	969	981
3	6	276	232
4	6	398	373
5	6	1401	-1375
6	6	301	269
7	6	968	-968
8	6	382	-291
11	6	352	344
2	7	1123	1168
3	7	433	-434
4	7	486	-498
5	7	363	-309
6	7	860	-810
7	7	321	254
9	7	434	356
10	7	553	554
1	8	708	740
2	8	1012	-1022
4	8	1270	-1260
5	8	619	-602
8	8	749	702
10	8	345	287
1	9	577	-570
2	9	433	-439
3	9	1551	-1560
5	9	741	-696
6	9	296	302
7	9	568	519
9	9	599	607
1	10	1193	-1205
2	10	670	-711
4	10	686	-674
5	10	1138	1108
7	10	511	509
2	11	985	-995
4	11	346	364
6	11	898	852
1	12	884	-892
2	12	365	397
4	12	1070	1112
7	12	351	434
8	12	499	-400
1	13	469	467
3	13	1078	1052
5	13	538	508
7	13	379	-387
9	13	514	-492
1	14	808	785
2	14	534	523
4	14	479	478
5	14	340	-369
7	14	408	-408
2	15	507	498
4	15	407	-346
6	15	622	-623
1	16	556	590
2	16	416	-417
4	16	422	-393
3	17	636	-604

L = 3

H	K	FO	FC
4	-12	318	-304
1	0	2751	-2295
3	0	1693	-1706
7	0	1316	1355
9	0	671	681
11	0	348	-360
1	1	721	-677
2	1	1239	-1269

3	1	748	740
4	1	930	-959
5	1	726	742
6	1	565	570
7	1	680	655
8	1	829	786
9	1	338	-367
1	2	288	-275
3	2	389	-405
4	2	1626	1617
5	2	227	-194
6	2	959	939
10	2	539	-581
1	3	1879	-1757
2	3	1272	1331
3	3	841	862
4	3	804	794
5	3	1612	1604
6	3	691	-684
8	3	469	-489
9	3	385	-381
11	3	391	-358
1	4	1360	1313
3	4	1983	1979
5	4	306	-293
6	4	366	284
7	4	977	-971
9	4	543	-525
1	5	352	405
2	5	1499	1540
3	5	340	-350
4	5	639	655
5	5	1266	-1246
6	5	594	-580
8	5	650	-600
9	5	313	208
1	6	866	823
2	6	250	269
3	6	466	429
4	6	1500	-1463
6	6	1102	-1053
8	6	300	259
10	6	624	582
1	7	995	1038
2	7	581	-607
3	7	954	-940
5	7	1298	-1265
7	7	524	-518
8	7	365	316
9	7	636	570
11	7	402	344
1	8	1741	-1718
3	8	1091	-1075
4	8	651	-621
7	8	947	911
9	8	424	443
1	9	371	-372
2	9	1644	-1664
4	9	889	-908
6	9	614	625
8	9	602	598
1	10	316	-316
2	10	384	-361
3	10	818	-829
4	10	677	669
6	10	604	584
10	10	397	-372
1	11	842	-801
2	11	648	649
3	11	597	594
5	11	1193	1111
1	12	550	519
3	12	942	965
6	12	482	482
7	12	603	-575
2	13	1341	1317
4	13	310	359
6	13	456	-374
8	13	618	-599
1	14	689	668
3	14	561	511
4	14	506	-526
7	14	557	-488
1	15	550	538
3	15	416	-347
5	15	686	-663
1	16	365	-367
3	16	463	-387
4	16	628	-609
2	17	742	-709
0	18	340	-285
1	18	407	-411
3	18	525	-421

L = 4

H	K	FO	FC
3	-11	295	264
2	-5	256	222
2	0	3584	-3341
6	0	1130	1156
8	0	660	635
10	0	362	-405
1	1	1807	-1705
2	1	812	796
3	1	690	-712
4	1	1087	1056
5	1	1005	982
6	1	411	395
7	1	1036	1051
8	1	662	-631
10	1	435	-363
1	2	457	-416
2	2	1273	-1265
3	2	2277	2241
4	2	526	518
5	2	1416	1377
6	2	319	261
9	2	680	-658
1	3	1053	995
2	3	301	373
4	3	1755	1752
5	3	1094	-1068
7	3	635	-655
8	3	506	-441
10	3	504	-461
1	4	534	-486
2	4	2089	2044
3	4	324	329
6	4	1338	-1291
8	4	423	-396
12	4	483	414
1	5	2085	2027
3	5	951	918
4	5	984	-997
5	5	833	-856
7	5	847	-830
2	6	377	387
3	6	1490	-1464
4	6	589	-571
5	6	1106	-1078
7	6	389	322
8	6	346	-290
9	6	716	727
1	7	809	-797
2	7	1053	-1088
4	7	1406	-1410
6	7	595	-629
7	7	539	543
8	7	505	469
10	7	478	498
2	8	1045	-1053
3	8	625	-640
5	8	549	-499
6	8	844	794
8	8	533	479
1	9	1303	-1305
2	9	447	397
3	9	934	-919
4	9	337	316
5	9	827	778
6	9	388	360
7	9	791	748
1	10	351	-351
2	10	977	-1012
3	10	952	944
5	10	727	722
6	10	516	495
7	10	506	-440
9	10	492	-466
2	11	514	537
4	11	1204	1193
8	11	521	-476
1	12	294	272
2	12	894	891
3	12	604	621
5	12	446	386
6	12	727	-667
9	12	368	-326
1	13	1153	1122
3	13	320	311
5	13	457	-457
7	13	689	-732
2	14	436	422
3	14	564	-592
6	14	554	-479
2	15	449	-439
4	15	672	-680
2	16	467	-406
3	16	521	-544
4	16	315	8
5	16	430	-399
1	17	701	-689

L = 5

H	K	FO	FC
1	0	1048	-1017
3	0	272	332
5	0	1517	1515
7	0	1028	1077
9	0	532	-509
11	0	501	-473
1	1	985	920
2	1	419	-438
3	1	1518	1483
4	1	752	748
5	1	240	230
6	1	976	1013
7	1	771	-764
9	1	403	-426
10	1	460	-445
1	2	484	-420
2	2	2326	2308
4	2	1230	1235
5	2	381	355
6	2	334	-317
8	2	837	-821
1	3	289	-232
2	3	611	652
3	3	1957	1899
4	3	677	-676
6	3	824	-788
7	3	690	-680
9	3	473	-521
10	3	381	301
1	4	1776	1747
3	4	355	-321
4	4	564	535
5	4	1932	-1898
7	4	503	-512
8	4	376	-329
11	4	457	432
2	5	655	648
3	5	714	-727
4	5	958	-956
6	5	1195	-1190
7	5	527	538
10	5	495	470
1	6	946	942
2	6	1510	-1528
4	6	1245	-1223
7	6	442	-411
8	6	905	851
1	7	1474	-1426
2	7	258	-231
3	7	1120	-1127
4	7	610	578
7	7	731	652
9	7	735	679
1	8	1385	-1389
2	8	715	-726
3	8	377	361
4	8	692	-676
5	8	783	762
6	8	425	403
7	8	538	605
11	8	383	-281
1	9	444	444
2	9	873	-864
3	9	282	254
4	9	625	606
6	9	898	910
10	9	367	-373
1	10	649	-639
2	10	1025	1026
4	10	1014	1045
5	10	788	734
6	10	366	-379
8	10	591	-550
1	11	591	544
2	11	369	420
3	11	1152	1142
7	11	586	-575
9	11	396	-361
1	12	891	896
2	12	661	649
4	12	304	270
5	12	780	-780
8	12	444	-430
2	13	475	485
4	13	563	-565
6	13	606	-610
1	14	462	484
2	14	686	-688
4	14	395	-411
5	14	476	-451
1	15	570	-541
3	15	725	-707
7	15	372	419
1	16	502	-509
2	16	496	-469
5	16	435	361
2	17	372	-364
4	17	544	496

L = 6

H	K	FO	FC
4	-11	353	-297
2	0	346	-283
4	0	2680	2658
6	0	1014	1038
8	0	649	-679
10	0	652	-621
1	1	926	-891
2	1	1287	1297
3	1	1167	1147
4	1	353	346
5	1	1215	1201
6	1	717	-724
8	1	516	-500
9	1	557	-548
1	2	2083	1942
2	2	563	-558
3	2	1223	1204
4	2	846	832
5	2	779	-785
6	2	291	-348
7	2	1111	-1102
9	2	397	-410
11	2	357	308
1	3	868	822
2	3	1875	1843
3	3	579	-594
4	3	672	651
5	3	621	-629
8	3	504	-496
3	4	887	828
4	4	1972	-1878
6	4	613	-610
7	4	384	-317
8	4	344	350
10	4	539	492
1	5	849	869
2	5	1061	-1058
3	5	1034	-1039
4	5	480	-495
5	5	1262	-1266
6	5	677	672
9	5	532	543
1	6	1503	-1490
3	6	852	-844
4	6	290	-247
5	6	326	356
7	6	1032	1054
9	6	327	292
2	7	1365	-1373
3	7	543	517
5	7	297	288
6	7	729	707
8	7	846	834
1	8	392	-389
2	8	552	506
3	8	530	-575
4	8	943	914
6	8	697	683
7	8	460	414
8	8	398	-403
10	8	439	-468
1	9	811	-794
2	9	401	393
3	9	757	738
5	9	1222	1194
9	9	458	-454
1	10	793	761
3	10	1045	1039
4	10	769	784
5	10	356	-393
7	10	661	-586
1	11	283	136
2	11	1542	1530
6	11	752	-734
8	11	430	-407
1	12	796	800
2	12	335	-285
3	12	336	358
4	12	506	-506
7	12	440	-461
1	13	306	319
3	13	594	-571
5	13	617	-527
1	14	770	-695
3	14	364	-377
4	14	495	-503
6	14	391	-379
7	14	543	511
2	15	732	-745
6	15	446	404
1	16	475	-489
3	16	431	-375
3	17	459	442

L = 7

H	K	FO	FC
1	0	311	249
3	0	1789	1735
5	0	916	904
7	0	495	-481
9	0	615	-643
1	1	1269	1239
2	1	1467	1475
3	1	424	401
4	1	882	933
5	1	817	-814
7	1	817	-836
8	1	554	-594
9	1	309	213
2	2	1430	1476
3	2	572	516
4	2	930	-928
6	2	1173	-1169
10	2	346	467
1	3	1656	1605
2	3	1336	-1259

```
 3  3  595  588
 4  3  800 -806
 5  3 1346-1351
 7  3  479 -474
 8  3  514  456
 1  4  339  380
 2  4  406  375
 3  4 1681-1674
 5  4  880 -871
 7  4  661  663
 9  4  626  614
 1  5  731 -725
 2  5 1006-1001
 3  5  300 -266
 4  5 1104-1112
 5  5  671  682
 8  5  750  734
 1  6  781 -725
 2  6 1050-1037
 3  6  370 -383
 4  6  490  460
 6  6 1099 1103
 8  6  399  348
 9  6  405  358
10  6  420 -383
 1  7 1710-1710
 2  7  527  503
 4  7  510  527
 5  7  647  690
 7  7  910  903
 8  7  346 -240
 1  8  632  623
 2  8  732 -762
 3  8 1221 1206
 5  8  493  500
 6  8  540  546
 7  8  440 -422
 9  8  635 -643
 1  9  287  306
 2  9  818  831
 4  9 1291 1257
 7  9  366 -275
 8  9  595 -536
10  9  412 -281
 2 10  946  956
 3 10  551  530
 6 10  726 -660
 8 10  356 -144
 1 11 1295 1293
 3 11  287  299
 4 11  411 -460
 5 11  875 -823
 7 11  523 -502
 3 12  628 -610
 4 12  307 -340
 6 12  344 -369
 0 13  376  327
 2 13  702 -702
 4 13  826 -797

 8 13  459  490
 2 14  385 -385
 3 14  565 -563
 6 14  491  485
 1 15  776 -787
 5 15  442  398
 2 16  460 -397
 3 16  473  380

   L =  8
 H  K   FO   FC
 3-12  309  273
 2-11  355 -324
 2  0 1348 1324
 4  0 1389 1384
 6  0  435 -554
 8  0  754 -769
 1  1 1333 1294
 3  1 1214 1188
 4  1  823 -831
 6  1  782 -796
 7  1  695 -744
 9  1  409 -420
10  1  443  452
 1  2 1277 1269
 3  2  700 -682
 4  2  335  375
 5  2 1434-1475
 6  2  550 -572
 7  2  425 -401
 9  2  456  526
 1  3  908 -883
 2  3  386  371
 3  3  786 -745
 4  3 1063-1064
 6  3  610 -672
 7  3  384  469
 1  4  285  256
 2  4 1642-1649
 4  4  988 -998
 6  4  811  843
 8  4  536  577
 0  5  330 -360
 1  5 1025-1008
 2  5  377 -358
 3  5 1424-1406
 4  5  875  891
 6  5  406  440
 7  5  968 1015
 9  5  335  413
 1  6 1064-1051
 2  6  323 -339
 3  6  546  547
 5  6  909  903
 7  6  387  345
 9  6  499 -456
 1  7  606  615
 3  7  538  530
 4  7  634  660

 6  7  718  745
 1  8  762 -719
 2  8 1498 1482
 4  8  369  389
 5  8  637  645
 6  8  321 -335
 8  8  725 -727
 1  9  662  625
 3  9 1098 1106
 7  9  671 -703
 1 10 1053 1077
 2 10  596  629
 3 10  349 -283
 4 10  395  385
 5 10 1031 -977
 4 11  915 -891
 6 11  577 -589
 1 12  445  416
 2 12  926 -916
 4 12  337 -264
 5 12  406 -375
 8 12  357  349
 1 13  757 -786
 3 13  657 -640
 7 13  535  501
 1 14  415 -411
 2 14  571 -557
 5 14  463  452
 4 15  483  521
 2 16  492  479
 1 17  356  351

   L =  9
 H  K   FO   FC
 1  0 2136 2047
 3  0  260  313
 5  0  767 -814
 7  0 1085-1112
11  0  374  348
 2  1 1008  994
 3  1  885 -894
 5  1  837 -849
 6  1  516 -508
 8  1  347 -284
 9  1  582  582
 2  2  705 -706
 4  2 1489-1490
 8  2  445  480
10  2  414  441
 2  3 1094-1109
 3  3 1132-1117
 5  3  962 -950
 6  3  498  482
 7  3  373  417
 9  3  454  452
 1  4 1639-1603
 3  4 1073-1049
 4  4  331 -281
 5  4  872  891

 7  4  720  754
 1  5  436 -461
 2  5 1439-1403
 3  5  853  828
 5  5  633  594
 6  5  796  816
 8  5  591  608
 1  6  523 -546
 2  6  641  639
 4  6 1136 1124
 6  6  338  395
 7  6  466  449
 8  6  541 -518
10  6  362 -368
 2  7  434  415
 3  7  832  829
 5  7  561  482
 6  7  394 -423
 9  7  483 -538
 1  8 1224 1233
 3  8  575  552
 4  8  663  636
 5  8  500 -441
 7  8  756 -807
 2  9 1126 1148
 6  9  766 -777
 1 10  649  629
 2 10  564 -578
 3 10  344  377
 4 10 1054-1066
 1 11  352  327
 3 11  842 -845
 5 11  656 -640
 6 11  406  283
 1 12  762 -724
 2 12  381 -322
 3 12  446 -431
 4 12  355 -334
 5 12  405  365
 7 12  447  417
 2 13  641 -651
 6 13  609  593
 1 14  634 -649
 4 14  416  440
 3 15  662  633
 5 15  451  471
 0 16  383 -277
 1 16  432  419

   L = 10
 H  K   FO   FC
 1-14  344 -291
 0 -3  290 -167
 2  0  280  296
 4  0  633 -635
 6  0 1305-1343
10  0  444  513
 1  1 1068 1030
 2  1 1065-1051

 4  1  659 -638
 5  1  737 -797
 6  1  355 -351
 7  1  374 -366
 8  1  536  571
 1  2  535 -606
 2  2  441  410
 3  2 1496-1484
 5  2  477 -442
 7  2  793  788
 9  2  587  611
 1  3  858 -844
 2  3 1114-1117
 4  3 1028-1065
 5  3  499  540
 8  3  422  481
 1  4  529 -520
 2  4 1048-1041
 4  4  752  732
 6  4  863  937
 1  5  884 -902
 2  5  727  748
 4  5  521  533
 5  5  941  914
 6  5  356 -379
 7  5  564  612
 1  6  652  715
 3  6 1196 1183
 6  6  387  397
 7  6  562 -570
 9  6  477 -469
 1  7  503  471
 2  7  949  952
 4  7  812  811
 5  7  323 -307
 8  7  652 -654
 2  8  537  492
 3  8  438  434
 4  8  566 -574
 6  8  753 -727
 1  9 1182 1177
 2  9  366 -377
 5  9  974 -967
 7  9  421 -375
 1 10  327 -334
 2 10  344  348
 3 10  820 -839
 4 10  376 -344
 6 10  431 -396
 7 10  463  395
 1 11  324 -266
 2 11  764 -741
 4 11  750 -812
 8 11  409  437
 2 12  381 -385
 3 12  551 -547
 4 12  512  523
 6 12  384  416
 1 13  741 -743

 5 13  571  533
 3 14  450  416
 4 14  381  277
 2 15  724  660
 4 15  436  421

   L = 11
 H  K   FO   FC
 3-10  356 -328
 3 -6  326  217
 1  0  330  330
 3  0  586 -621
 5  0  551 -499
 9  0  676  663
 1  1 1208-1178
 3  1  461 -466
 4  1 1127-1129
 6  1  461 -519
 7  1  704  702
 1  2  324  223
 2  2 1582-1580
 4  2  726 -769
 5  2  429 -444
 6  2  754  775
 8  2  644  637
 1  3  816 -793
 3  3  843 -850
 4  3 1165 1147
 5  3  348  356
 6  3  316  441
 7  3  540  591
 1  4  850 -844
 3  4  796  801
 5  4 1070 1096
 9  4  385 -428
 1  5  478  457
 3  5  590  606
 4  5  831  820
 5  5  380 -417
 6  5  555  584
10  5  444 -467
 2  6 1207 1206
 4  6  303  278
 5  6  334  365
 6  6  562 -592
 8  6  487 -549
 1  7 1065 1066
 3  7  846  861
 7  7  740 -768
 1  8  478  511
 2  8  440  436
 3  8  557 -626
 5  8  847 -845
 9  8  481  424
 1  9  420 -468
 4  9  940 -907
 6  9  341 -381
 7  9  376  259
 2 10  811 -834

 5 10  353 -430
 6 10  434  501
 8 10  390  302
 1 11  665 -662
 3 11  725 -731
 7 11  469  515
 1 12  463 -517
 2 12  534 -553
 3 12  427  431
 5 12  661  623
 4 13  578  611
 6 13  368  472
 2 14  420  420
 1 15  622  569
 3 15  427  392

   L = 12
 H  K   FO   FC
 2  0 1001-1048
 4  0  728 -772
 6  0  383 -483
 8  0  747  775
10  0  357  293
 2  1  312 -322
 3  1  799 -837
 5  1  539 -576
 6  1  526  584
 8  1  409  404
 1  2 1363-1367
 3  2  523 -519
 4  2  330 -320
 5  2  768  829
 7  2  618  614
 2  3 1034-1044
 3  3  806  836
 4  3  399  373
 5  3  456  496
 6  3  767  810
 7  3  378 -371
 2  4 1005 1031
 4  4 1148 1207
 8  4  412 -491
 2  5  533  591
 3  5  797  804
 5  5  467  503
 9  5  421 -474
 1  6 1127 1099
 4  6  306  358
 5  6  543 -606
 6  6  395  315
 7  6  598 -630
 2  7  628  654
 3  7  336 -328
 4  7  408 -417
 6  7  786 -810
 1  8  374  381
 2  8  491 -533
 4  8  752 -810
 5  8  355 -264
```

8	8	481	446
3	9	892	-881
5	9	373	-355
1	10	802	-814
3	10	312	-201
4	10	516	-519
5	10	418	515
2	11	647	-671
6	11	623	667
1	12	424	-464
4	12	681	701
3	13	621	599
1	14	551	487
2	14	353	314

L = 13

H	K	FO	FC
2	-7	309	-316
1	-2	313	269
1	0	1232	-1225
3	0	1051	-1057
5	0	371	-308
7	0	721	714
9	0	416	437
1	1	580	-549
2	1	914	-950
4	1	405	-399
5	1	385	331
6	1	463	507
7	1	374	405
8	1	349	417
2	2	341	-341
4	2	942	972
6	2	780	822
1	3	1051	-1074
2	3	570	624
4	3	424	445
5	3	854	910
1	4	665	668
3	4	1084	1140
7	4	470	-568
9	4	387	-406
1	5	614	625
2	5	980	992
4	5	589	580
5	5	344	-452
8	5	474	-505
1	6	341	350
3	6	310	269
4	6	687	-701
6	6	657	-693
1	7	685	662
5	7	813	-768
1	8	591	-596
3	8	609	-654
7	8	557	551
2	9	810	-836
4	9	439	-442
3	10	484	-493
4	10	554	595
6	10	442	367
1	11	619	-582
5	11	721	761
3	12	573	609
4	12	377	300
2	13	520	554
4	13	348	296
1	14	362	294

L = 14

H	K	FO	FC
1	-2	303	294
2	0	894	-939
6	0	578	614
8	0	553	655
1	1	785	-804
2	1	326	363
3	1	570	-589
4	1	311	395
7	1	456	544
3	2	818	859
5	2	708	728
1	3	600	608
2	3	351	386
3	3	379	394
4	3	851	959
5	3	396	-374
2	4	988	1051
6	4	549	-663
0	5	388	343
1	5	1011	1059
3	5	347	349
4	5	567	-559
7	5	546	-586
3	6	618	-643
5	6	654	-634
1	7	398	-381
2	7	444	-418
4	7	611	-672
7	7	348	280
2	8	597	-607
3	8	393	-377
6	8	400	521
1	9	838	-824
3	9	476	-461
5	9	394	373
2	10	439	-405
3	10	555	548
5	10	516	480
6	10	358	327
4	11	618	698
2	12	551	529
1	13	638	626

L = 15

H	K	FO	FC
1	-10	351	-322
1	-7	343	325
1	0	1003	-1040
5	0	600	598
7	0	517	535
1	1	419	500
2	1	522	-502
3	1	513	510
4	1	401	419
6	1	501	542
2	2	713	773
4	2	582	697
8	2	372	-479
2	3	326	326
3	3	864	907
4	3	319	-256
6	3	418	-468
1	4	970	1034
5	4	773	-780
3	5	418	-476
6	5	444	-581
7	5	375	234
2	6	617	-650
4	6	567	-593
3	7	623	-682
1	8	532	-572
5	8	371	457
2	9	413	-455
2	10	585	553
4	10	553	547
5	10	398	348
3	11	650	674
1	12	413	427

L = 16

H	K	FO	FC
2	-2	332	-142
4	0	616	633
6	0	551	553
0	1	368	398
1	1	432	-461
2	1	561	569
5	1	400	474
1	2	783	826
3	2	564	649
7	2	404	-526
1	3	332	369
2	3	771	792
6	3	368	-454
4	4	788	-848
1	5	331	241
2	5	460	-462
3	5	426	-457
5	5	428	-516
0	6	363	360
1	6	670	-696
3	6	542	-574
2	7	645	-683
4	8	442	464
1	9	391	-405
3	9	332	365
3	10	582	531

L = 17

H	K	FO	FC
2	-5	355	-361
3	0	666	695
5	0	503	509
1	1	504	527
2	1	371	357
4	1	477	527
5	1	333	-231
2	2	564	602
6	2	581	-582
1	3	585	627
3	3	378	309
3	4	702	-742
5	4	374	-430
4	5	557	-573
2	6	494	-498
1	7	659	-629
2	7	315	194
3	8	439	420
2	9	358	373

L = 18

H	K	FO	FC
2	0	494	585
4	0	378	397
1	1	422	365
3	1	568	538
4	1	350	-330
1	2	554	642
5	2	574	-539
1	3	357	-290
3	3	353	-360
4	3	458	-469
2	4	601	-658
4	4	404	-440
1	5	403	-353
3	5	496	-552
1	6	515	-505
1	8	346	-298

L = 19

H	K	FO	FC
1	0	524	653
3	0	402	438
2	1	470	498
3	1	342	-315
3	3	344	-408
1	4	440	-491
2	5	368	-455

SECTION II. THE CHEMISTRY OF THIOMETHOXYL AND AMINO SECONDARY CARBENE COMPLEXES OF IRON

INTRODUCTION

In view of the projected shortage of crude oil, which is currently the primary feed stock for various organic compounds, interest in the Fischer-Tropsch reaction as an alternative source of organics has revived. The Fischer-Tropsch reaction converts a mixture of H_2 and CO gases, when passed through a hot bed of catalyst, composed of transition metals on a solid support, under high pressure conditions, into hydrocarbons and oxygenated organic molecules (Eqn. 1).

$$CO + H_2 \xrightarrow[\Delta]{\text{metal}} \text{alkanes, alkenes, alcohols} \ldots \qquad (1)$$

The mechanism(s) of this reaction remains elusive but most of the transformations are believed to take place on the activated metal surfaces; metal coordinated C[1], CHO[2], CH_2, CHOH[3], CH_2OH are among the plausible transient species[4-6]. Current advances in the syntheses of these organometallic intermediates undoubtedly would shed some light on the mystery of this catalytic reaction.

Most recently, the chemistry of isolated primary carbene complexes has been explored. Schrock and coworkers showed that $Cp_2TaMe(CH_2)$[7] disproportionates thermally to give the metallacyclopropane (Eqn. 2). Brookhart et al.[8], demonstrated that

$CpdppeFeCH_2^+$, which only can be generated in-situ, transfers the methylene moiety to olefins affording cyclopropanated products (Eqn. 3).

$$2Cp_2TaCH_3(CH_2) \xrightarrow{\Delta} Cp_2\overline{Ta\overset{}{C}H_2\overset{}{C}}H_2 \qquad (2)$$

$$\begin{array}{lll} Cp(dppe)FeCH_2OCH_3 & \xrightarrow{H^+} & [Cp(dppe)FeCH_2]^+ \\ & & \quad\searrow \\ & & \qquad Cp(dppe)Fe(\eta^2\text{-}C_2H_4)^+ \end{array} \qquad (3)$$

Due to its inherently unstable nature, the iron complex decomposes to the η^2 olefin complex, $Cp(dppe)Fe(C_2H_4)^+$ (Eqn. 3). The reaction turns out to be a general pathway for the decomposition of other methylene compounds. Thus, $CpM(CO)_2(PPh_3)(C_2H_4)^+$ (M = W,Mo) is formed when the methylene complex is heated[9] (Eqn. 4).

$$M'CH_2^+ \xrightarrow{\Delta} M'(C_2H_4)^+ \qquad (4)$$

$M' = CpMo(CO)_2PPh_3,\ CpW(CO)_2PPh_3$

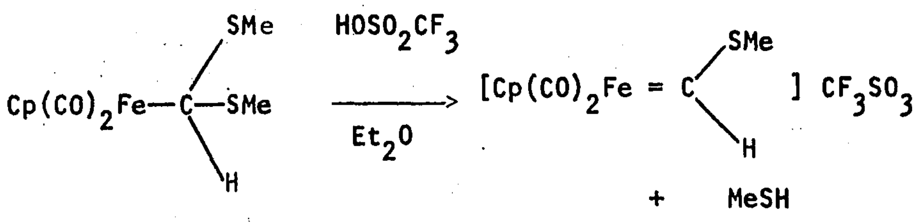
To enhance the stability of methylene complexes, CO ligands are commonly replaced with electron-donating ligands, such as tertiary phosphines. Alternatively, replacement of one of the carbene hydrogen atoms with an electron-donating group results in a secondary carbene complex which is often strikingly more stable. Thus far, amino[10-22], oxyl[19,23-25], thioalkoxyl[19,26-28], silyl[29-31], alkyl[30,32-33,34-41] and aryl[9,31,42-46] carbene complexes have been successfully produced. Collectively, the first three types are often referred to as Fischer-type carbenes whereas the latter three are denoted as alkylidene complexes.

Synthesis

Methods for the preparations of secondary carbene complexes are very specific, and may be classified into five categories: acid-assisted elimination, base-assisted elimination, nucleophilic substitution, protonation and alkylation, and hydride addition.

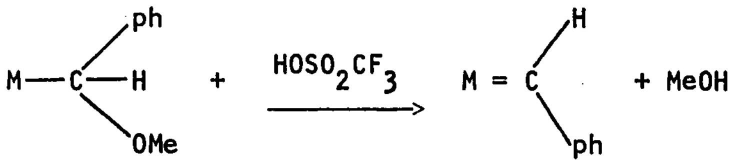
Acid-assisted elimination

Bronsted and Lewis acid-promoted eliminations are the most common synthetic schemes for preparing secondary carbene compounds. McCormick and Angelici[27] utilized this method in preparing $\{Cp(CO)_2Fe[CH(SMe)\}CF_3SO_3$ by expelling MeSH from $Cp(CO)_2FeCH(SMe)_2$ With CF_3SO_3H (Eqn. 5).



(5)

Similarly, $Cp(CO)_2Fe(CHPh)^+$[45], $(CO)_5W(CHPh)$[43] and a few other benzylidene complexes were obtained from the reactions of acids with the corresponding metal ether precursors (Eqn. 6)



(6)

$M = Cp(CO)_2Fe, (CO)_5W$

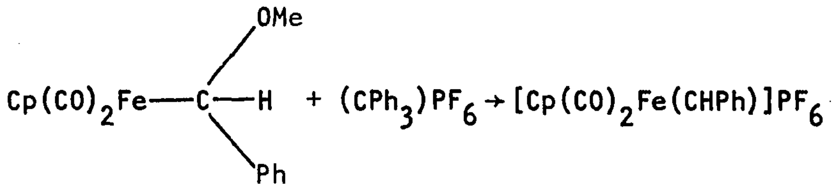
By far the most versatile, but often non-selective, lewis acid for this transformation is the trityl cation, Ph_3C^+. This cation has been successfully employed in the preparation of $Cp(CO)(L)Fe[CH(OR)]^+$[24] by means of hydride abstraction from $Cp(CO)(L)FeCH_2OR$ (Eqn. 7).

$$Cp(CO)(L)FeCH_2OR + (Ph_3C)PF_6 \longrightarrow \{Cp(CO)(L)Fe[CH(OR)]\}PF_6 + HCPh_3 \qquad (7)$$

$L = CO, PPh_3$

$R = Me, Et$

Likewise, $[Cp(NO)(PPh_3)Re(CHPh)]^+$[42] was isolated from the reaction of the benzyl precusor with trityl cation. This reagent is not limited to hydride removal; abstraction of methoxide ion from a metal ether complex also occurs under the proper conditions. Such process was observed in the reaction of $Cp(CO)_2Fe[CH(Ph)(OMe)]$ and trityl, affording $[Cp(CO)_2Fe(CHPh)]PF_6$[45] (Eqn. 8)



$$Cp(CO)_2Fe{-}C(OMe)(H)(Ph) + (CPh_3)PF_6 \rightarrow [Cp(CO)_2Fe(CHPh)]PF_6 \qquad (8)$$

Base-assisted elimination

Elimination with base is a relatively rare reaction in organometallic chemistry. A few Ta and Nb neopentyl complexes have been observed to undergo α-proton elimination in the presence of a Grignard reagent. Schrock et al., accidently prepared $((Me)_3CCH_2)_3TaCHC(Me)_3$[7] by reacting $Cl_2Ta(CH_2C(Me_3))_3$ with $LiCH_2CMe_3$. Presumably, the reaction proceeded through the pentaneopentyl tantalum complex; α-hydrogen abstraction from one of the ligands afforded the observed secondary carbene (Eqn. 9).

$$Cl_2Ta(CH_2R)_3 + 2LiCH_2R \rightarrow [Ta(CH_2R)_5] \rightarrow RCH_3 + (RCH_2)_3TaCHR \qquad (9)$$

$R = t\text{-}Bu$

It was suggested that the high acidity of the α-hydrogen is faciliated by steric crowding about the metal. Since this initial success, series of Nb and Ta alkylidenes have been synthesized in a similar fashion[40].

Nucleophilic substitution

A number of amino hydrido carbenes have been obtained from the reaction of iminyl chloride with organometallic nucleophiles. Lappert et al., showed that the oxidative addition of N,N dimethylchloromethyl enamine chloride, $(Me_2NCHCl)Cl$, to $(PEt_3)_3RhCl$ resulted in the formation of $(PEt_3)_2\ RhCl_3(CHNMe_2)$[13]. Analogously, other Rh[12], Pt[13], Ru[14] and Ir[14] secondary amino carbene complexes have been prepared (Eqn. 10).

$$(PEt_3)_3RhCl + [Me_2NCHCl]Cl \rightarrow \begin{array}{c}(PEt_3)_2Cl_3Rh(CHNMe_2)\\ + \\ PEt_3\end{array} \qquad (10)$$

The metal carbonyl anions, $Cr(CO)_5^{2-}$ and $Fe(CO)_4^{2-}$[10,14], also react with the iminium chloride to yield amino carbenes (Eqn. 11). Secondary carbene complexes of Mn, Re, V, Cr, Mo, W, Co have been synthesized by this method[14].

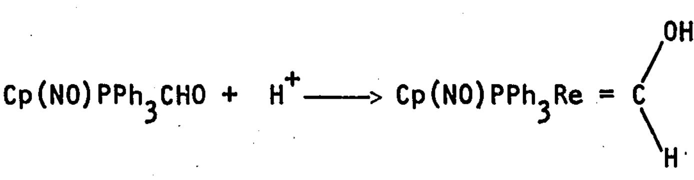
$$M^{2-} + (Me_2NCHX)Cl \longrightarrow MCHNMe_2 \qquad (11)$$

$$M = Cr(CO)_5,\ Fe(CO)_4; \qquad X = H,\ Cl,\ SMe$$

Despite these successes in generating secondary amino carbenes, this novel method has not been extended to the preparations of other classes of carbenes.

Protonation and alkylation

Conversion of metalacyls to the analogous carbene complexes simply by alkylation marked a milestone in organometallic chemistry[47-48]. Due to the instability of M[C(OH)R], the parallel protonation reaction is rarely cited[47-48]. Gladysz et al., showed that $Cp(NO)PPh_3Re[CH(OH)]^+$ [23] may be prepared by the protonation of the formyl complex (Eqn. 12)



$$Cp(NO)PPh_3CHO + H^+ \longrightarrow Cp(NO)PPh_3Re=C\begin{matrix} OH^+ \\ H \end{matrix} \qquad (12)$$

Similarly, a number of iminoyl formyls (Rh[15-16], Os[19], Pt[11,18], accept a proton to give carbenes as indicated in Eqn. 13.

$$\begin{tikzcd} \mathrm{trans(PPh_3)_2(CO)_2(Cl)Os(CHNMe)} + \mathrm{H^+} \arrow[d] \\ \mathrm{trans(PPh_3)_2(CO)_2(Cl)Os(CHNHMe)^+} \end{tikzcd} \qquad (13)$$

Protonation of an η'-cyclopropyl metal complex produced an ethyl secondary carbene compound (Eqn. 14). However, this complex underwent facile hydrogen rearrangement to give the η^2-propene derivative[34].

$$\begin{tikzcd} \mathrm{Cp(CO)_2Fe(\overline{CHCH_2CH_2})} + \mathrm{H^+} \arrow[r] & \mathrm{Cp(CO)_2Fe(CHEt)^+} \arrow[d] \\ & \mathrm{Cp(CO)_2Fe(\eta^2\text{-}H_2C{=}CHCH_3)^+} \end{tikzcd} \qquad (14)$$

Collins and Roper[19] found that a formyl complex, $\mathrm{(PPh_3)_2(CO)L(Cl)Os(CHO)}$ when alkylated with $\mathrm{CF_3SO_3Me}$ yielded the corresponding air stable carbene compound $\mathrm{\{(PPh_3)_2(CO)L(Cl)Os[CH(OMe)]\}CF_3SO_3}$ (Eqn. 15).

$$(PPh_3)_2(CO)L(Cl)Os(CHX) + CF_3SO_3Me \longrightarrow \{(PPh_3)_2CO(L)(Cl)Os[CH(XMe)]\}^+CF_3SO_3 \qquad (15)$$

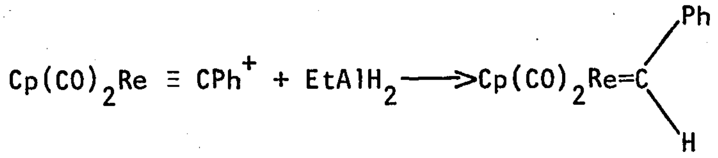
X = O, S

L = (p-tolyl)NC

Analogously, the first sulfur stabilized secondary carbene, $\{(PPh_3)_2(CO)L(Cl)Os[CH(SMe)]\}CF_3SO_3$ was obtained (Eqn. 15).

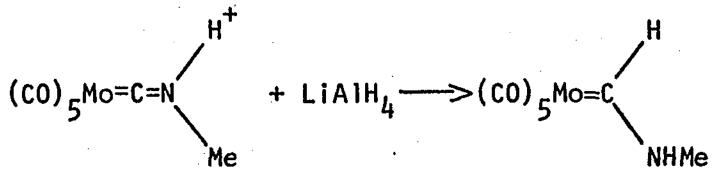
Hydride addition

Hydride attack on metal-coordinated carbynes leading to the production of secondary alkyl carbene complexes was initially discovered by Fischer and Frank[46], thus, $Cp(CO)_2ReCPh^+$ was reduced with $EtAlH_2$ to afford $Cp(CO)_2Re(CHPh)$ (Eqn. 16).



$$Cp(CO)_2Re \equiv CPh^+ + EtAlH_2 \longrightarrow Cp(CO)_2Re{=}C(Ph)(H) \qquad (16)$$

This α-hydride addition technique has also been successfully employed in the synthesis of an amino carbene[22] (Eqn. 17).



$$(CO)_5Mo{=}C{=}N^+(H)(Me) + LiAlH_4 \longrightarrow (CO)_5Mo{=}C(H)(NHMe) \qquad (17)$$

The above method is a useful technique for obtaining otherwise inaccessible secondary carbene complexes. However, the unavailability of suitable carbyne complexes has reduced the applicability of this approach.

In contrast to carbynes, isocyanide complexes are relatively abundant. Treichel et al.[17] found that a number of di and tri-isocyanide compounds reacted with borohydride to give boro-heterocyclic metal carbene complexes (Eqns. 18 and 19).

$$Cp(CO)Fe(CNMe)_2^+ + BH_4^- \longrightarrow Cp(CO)Fe(CHNMe)_2BH_2 \qquad (18)$$

$$Cp(Fe(CNMe)_3^+ + BH_4^- \longrightarrow CpFe(CHNMe)_3BH \qquad (19)$$

Quite recently[25], metal carbonyls of group VI transition metals and Nb have been found to be susceptible to reduction with organometallic hydrides, giving oxo-carbene complexes (Eqn. 20).

$$Cp_2MCO + (Me_5C_5)_2ZrH_2 \longrightarrow Cp_2M[CH(OZrH(Me_5C_5)_2)] \qquad (20)$$

$$M = W, Mo, Cr, Nb(H)$$

Miscellaneous

A number of interesting secondary carbene preparations which do not fit into the previous discussions are summarized in Table 1.

Table 1. Other secondary carbene preparations

Reaction	Reference
$Ta(CHR)(PEt_3)_2Cl_3 + (OR)_4WO \rightarrow Ta(OR)_4Cl + Cl_2(PEt_3)_2(O)W(CHR)$ R = t-Bu	38
$[(PPh_3)Cl\overline{PtCH_2N(Me)_2CH_2N}(Me)_2]Cl \xrightarrow{\Delta} Cl_2(PPh_3)PtCHN(Me)_2$	20
$(Cp(NO)PPh_3ReCH_2)_2SMe^+ \xrightarrow{\Delta} Cp(NO)PPh_3ReMe +$ $[Cp(NO)PPh_3ReCHSMe]^+$	26
$MCl_6 + LiCH_2SiMe_3 \longrightarrow (Me_3SiCH_2)_3(MCHSiMe_3)$ [a]	29
$Cp_2ZrMe(\eta^2MeCHO) + Cp_2WH_2 \longrightarrow Cp_2W(CHMe) + Cp_2Zr(OH)(Me)$	41
$TPPFeCl_2 + PhSCHCl_2 + Fe^0 \longrightarrow TPPFe(CHSPh)$	28
$CpRe(NO)PPh_3(CH_2OMe) + Me^+ \longrightarrow CpRe(NO)PPh_3[CH(OMe)]^+$	23
$CpMo(CO)_3CH_2OMe + Ph_3C^+ \longrightarrow CpMo(CO)_3Me + CpMo(CO)_3[CH(OMe)]^+$	9

[a] Not fully characterized.

Chemical Properties

The chemistry of metal-coordinated carbon ligands is rich and varied. Most of the chemical reactivity studies are on alkyl carbene, alkylidene, complexes. By and large, alkylidenes undergo carbene ligand transfer to olefins to give cyclopropane products[49], as exemplified in the reaction of $Cp(CO)_2Fe(CHPh)^+$ and propene[45] (Eqn. 21).

$$\mathrm{Cp(CO)_2FeCHPh^+ + H_2C{=}CHMe \longrightarrow Ph\overline{CHCH_2C}HMe} \qquad (21)$$

Dimerization of carbene ligands leading to olefins is frequently observed[43,45] (Eqn. 22).

$$\mathrm{Cp(CO)_2Fe(CHPh)^+ \longrightarrow PhCH{=}CHPh\ (cis\ and\ trans)} \qquad (22)$$

Similar reactions have also been found in methylidene complexes, although the conditions are milder than those in Eqns. 21 and 22 due to more favorable steric and electronic considerations. Such similarity has encouraged catalytic studies on alkylidenes. Several alkylidenes have been discovered to be catalytically active in promoting olefin metathesis[38,40]. In this reaction, the olefin and carbene groups are presumed to unite to form a puckered metallocyclobutane intermediate[43], subsequent scission results in overall alkyl exchange[38] (Eqn. 23)

$$Cl_2(PEt_3)_2W(O)(CHR) + \text{2-pentene} + AlCl_3 \longrightarrow Cl_2(PEt_3)_2W(O)(CHR') + RCH{=}CHR' \qquad (23)$$

R=t-Bu

R'=Me, Et

Schrock found that the highly polarized metal carbene bond of $(RCH_2)_3Ta(CHR)$ may be regarded as being similar to a Wittig reagent; as in the Wittig reaction, the carbene transfers to organic acyls under mild conditions, giving olefins in high yields[40] (Eqn. 24).

$$(RCH_2)_3Ta(CHR) + EtOCHO \longrightarrow EtOCHCHR \qquad (24)$$

R = t-Bu

Intramolecular β-H migration is very common in alkylidene complexes. For instance, $Cp(CO)_2Fe(CHEt)^{+}$[34], generated in situ from $Cp(CO)_2Fe(\overline{CHCH_2CH_2})$ and acid, undergoes a facile 1,2 shift to achieve the η^2-propene complex (Eqn. 14). Likewise, other β-H containing alkylidene complexes convert to their olefinic comlexes upon heating[32,41].

Although the chemistry of heteroatom stabilized, Fischer-type, secondary carbenes has recently been explored, little is known. Hence, their chemical reactivities are deferred and will be discussed in the subsequent sections.

Spectroscopic Properties

The most commonly used analytical technique for elucidating carbene complex structure is 'H NMR. The electron deficient C_{carb} causes the carbene hydrogen resonance to be at very low fields, ranging from 9 to 18 δ. Temperature dependent 'H NMR studies also provide a means of estimating rotational barriers around the $M-C_{carb}$ and $C_{carb}-X$ bonds. Schrock[40] calculated the M-C rotational barrier in $Cp_2Ta(CH_2Ph)(CHPh)^+$ to be about 19.2 kcal/mole, which is 1.8 kcal/mole lower than that of $Cp_2Ta(Me)(CH_2)^+$, whose metal-C_{carb} bond is essentially a double bond based on an x-ray crystallographic study. The lower rotational barrier in $Cp_2Ta(CH_2Ph)(CHPh)^+$ was interpreted as indicating an increase in $C_{carb}-C_{ipso}$ double bonding at the expense of M-C bonding and is in accord with the x-ray data[31]. Brookhart et al.[50], noted that the rotational energy about the $C_{carb}-C_{ipso}$ bond of $Cp(CO)_2Fe[CH(p\text{-tolyl})]^+$ is estimated to be 1.3 kcal/mole higher than the phenyl analog by variable temperature 'H NMR experiments. This significant change was taken to indicate that the aryl π electrons are delocalized over the C_{carb}; this results in an accumulation of cationic character on the ring and an increase in the C_{carb}-C_{ipso} bond strength by means of π overlap. The extent of such electron redistribution chiefly depends on the electron donating abilities of para and ortho substituents of the aryl. Methyl is found to be more electron donating than hydrogen based on the pioneering works by Hammett in organic aryl systems[51]. Hence, the para-tolyl secondary carbene must have greater C_{carb}-C_{ipso} double bond character than its phenyl counterpart.

Although the barriers for rotation in heteroatom-stabilized secondary carbenes have not yet been determined, the general consensus is that the C_{carb}-X rotational barrier is expected to be substantially higher than that for the C_{carb}-C rotation of in alkylidenes, due to more favorable X to C_{carb} π-backbonding. For example, the methyl resonances (syn and anti relative to the carbene hydrogen) in $RhCl_3(PEt_3)_2(CHNMe_2)$, figure 1, do not coalesce even at 150°C.[12] This suggests strong

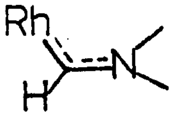


Figure 1. Structure of $RhCHNMe_2$

C-N π-bond character which is confirmed by an x-ray structural determination which shows the C-N bond to be significantly shorter than a typical C-N single bond.

^{13}C NMR is also a valuable technique for establishing the presence of a carbene ligand[52]. In general, the C_{carb} resonance of secondary carbene complexes occurs in the range of 190-350 PPM downfield from TMS. With few exceptions, Ta and Nb alkylidenes and Fischer-type carbenes appear below 300 PPM; they are also less electrophilic and less prone to decompose than those at low fields (300-350 PPM).

Structural and Bonding

Owing to the inherent instability of alkylidenes, few single crystal x-ray structural determinations of secondary carbene complexes have been described. Schrock[40] reported the Ta-C_{carb} distance in $Cp_2Ta(CH_2Ph)(CHPh)$ to be slightly longer than the full double bond found in $Cp_2Ta(Me)(CH_2)$ and the Ta-C_{carb}-C_{ipso} angle to open up 15° from the idealized sp^2 hybridized angle of 120°. More strikingly, the analogous bond in the 14-eletron complex, $(Me_5C_5)Ta(CH_2Ph)_2(CHPh)$[44] is marginally longer than that in the carbyne, $(Me_5C_5)Ta(PMe_3)_2Cl(CPh)$, and the Ta-$C_{carb}$-C angle is 166° which amounts to being bent 5° from the analogous angle of the carbyne. Since the carbenic phenyl rings in both cited benzylidenes are twisted out of the Ta-C_{carb}-C_{ipso} plane by as much as 40°, p-p back bonding is virtually negligible; this is reflected in the observation of little or no shortening of the C_{carb}-C_{ipso} bonds. These data point to a strong M-C_{carb} interaction and weak C_{carb}-C_{ipso} π overlap. These conclusions are also valid in the cases of $Cp_2W(CHPh)$[41] and $Cl_2(PEt_3)_2W(O)[CH(CMe_3)]$[38] where both structures exhibit remarkable resemblance to the tantalum complexes.

With the exception of the metal oxyl carbene complex[25], all reported structural studies of Fischer-type secondary carbenes are amino carbenes[12,15,20,53]. By and large, the C_{carb} and N are approximately planar with an M-C-N angle in the range of 125-140°. The observed deviations from the ideal 120° are presumably due to the smallness of the carbene hydrogen. The metal-C_{carb} and C_{carb}-N distances are invariably shorter than expected for their respective single bonds. Thus, d-p and p-p interactions must both be important in amino carbenes. In $Cp_2W[CH(OZrH(Me_5C_5)_2)]$[25], the W-$C_{carb}$ distance is shorter than that in $(CO)_5W(CPh_2)$[54] which has a W-C_{carb} double bond; the C-O in $Cp_2W[CH(OZrH(Me_5C_5)_2)]$ is marginally shorter than a single bond which suggests that W-C_{carb} d-p π-back bonding is more important than the C_{carb}-O p-p π bonding. However, this result is probably not general for monometallic oxyl carbenes owing to the fact that the Zr atom in this carbene complex competes with the C_{carb} for the oxygen lone pairs; this leads to a weakening of the C-O π-interaction.

The Present Research

The chemistry of sulfur-containing organometallic compounds has been a long-time interest in this laboratory. More recently, we have extended our studies into sulfur-stabilized carbene complexes of transition metals. In the course of these investigations, we synthesized the first iron thiomethoxyl hydrido carbene, $Cp(CO)_2Fe[CH(SMe)]^+$ [27]. Despite our earlier studies and recent investigations by other groups of $\{(PPh_3)_2(CO)_2(Cl)Os[CH(SMe)]\}^+$ [19], $CpRe(NO)PPh_3[CH(SMe)]^+$ [26] and $TPPFe[CH(SPh)]$[28], little is known about the reactivity of thioalkoxyl secondary carbene complexes. Thus, we have examined the chemical and physical properties of $Cp(CO)_2Fe[CH(SMe)]^+$ and its immediate derivatives.

EXPERIMENTAL

General Procedure

All reactions were carried out under an N_2 atmosphere at room temperature, unless specified otherwise. Schlenk ware and a vacuum manifold were standard equipment for carrying out the reactions. A 500 ml 3 neck-flask equipped with a stopcock in the bottom was used for amalgam reductions. Low pressure (1-5 atmospheres) reactions were conducted in a pop bottle sealed with a neoprene lid and metal cap.

The exchange of PF_6^- with other anions was performed by dissolving the desired complex in either acetone containing 10 eqv. of $(NH_4)PF_6$ or acetonitrile with 10 eqv. of KPF_6 solution. The mixture was allowed to metathesize for ½ hr, and the solvent was removed under reduced pressure supplied by a vacuum manifold which was about 1 torr. The resulting residue was extracted with CH_2Cl_2, the combined extracts were filtered through a frit, and the resulting solution volume was concentrated under reduced pressure. A layer of a less polar organic solvent (Et_2O, hexane, EtOH) was placed over the CH_2Cl_2 solution, and the mixture was slowly chilled to -20° to induce crystallization.

Solvents

For our studies, CH_2Cl_2 was distilled from CaH_2 under an N_2 atmosphere. The solvent MeCN was dried over CaH_2 to remove most of the moisture and then decanted into a fresh CaH_2-containing flask for distillation. The distilled fraction was then re-distilled from P_2O_5. The CaH_2 and P_2O_5 dryings were repeated once more before storing in a Schlenk flask under a nitrogen atmosphere for later use. The solvent Et_2O was distilled from K and benzophenone. Tetrahydrofuran was distilled from Na and benzophenone and used immediately. Hexane was purged with N_2 and stored over 5 Å molecular sieves. Acetone was distilled from P_2O_5 twice before use. Methanol was distilled from Mg and a catalytic amount of I_2 after standing for 12 hr.

Instrumentation

Infrared spectra were recorded on a Perkin-Elmer 281 spectrophotometer; NaCl cells with 1 mm path length were commonly used except for THF solutions when 0.1 mm thick cells were used. The instrument was calibrated with gaseous CO, and the band positions are believed to be accurate to within 2 cm^{-1}.

Proton NMR spectra were obtained with Varian 360 or Hatachi R20B (60 MHz) spectrometers. ^1H NMR spectra for variable-temperature studies and low concentration samples were recorded on a JEOL FX90Q (89.55 MHz) Fourier transform spectrometer. ^{13}C NMR spectra were obtained with a Bruker WM300 (75.43 MHz) or a JEOL FX90Q (22.50 MHz) Fourier transform spectrometer. ^{31}P spectra were run on a Bruker WM300 (121.44 MHz) instrument. Five mm diameter NMR sample tubes were used for all spectra; $Cr(acac)_3$ (35 mg/ml) was added, unless specified otherwise, for ^{13}C and ^{31}P samples to reduce data acquisition time. Tetramethylsilane (TMS) or deuterated solvent was used as an internal standard for ^1H and ^{13}C NMR spectra. H_3PO_4 capillary insert was employed as the internal reference for ^{31}P NMR spectra. Chemical shifts for ^1H NMR bands are reported in δ units relative to TMS; ^{31}P resonances appeared upfield from H_3PO_4 and are assigned negative values.

GC traces were recorded on a Varian 1700 gas chromotograph equipped with a 30-foot 5% SE30 capillary column. Mass spectra and GC-MS spectra were performed on a Finnigan 400 GC-MS with INCOS 2300 data system, GC Model 9610. Decomposition and melting points were determined with a Thomas Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were made by the Ames Laboratory.

Reagents

Organic All alkyl phosphines and $P(OPh)_3$ were purchased from Strem Chemical and used without further purification. A sample of $P(OCH_2)_3CMe$ was kindly supplied by Steve Socol; PCl_3 and $ClPPh_2$ were distilled before use. CH_2N_2/Et_2O[55], $ClCH_2SMe$[56], $HC(SMe)_3$[57] and CyNC[58] were synthesized according to the literature procedures, and CH_2N_2/Et_2O was dried with anhydrous Na_2CO_3 before use. All amines except volatile ones (Me_2NH, $MeNH_2$, NH_3) were stored over KOH overnight and distilled from BaO. $Me_3NO \cdot 2H_2O$ was obtained from Aldrich and dried by benzene azeotropic distillation.

Inorganic Samples of $LiAlH_4$, $LiAlD_4$, $LiAl(OBu^t)_3H$ and n-BuLi (2.5 M in hexane) were available from Alfa; $Li(BEt_3H)$ (1 M in THF), HBF_4-Et_2O and CF_3SO_3H were purchased from Aldrich; $Mn_2(CO)_{10}$

and $(Cp(CO)_2Fe)_2$ were obtained from Strem Chemical, and CH_3SO_3F was acquired from Tridom Chemical (Fluka). Other chemicals were also commercially available.

Synthesis, Reactions and X-Ray Structure

Secondary carbene complexes and derivatives of iron

Synthesis of $Cp(CO)_2Fe[CH(SMe)_2]$ from $\{Cp(CO)_2Fe[C(SMe)_2]\}PF_6$ and $Li(AlH_4)$ A solution of 100 ml of THF containing $\{Cp(CO)_2Fe[C(SMe)_2]\}PF_6$,[1],(0.10 g, 0.23 mmol) was treated with $Li[AlH_4]$ (0.020 g, 0.47 mmol); the yellow solution turned dark brown immediately and evolution of gas was apparent. The mixture was stirred for an additional 20 min, and the solvent was then removed under reduced pressure to afford a stenchy brown solid. The residue was then extracted by rapidly stirring for 30 min with 20 ml of hexane. The resulting extract was then filtered through Celite on a glass frit under an N_2 atmosphere. Upon evaporation under reduced pressure, a yellow oil of $Cp(CO)_2Fe[CH(SMe)_2]$ (0.056 g, 85%),[2], was obtained. The IR and ^1H NMR spectra of the oily [2] were in accord with the previously recorded spectra of this compound[27]; the oil was used in subsequent reactions without further purification.

When this reaction was scaled up 10-fold, the major organometallic product obtained upon extraction was $[Cp(CO)_2Fe]_2$,[3].

Synthesis of $Cp(CO)_2Fe[CH(SMe)_2]$,[2], from $\{Cp(CO)_2Fe[C(SMe)_2]\}PF_6$,[1], and $Li(Et_3BH)$ A suspension of [1] (2.0 g, 4.6 mmol) in 20 ml of THF was treated dropwise with $Li(Et_3BH)$ (4.8 ml, 4.8 mmol), diluted with 5 ml of THF, via a 25 ml addition funnel in a period of 15 min. The deep brown mixture was allowed to react for an additional 20 min; the solvent was removed in vacuo, affording a brown oil. The oil was extracted as described in the preceding synthesis to furnish [2](1.3 g, 85%).

Synthesis of $Cp(CO)_2Fe[CH(SMe)_2]$,[2], from $\{Cp(CO)_2Fe[C(SMe)_2]\}PF_6$,[1], and $Li(Al(OBu^t)_3H$ A sample of [1] (2.0 g, 4.6 mmol) was suspended in 20 ml of THF, $Li(Al(OBu^t)_3H)$ (1.5 g, 5.8 mmol) was added, and the mixture was stirred for 30 min. The solvent was then evaporated under vacuum, and the resulting residue was extracted as noted above. This gave a mixture of [2] and a white inert solid which totaled 1.5 g. The concentration of [2] in the mixture was determined by the intensities of the ν(CO) absorbances of the complex to be 80-85%.

Reaction of $[Cp(CO)_2Fe]Na$ and $[HC(SMe)_2]PF_6$ The organic cation[59] was synthesized by adding $HC(SMe)_3$(1.0 g, 6.5 mmol) in 10 ml of Et_2O to a rapidly stirred 5 ml CH_2Cl_2 solution of $(CPh_3)PF_6$ (2.3 g, 5.8 mmol) at -40°C. After mixing for 10 min, a white precipitate was apparent. The solvent was carefully decanted via canula, and the white solid was washed with dried Et_2O at -40°C twice, and the remaining solvent was removed under vacuum to give $[HC(SMe)_2]PF_6$ (1.1 g, 75%). The cation is sensitive to water and is best used immediately.

A 10 ml THF solution of $Na[Cp(CO)_2Fe]$[60], synthesized from

$[Cp(CO)_2Fe]_2$ (0.77 g, 4.4 mmol) and 3% sodium amalgram, was transferred to a 10 ml THF solution of $[HC(SMe)_2]PF_6$ (1.1 g, 4.4 mmol) at -78°C. The pale yellow solution turned dark at once and the only identifiable product from the IR spectrum of the reaction mixture was $[Cp(CO)_2Fe]_2$,[3]. Analogously, when $K[Cp(CO)_2Fe]$[61] was used, the outcome was identical.

Reaction of $[Mn(CO)_5]Li$ and $[HC(SMe)_2]PF_6$ Into a THF solution of $Mn_2(CO)_{10}$ (0.10 g, 0.26 mmol), $(Et_3BH)Li$ (0.57 ml, 0.57 mmol) was dripped at -78 C; evolution of H_2 was evident[62]. After 30 min of mixing, the solution of the resulting $[Mn(CO)_5]Li$ was transferred to a THF solution of $[HC(SMe)_2]PF_6$ (0.12 g, 0.46 mmol) at -78°C using a cannula tube. The resulting mixture was slowly warmed to room temperature by removing the cold bath. The solvent was then removed under reduced pressure, and the resulting residue was loaded onto a 3x35 cm Florisil column and eluted with hexane. Two yellow bands were collected; the first band was identified by IR to be $Mn_2(CO)_{10}$; the second band was partially characterized and is believed to be $(CO)_5Mn[CH(SMe)_2]$ (7 mg, 5%).

$^1H(CDCl_3)$: 5.00(CH), 2.69(SMe)

Preparation of $\{Cp(CO)_2Fe[CH(SMe)]\}X;X:CF_3SO_3,[4],BF_4,[5]$ A rapidly stirred solution containing [2] (0.10 g, 0.35 mmol) in 15 ml of Et_2O was treated dropwise via a syringe with CF_3SO_3H until precipitation ceased (ca. 50 µl); a golden precipitate and MeSH, identified by its disagreeable odor, were found. The solvent was carefully removed by decantation, and the remaining solid was washed a few times with dry Et_2O and pumped dry to afford $\{Cp(CO)_2Fe[CH(SMe)]\}CF_3SO_3$,[4], (0.10 g, 74%). The complex is very sensitive to water and modestly to light and should be stored in the dark under N_2 at -20°C. Even taking those precautions, decomposition of [4] is apparent after 2 weeks of storage. Thus, it is best used immediately.

$IR(CH_2Cl_2)$: 2067 s, 2026 s (2069 s, 2029 s were previously reported)

$^1H(CF_3SO_3H)$: 15.79(CH), 5.86(Cp), 3.59(SMe)

(CD_2Cl_2): 14.86(br, CH), 5.11(Cp), 3.00(SMe)

A ^{13}C NMR spectrum of the compound was not obtained due to extensive decomposition during data acquisition even without the addition of $Cr(acac)_3$ which apparently accelerates the decomposition.

Like CF_3SO_3H, HBF_4-Et_2O also produced the corresponding carbene complex, $\{Cp(CO)_2Fe[CH(SMe)]\}BF_4$,[5], in 75% upon reaction with [2]. It exhibited similar spectral and stability characteristics to [4].

$IR(CH_2Cl_2)$: 2067 s, 2028 s

Preparation of $\{Cp(CO)_2Fe[CH(SMe)]\}PF_6$,[6] A solution of [2] (0.20 g, 0.70 mmol) in 15 ml of dry Et_2O was transferred via a cannula to a rapidly stirred solution of $(CPh_3)PF_6$ (0.18 g, 0.63 mmol) in 10 ml of CH_2Cl_2. The resulting orange solution was slowly warmed to room temperature; a yellow precipitate was formed. An additional 15 ml of Et_2O was added to induce further precipitation. The suspension was filtered through a fine frit, and the remaining solid was washed with Et_2O then dried under vacuum to afford the (0.20 g, 75%) crude product $\{Cp(CO)_2Fe[CH(SMe)]\}PF_6$,[6]. The substance is sparingly soluble in CH_2Cl_2 and was recrystallized from CH_2Cl_2/Et_2O to afford golden plate-like crystal of [6], though, it was found to occlude diethyl ether as established by its ^1H NMR spectrum.

IR(CH_2Cl_2): 2069 s, 2029 s

^1H (CD_2Cl_2): 15.24(br,CH), 5.15(Cp), 3.12(SMe)

^{13}C: not obtainable due to rapid decomposition in solution.

Reaction of $Cp(CO)_2FeCH_2SMe$,[7], and $(CPh_3)PF_6$ A sample of $(CPh_3)PF_6$ (0.15 g, 0.38 mmol) was added to a rapidly stirred CH_2Cl_2 solution of $Cp(CO)_2FeCH_2SMe$,[7], (0.10 g, 0.42 mmol)[63], synthesized from $[Cp(CO)_2Fe]Na$ and $ClCH_2SMe$, at -78°C. The solution was gradually warmed to room temperature, and an IR spectrum of the reaction mixture was obtained which revealed the presence of a small amount of [6](∿5%) and the disappearance of the iron thioether complex. Since little of the desired product was obtained, no further purification was conducted.

Preparation of $\{Cp(CO)_2Fe[CD(SMe)]\}CF_3SO_3$ A sample of [1] (0.10 g, 0.23 mmol) was suspended in 100 ml of THF, $Li(AlD_4)$ (0.025 g, 0.60 mmol) was added, and the mixture was allowed to stir for 20 min. The resulting brown solution was evaporated to dryness, and the remaining residue was extracted with hexane. Workup as for [2] gave $Cp(CO)_2Fe[CD(SMe)_2]$ (0.046 g, 70%). The crude product was then dissolved in 10 ml of Et_2O, and 30 µl of CF_3SO_3H was added. Following the established work up procedures for [4], $\{Cp(CO)_2Fe[CD(SMe)]\}CF_3SO_3$ (0.041 g, 65%) was isolated. The ν(CO) absorptions of this product are identical to those of [4].

<u>Reaction of $\{Cp(CO)_2Fe[CH(SMe)]\}CF_3SO_3$ with $MePPh_2$</u> Freshly prepared [4] (0.12 g, 0.31 mmol) was suspended in 10 ml of CH_2Cl_2; $MePPh_2$ (0.10 g, 0.51 mmol) was added. The mixture was stirred for 20 min, giving a golden yellow solution. The solvent was removed under vacuum, and the resulting oily residue was washed a few times to remove excess phosphine. The anion of the remaining oil was metathesized with KPF_6 in CH_3CN. Recrystallization from CH_2Cl_2-Et_2O at -20°C afforded deep orange crystals of $\{Cp(CO)_2Fe[CH(SMe)(MePPh_2)]\}PF_6$, [8], (0.13 g, 72%). Complex [8] is moisture and air stable and can be stored indefinitely at -20°C under an N_2 atmosphere.

Anal. calcd.: for $C_{22}H_{22}O_2SP_2F_6Fe$, C: 45.37, H: 3.78

Found: C: 46.00, H: 4.08

IR(CH_2Cl_2): 2021 s, 1971 s

$^1H(CD_3CN)$: 7.7(m, Ph), 5.16(Cp), 3.75(d, J_{PH} = 2.93, CH), 2.45(d, J_{PH} = 12.46, PMe), 1.36(d, J_{PH} = 0.73, SMe)

$^{13}C(CD_3CN)$: 214.5(CO), 134.7(d, J_{PC} = 3.9); 133-130; 127.7; 126.6; 124.3; 132.2 [Ph], 89.3(Cp), 22.5(SMe) 7.5(d, J_{PC} = 25.4, CH), 5.4 (d, J_{PC} = 11.72, PMe)

Reaction of $\{Cp(CO)_2Fe[CH(SMe)]\}BF_4$ with PPh_3 To a CH_2Cl_2 suspension of [5] (0.10 g, 0.31 mmol), PPh_3 (0.16 g, 0.62 mmol) was introduced. The mixture was stirred until all of [5] went into solution (ca. 30 min). The solvent was then removed under reduced pressure, and the residue was washed with Et_2O. It was recrystallized from CH_2Cl_2-Et_2O at -20°C giving $\{Cp(CO)_2Fe[CH(SMe)(PPh_3)]\}BF_4$, [9a], (0.16 g, 86%). Complex [9a] is a bright yellow, air-stable material; it may be stored at -20°C under an N_2 atmosphere for months with no noticeable physical changes.

Anal. Calcd.: $C_{27}H_{24}O_2PSF_4BFe$, C: 55.32, H: 4.10

Found: C: 55.23, H: 4.06

$IR(CH_2Cl_2)$: 2027 s, 1975 s

$^1H(CD_3CN)$: 7.35(m, Ph), 5.25(Cp), 4.28(d, J_{PH} = 1.46, CH) 1.67(d, J_{PH} = 0.74, SMe)

$^{13}C(CD_3CN)$: 215.5(d, J_{PC} = 5.86, CO), 213.0(CO), 135.1(d, J_{PC} = 7.81); 130.5(d, J_{PC} = 11.72); 125.7; 122.0; 120.6 [Ph], 89.7(Cp), 23.2(SMe), 6.0(d, J_{PC} = 25.39, CH)

Preparation of {Cp(CO)$_2$Fe[CH(SMe)(PPh$_3$)]}PF$_6$,[9b] Complex [4] (0.12 g, 0.31 mmol) was allowed to react with PPh$_3$ (0.16 g, 0.62 mmol) to give an oily product, the residue was metathesized with [NH$_4$]PF$_6$ in acetone. Upon workup and recrystallization from CH$_2$Cl$_2$-Et$_2$O at -20°C, {Cp(CO)$_2$Fe[CH(SMe)(PPh$_3$)]}PF$_6$,[9b], was obtained in 82% yield.

IR(CH$_2$Cl$_2$): 2027 s, 1975 s

^{31}P(CD$_3$CN): 31.7(PPh$_3$), -142.3(h, J_{PF} = 706.26, PF$_6^-$)

Preparation of {Cp(CO)$_2$Fe[CH(SMe)(PPh$_2$Cl)]}BF$_4$,[10] A freshly distilled sample of PPh$_2$Cl (0.14 g, 0.62 mmol) was injected into a suspension of [5] (0.10 g, 0.31 mmol) in 10 ml of CH$_2$Cl$_2$. The reaction was allowed to proceed for 30 min. Upon purification and recrystallization from CH$_2$Cl$_2$-Et$_2$O at -20°C, dark orange crystals of {Cp(CO)$_2$Fe[CH(SMe)(PPh$_2$Cl)]}BF$_4$,[10], (0.11 g, 62%) were obtained. The material decomposes when exposed to the ambient environment for a few hours.

IR(CH$_2$Cl$_2$): 2030 s, 1982 s

^{1}H(CD$_3$CN): 7.7(m, Ph), 5.21(Cp), 4.16(d, J_{PH} = 11.73, CH)
1.65(SMe)

^{13}C(CD$_3$CN): 214.4(d, J_{PC} = 5.86, CO), 213.2(CO), 136.3;
134.0; 133.6; 126.5; 122.7 [Ph], 89.3(Cp),
22.7(SMe), 12.7(d, J_{PC} = 15.62, CH)

Reaction of $\{Cp(CO)_2Fe[CH(SMe)]\}BF_4$ with PCl_3 A sample of [5] (0.10 g, 0.31 mmol) reacted with 100 µl of freshly distilled PCl_3 in 10 ml of CH_2Cl_2. An infrared spectrum of the solution showed two strong ν(CO) bands (2031, 1982 cm^{-1}) which are consistent with the phosphine adduct, $\{Cp(CO)_2Fe[CH(SMe)(PCl_3)]\}BF_4$,[11]. However, the product was not sufficiently stable to be isolated; thus, satisfactory NMR data for [11] were not obtained.

Preparation of $\{Cp(CO)_2Fe[CH(SMe)(P(OPh)_3)]\}PF_6$,[12] A sample of $P(OPh)_3$ (0.20 g, 0.67 mmol) was allowed to react with [4] (0.12 g, 0.31 mmol) in CH_2Cl_2 for 30 min. The resulting solution was pumped dry; the residue was metathesized with KPF_6 in MeCN, and recrystallized from CH_2Cl_2-Et_2O at -20°C, affording dark brown crystals of $\{Cp(CO)_2Fe[CH(SMe)(P(OPh)_3)]\}PF_6$,[12], (0.15 g, 72%). Compound [12] is quite stable toward moisture and air.

Anal. Calcd.: $C_{27}H_{24}O_5SP_2F_6Fe$, C: 46.83, H: 3.47

Found: C: 46.03, H: 3.66

IR(CH_2Cl_2): 2032 s, 1986 s

$^1H(CD_3CN)$: 7.35(m, Ph), 5.25(Cp), 3.41(d, J_{PH} = 7.33, CH) 2.12(d, J_{PH} = 1.71, SMe)

$^{13}C(CD_3CN)$: 214.5; 213.6 [CO], 150.7(d, J_{PC} = 13.68); 131.7; 128.3(d, J_{PC} = 3.90); 120.6 [Ph], 88.1(Cp), 20.5(SMe, 10.78(d, J_{PC} = 130.86, CH)

Preparation of $\{Cp(CO)_2Fe[CH(SMe)(P(OCH_2)_3CMe)]\}X$, X = CF_3SO_3([13a]), PF_6([13b]) A freshly sublimed sample of $P(OCH_2)_3CMe$ (0.10 g, 0.68 mmol) reacted with [4] (0.12 g, 0.31 mmol) to give a crude mixture of $\{Cp(CO)_2Fe[CH(SMe)(P(OCH_2)_3CMe)]\}CF_3SO_3$,[13a], upon evaporation. The mixture was washed with Et_2O and then recrystallized from CH_2Cl_2-Et_2O at -20°C to yield a golden powder of [13a] (0.14 g, 87%). This compound exhibits remarkable stability toward air; it eventually turned black when exposed to laboratory lighting for few days under N_2.

IR(CH_2Cl_2): 2041 s, 1992 s

Since [13a] was obtained in powder form and was not suitable for a single crystal X-ray determination, it was metathesized with $(NH_4)PF_6$ in acetone. [13b] was isolated in 64% yield from CH_2Cl_2-Et_2O at -20°C. Microscopic crystals were found which were suitable for X-ray analysis.

IR(CH_2Cl_2): 2042 s, 1992 s

$^1H(CD_3CN)$: 5.13(Cp), 4.74(d, J_{PH} = 5.37, OCH_2), 2.67(d, J_{PH} = 2.44, CH), 2.22(SMe), 0.94(CMe)

$^{13}C(CD_3CN)$: 214.0(d, J_{PC} = 3.66); 213.1[CO], 87.4(Cp), 80.7(d, J_{PC} = 6.1, OCH_2), 36.3(d, J_{PC} = 34.2, $\underline{C}Me$), 23.5(SMe), 13.0($C\underline{Me}$), -5.1(d, J_{PC} = 101.32, CH)

$^{31}P(CD_3CN)$: 60.4($P(OCH_2)_3CMe$), -142.3 (h, J_{PF} = 708.01, PF_6^-)

Crystal data {$Cp(CO)_2Fe[CH(SMe)(P(OCH_2)_3CMe)]$}$PF_6$, MW 530.0, monoclinic, $P2_1/c$, a = 10.359(3), b = 12.284(4), c = 16.234(4) Å, β = 95.25(3), V = 2056.9 Å^3, $\rho_{calcd.}$ = 1.711 g/cm^3, Z = 4.

Data acquisition The title compound yielded yellow plate-like crystals which were readily indexed using 12 independent reflections and an automatic indexing procedure.[64]

The data were collected at ambient temperature with graphite-monochromated Mo Kα (λ = 0.70979 Å) radiation on an automated four-circle diffractometer designed and built at the Ames Laboratory; ω-scan; 4151 reflections measured in almost 4 octants; $2\theta \leq 45°$; decomposition corrections applied; 2502 reflections with $I \geq 3\sigma_I$ after averaging; agreement between equivalent reflections is 4.2%.

The position of the Fe atom was located by analysis of a sharpened three-dimensional Patterson function. All the remaining non-hydrogen and H_1 atoms were found by successive structure factor and electron density map calculations; a combination of block and full-matrix least-square refinement[65] of all non-hydrogen atoms was carried out. As expected for the PF_6^-, packing disorder resulted in high conventional and weighted residuals of R = 0.082 and R_w = 0.109, respectively. The scattering factors[66] were modified for anomalous dispersion effects.[67] The bond angles (Table 5), bond distances (Table 6), final atom positional parameters (Appendix I), thermal parameters

(Appendix 2) and structural factors (Appendix 3) are summarized as indicated.

Pyrolysis of $\{Cp(CO)_2Fe[CH(SMe)(PPh_3)]\}BF_4$ A 13 mg sample of [9a] was sealed in a 2 ml prescored ampule under an atmosphere of N_2. The bottom 1/3 portion of the ampul was submerged in an oil bath maintained at 200°C for 2 min, gas evolution was apparent. The ampule was then removed from the bath and cooled to room temperature; it was broken open leaving a mixture of an amber oil and a brown residue. The oily product was separated from the mixture simply by extraction with CCl_4; it was found to consist of 4 major products by GC. They were determined by their GC-MS spectra to be cis and trans 1,2 bis(thiomethoxyl) ethylene, trithiomethoxylmethane and ferrocene. The remaining residue was recrystallized from CH_2Cl_2-Et_2O at -20°C, affording bright yellow crystals of $[Cp(CO)_2FePPh_3]BF_4$ (10.4 mg, 88%). This product was characterized by its IR and ^1H NMR spectra, which are consistent with reported data[68] for this compound.

GC-MS spectra of the CCl_4 solution (m/e)

Cis/trans MeSCH=CHSMe: 122(M + 2 for ^{34}S isotope; Calcd. 8.8%, found 8.6%), 120(M), 105(M-Me)

$HC(SMe)_3$: 156(M + 2 for ^{34}S isotope; Calcd. 13.2%, found 10.4%), 154(M), 107(M-SMe)

Cp_2Fe: 186(M), 121(M-Cp), 56(M-2Cp)

Pyrolysis of $\{Cp(CO)_2Fe[CH(SMe)(P(OCH)_3CMe]\}PF_6$ A 30 mg sample of [13b] was heated at 180°C for 2 min as described in the preceding experiment. The resulting material was recrystallized from CH_2Cl_2-Et_2O at -20°C affording a brown powder of $[Cp(CO)_2FeP(OCH_2)_3CMe]PF_6$ (17 mg, 65%). The complex was characterized by its IR, ^1H and ^{13}C NMR spectra, which are in accord with those of an authentic sample prepared from the reaction of $[Cp(CO)_2FeTHF]BF_4$[69] and $P(OCH_2)_3CMe$.

$IR(CH_2Cl_2)$: 2078 s, 2039 s

$^1H(CD_3CN)$: 5.44(d, J_{PH} = 1.22, Cp), 4.43(d, J_{PH} = 5.13, OCH_2), 1.93(CMe)

$^{13}C(CD_3CN)$: 206.7(d, J_{PC} = 39.06, CO), 88.7(Cp), 78.7(d, J_{PC} = 5.86 OCH_2), 33.0(d, 39.15, <u>C</u>Me), 14.4(C<u>Me</u>)

Synthesis of $\{Cp(CO)_2Fe[CH(SMe)(Ph_2PH)]\}CF_3SO_3$, [14] Diphenylphosphine (0.12 g, 0.64 mmol) was added to [4] (0.12 g, 0.31 mmol) in 10 ml of CH_2Cl_2. The mixture was stirred for 20 min and then diluted with 10 ml of heptane. The solution volume was gradually reduced in vacuo until complete precipitation occurred; this gave a bright yellow, malodorous solid. The material was dissolved in a minimum amount of $MeNO_2$ and a layer of diethylether was added to induce crystallization at -20°C; $\{Cp(CO)_2Fe[CH(SMe)(PPh_2H)]\}CF_3SO_3$, [14], (0.11 g, 62%) was isolated. Compound [14] is not very soluble in most organic solvents and only sparingly soluble in nitromethane.

Anal. Calcd.: $C_{22}H_{20}O_5S_2F_3PFe$, C: 46.16, H: 3.50

Found: C: 45.82, H: 3.54

IR(CH_2Cl_2): 2033 s, 1980 br

$^1H(CD_3CN)$: 7.72(m, Ph), 7.45(dd, J_{PH} = 501.31; J_{HH} = 10.63, PH), 5.14(Cp), 3.46(dd, J_{PH} = 1.47; J_{HH} = 10.63, CH), 1.59(d, J_{PH} = 0.73, SMe)

$^{13}C(CD_3NO_2)$: 214.9(d, J_{PC} = 5.86); 213.8[CO], 135-130(Ph), 88.5(Cp), 23.3(SMe), 5.6(d, J_{PC} = 21.49, CH)

Preparation of {Cp(CO)$_2$Fe[CH(SMe)(HPCy$_2$)]}CF$_3$SO$_3$,[15]. Into a CH_2Cl_2 solution of [4] (0.12 g, 0.31 mmol), HPCy$_2$ (0.10 g, 0.51 mmol) was introduced. Upon initial workup as in the preceding synthesis, 0.12 g crude product of {Cp(CO)$_2$Fe[CH(SMe)(HPCy$_2$)]}CF$_3$SO$_3$,[15], was obtained. The material was recrystallized from THF-hexane giving [15] (0.069 g, 39%). This material is bright yellow and is very soluble in polar organic solvents.

Anal. Calcd.: $C_{22}H_{32}O_5S_2F_3PFe$, C: 45.21, H: 5.48

Found: C: 45.47, H: 5.23

IR(CH_2Cl_2): 2025 s, 1975 s

$^1H(CD_3CN)$: 5.78(d, m, J_{PH} = 439, PH), 5.16(Cp), 3.18(d, d,

J_{PH} = 1.47, J_{HH} = 2.93, CH), 2.21(d, J_{PH} = 1.10, SMe), 1.83(m, Cy)

$^{13}C(CD_3CN)$: 216.2(br, CO), 215.0(CO), 89.2(Cp), 34-26(Cy), 23.3(SMe), -1.3(d, J_{PC} = 19.53, CH)

Synthesis of $\{Cp(CO)_2Fe[CH(SMe)(PhPH_2)]\}CF_3SO_3$,[16] Phenylphosphine (0.10 g, 0.90 mmol) was injected into a CH_2Cl_2 suspension of [4] (0.12 g, 0.31 mmol). After the reaction had proceeded for 20 min, a yellow homogeneous solution was obtained. It was diluted with 10 ml of heptane; slow evaporation under reduced pressure furnished a yellow precipitate. The solid was recrystallized from CH_2Cl_2-Et_2O at -20°C affording $\{Cp(CO)_2Fe[CH(SMe)(PhPH_2)]\}CF_3SO_3$,[16], (0.089 g, 58%).

Anal. Calcd.: $C_{16}H_{16}O_5S_2F_3PFe$, C: 38.72, H: 3.23

Found: C: 37.84, H: 3.29

$IR(CH_2Cl_2)$: 2036 s, 1987 s

$^1H(CD_3CN)$: 7.7(m, Ph), 7.25(d, m, J_{PH} = 482.02, PH), 6.98(d, m, J_{PH} = 502.18, PH), 5.18(Cp), 3.06(d, d, J_{PH} = 1.28, J_{HH} = 9.9, CH), 1.79(SMe)

$^{13}C(CD_3COCD_3)$: 213.3(br); 212.3[CO], 135-130(Ph), 87.6(Cp), 22.2(SMe), 1.5(d, J_{PC} = 11.72, CH)

Preparation of $\{Cp(CO)_2Fe[CH(SMe)(CyPH_2)]\}PF_6$, [17] The reaction of H_2PCy (0.10 g, 0.86 mmol) and [4] (0.12 g, 0.31 mmol) in 10 ml of CH_2Cl_2 for 20 min gave a gummy residue after workup in according to the procedures described in the preceding synthesis. Therefore, the residue was metathesized with KPF_6 in MeCN. Upon recrystallization, $\{Cp(CO)_2Fe[CH(SMe)(CyPH_2)]\}PF_6$, [17], (0.080 g, 52%) was obtained. Like the other adducts, [17] is stable in air and can be maintained indefinitely at -20°C under N_2.

Anal. Calcd.: $C_{15}H_{22}O_2F_6SP_2Fe$, C: 36.15, H: 4.42

Found: C: 36.99, H: 4.45

IR(CH_2Cl_2): 2036 s, 1986 s

$^1H(CDCl_3)$: 6.16(d, m, J_{PH} = 470.84, PH), 5.83(d, m, J_{PH} = 472.29, PH), 5.15(Cp), 2.87(d, m, J_{PH} = 7.7, CH), 2.29(SMe), 1.90-1.41(m, Cy)

$^{13}C(CD_3CN)$: 214.2(d, J_{PC} = 5.86, CO), 213.8(CO), 87.6(Cp), 31.8(d, J_{PC} = 37.11), 28.3, 26.5, 25.9[Cy], 22.4(SMe), -4.3(d, J_{PC} = 19.53, CH)

$^{31}P(CDCl_3)$: 13.2(t, J_{PH} = 470.84, H_2PCy), -143.5(h, J_{PF} = 710.62, PF_6^-)

Thermal rearrangement of $\{Cp(CO)_2Fe[CH(SMe)(HPPh_2)]\}CF_3SO_3$,[14]

A 35 mg sample of [14] sealed in a prescored ampule was heated at 168°C for 2 min, which turned it into a caramel-like substance. The ampule was allowed to cool to room temperature, then broken open. Its contents were washed with Et_2O and then extracted with CH_2Cl_2. Filtration and evaporation of the CH_2Cl_2 solution followed by recrystallization from CH_2Cl_2-Et_2O at -20°C afforded pale yellow crystals of $\{Cp(CO)_2Fe[PPh_2(CH_2SMe)]\}CF_3SO_3$,[18], (7 mg, 20%). This compound was identified by its IR, ^1H and ^{31}P NMR spectra.

$IR(CH_2Cl_2)$: 2057 s, 2012 s

$^1H(CD_3NO_2)$: 7.7 (m, Ph), 5.38 (d, J_{PH} = 1.46, Cp)
3.82 (d, J_{PH} = 6.1, CH_2), 1.99 (d, J_{PH} = 1.46, SMe)

$^{31}P(CD_3CN)$: 63.69

Thermal rearrangement of $\{Cp(CO)_2Fe[CH(SMe)(HPCy_2)]\}CF_3SO_3$,[15]

By a procedure analogous to that used in the rearrangement of [14], 20 mg of [15] was heated at 200°C for 2 min; 4 mg (20%) of $\{Cp(CO)_2Fe[PCy_2(CH_2SMe)]\}CF_3SO_3$,[19], was obtained. This compound was identified by its IR and ^1H NMR spectra.

$IR(CH_2Cl_2)$: 2049 s, 2005 s

$^1H(CD_3CN)$: 5.41 (d, J_{PH} = 1.47, Cp), 3.21 (d, J_{PH} = 9.53, CH_2), 2.32 (d, J_{PH} = 1.84, SMe), 1.83 (m, Cy)

Preparations of $Cp(CO)_2Fe[CH(SMe)(PPh_2)]$,[20] A THF suspension of [14] (0.020 g, 0.035 mmol) was chilled at -78°C with an acetone-dry ice bath. It was then treated with 19 μl of n-BuLi (2.5 M in hexane), and the mixture was warmed to room temperature slowly, producing a pale orange solution. The solvent was removed at reduced pressure, and the remaining residue was extracted with hexane to yield an air-sensitive glassy product of [20] (0.013 g, 78%) upon evaporation.

$IR(CH_2Cl_2)$: 2008 s, 1958 s

$^1H(C_6D_6)$: 7.9-7.1 (m, Ph), 4.36 (Cp), 3.50 (d, J_{PH} = 4.39, CH) 1.56 (SMe)

The hexane-insoluble portion was recrystallized from CH_2Cl_2-Et_2O at -20°C, after having been washed with diethylether, to provide $\{Cp(CO)_2Fe[PPh_2(CH_2SMe)]\}CF_3SO_3$,[18], (0.001 g, 5%).

Like n-buthyl lithium, a 10-fold excess of Et_3N also worked well for the deprotonation reaction in THF and CH_2Cl_2 at room temperature. Between 75-80% of [20] and 8-12% of [18] were isolated.

Reaction of $Cp(CO)_2Fe[CH(SMe)(PPh_2)]$,[20], with $MeOSO_2F$ Into a 10 ml CH_2Cl_2 solution containing freshly prepared [20] (0.013 g, 0.031 mmol) from [14] and Et_3N in CH_2Cl_2, 20 μl of $MeOSO_2F$ was injected. The solution was evaporated under reduced pressure to leave a glassy residue. It was then washed with Et_2O, metathesized with KPF_6 in MeCN, and recrystallized from CH_2Cl_2-Et_2O at -20°C giving [8] (0.015 g, 82%).

Reaction of $\{Cp(CO)_2Fe[CH(SMe)]\}CF_3SO_3$,[4], with pyridine A sample of 0.5 ml of pyridine was added to a 10 ml CH_2Cl_2 solution of [4] (0.24 g, 0.62 mmol); a golden solution was obtained. The solution was then evaporated to dryness and washed a few times with ether to remove a trace amount of [2] leaving an oily substance. That material was allowed to recrystallize from CH_2Cl_2-Et_2O at -20°C for 24 hours to yield $\{Cp(CO)_2Fe[CH(SMe)(Pyr)]\}CF_3SO_3$,[21] (0.11 g, 38%) and traces of [2], [7] and [37]. The remaining mother-liquor was then diluted with Et_2O and placed in a -20°C freezer for recrystallization. After a few days, golden plate-like crystals of [21] (0.078 g, 27%) were obtained. They are very sensitive to moisture and decompose upon prolonged exposure to light. They may be kept indefinitely at -20°C under an inert atmosphere.

Anal. Calcd.: $C_{15}H_{14}O_5S_2F_3NFe$; C: 38.71, N: 3.01, H: 3.01

Found: C: 39.47, N: 2.97, H: 3.13

IR(CH_2Cl_2): 2022 s, 1974 s

$^1H(CDCl_3)$: 9.31 (d, J_{HH} = 5.49); 8.30 (t, J_{HH} = 6.96); 7.92 (t, J_{HH} = 6.60) [Pyr], 6.42 (CH), 5.10 (Cp), 1.92 (SMe)

$^{13}C(CDCl_3)$: 213.6; 213.2 [CO], 143.0; 141.9; 128.2 [Pyr], 87.2 (Cp), 64.5 (CH), 19.8 (SMe)

Synthesis of $\{Cp(CO)_2Fe[CH(NMe_2)]\}PF_6$, [22] A sample of [4] (0.24 g, 0.62 mmol) was suspended in 10 ml of CH_2Cl_2; 15 ml of gaseous Me_2NH was bubbled into the solution via a syringe. The golden solution turned yellow-brown. The solution was diluted with 10 ml of heptane; its volume was reduced to one-half under vacuum, and the remaining solvent was decanted affording a brown residue. The product was metathesized with $(NH_4)PF_6$ in acetone, recrystallized from CH_2Cl_2-Et_2O at -20°C to furnish [22] (0.070 g, 30%).

Anal. Calcd.: $C_{10}H_{12}O_2NPF_6Fe$; C: 31.68, H: 3.17, N: 3.70

Found: C: 31.68, H: 3.16, N: 3.49

IR(CH_2Cl_2): 2049 s, 2005 s

$^1H(CD_3CN)$: 10.79 (CH), 5.30 (Cp), 1.94 (d, J_{HH} = 2.6, NMe)
1.89 (d, J_{HH} = 2.2, NMe)

$^{13}C(CD_3CN)$: 234.9 (CH), 211.8 (CO), 88.8 (Cp), 55.9; 47.7
[NMe]

Synthesis of $\{Cp(CO)_2Fe[CH(NEt_2)]\}CF_3SO_3$, [23] Diethylamine (65 µl, 0.62 mmol) was added to a rapidly-stirred CH_2Cl_2 suspension of [4] (0.24 g, 0.62 mmol) and allowed to react for 2 min. Subsequent follow-up as described previously for [22] afforded, [23], (0.079 g, 31%).

IR(CH_2Cl_2): 2048 s, 2004 s

^1H(CD_3COCD_3): 11.30 (CH), 5.59 (Cp), 3.99 (q, J_{HH} = 7.3, NCH_2)
3.96 (q, J_{HH} = 7.3, NCH_2), 1.47 (t, J_{HH} = 7.3,
Me), 1.36 (t, J_{HH} = 7.3, Me)

^{13}C(CD_3CN): 232.4 (CH), 211.7 (CO), 88.9 (Cp), 58.8; 53.2
[NCH_2], 14.4; 13.2 [$NCH_2\underline{Me}$]

<u>Reaction of {Cp(CO)$_2$Fe[CH(SMe)(Pyr)]}CF_3SO_3,[21], with Et_2NH</u>

Diethylamine (14 µl, 0.12 mmol) was injected into a 5 ml CH_2Cl_2 solution containing [21] (0.03 g, 0.06 mmol). Subsequently, 10 ml of heptane was added. The resulting solution was slowly evaporated under vacuum until the bulk of the CH_2Cl_2 was removed; precipitation was apparent. The rest of the heptane was decanted, leaving a pale yellow precipitate. It was then recrystallized from CH_2Cl_2-Et_2O at -20°C to afford [23] (0.10 g, 42%).

<u>Synthesis of {Cp(CO)$_2$Fe[CH(NHMe)]}PF_6,[24]</u> Ten ml of gaseous methylamine was bubbled into a 10 ml CH_2Cl_2 solution containing [4] (0.24 g, 0.62 mmol). The resulting solution was stirred for 2 min and was then evaporated to dryness under reduced pressure; the remaining residue was then washed with Et_2O to remove [2], metathesized with $(NH_4)PF_6$ in acetone and recrystallized from CH_2Cl_2-Et_2O at -20°C to give [24] (0.063 g, 28%).

Anal. Calcd.: $C_9H_{10}O_2NPF_6Fe$: C: 29.50, N: 3.84, H: 2.74

Found: C: 29.72, N: 3.58, H: 2.75

IR(CH_2Cl_2): 2055 s, 2007 s

$^1H(CD_3CN)$: 10.90 (NH), 10.69 (CH), 5.29 (Cp), 3.33 (d, J_{HH} = 3.3, NMe)

$^{13}C(CD_3CN)$: 238.6 (CH), 211.2 (CO), 88.6 (Cp), 45.8 (NMe)

Preparation of {$Cp(CO)_2Fe[CH(NHCy)]$}CF_3SO_3, [25] To a 10 ml CH_2Cl_2 solution of [4] (0.24 g, 0.62 mmol), cyclohexylamine (80 µl, 0.62 mmol) was added. The mixture was stirred for 2 min and was then diluted with 10 ml of heptane. After the solution volume was reduced to one-half under reduced pressure, a yellow solution containing [2], and a pale yellow precipitate were evident. The solution was decanted, and the resulting residue was washed with Et_2O and then recrystallized from CH_2Cl_2-Et_2O at -20°C affording pale yellow analytically pure crystals of [25] (0.094 g, 35%). This substance is stable in air and may be stored indefinitely in the dark at -20°C under N_2.

Anal. Calcd.: $C_{15}H_{18}O_5NF_3SFe$, C: 41.20, H: 4.12, N: 3.20

Found: C: 41.23, H: 4.25, N: 3.16

IR(CH_2Cl_2): 2054 s, 2004 s

$^1H(CD_2Cl_2)$: 10.76 (CH), 10.55 (NH), 5.25 (Cp), 3.52 (br); 1.56 (m) [Cy]

$^{13}C(CD_3CN)$: 235.1 (CH), 211.3 (CO), 88.8 (Cp), 69.9; 32.5; 25.3; 25.1 [Cy]

Synthesis of $\{Cp(CO)_2Fe[CD(NHCy)]\}CF_3SO_3$,[26] A freshly prepared sample of $\{Cp(CO)_2Fe[CD(SMe]\}CF_3SO_3$ (0.10 g, 0.26 mmol) was allowed to react with 32 μl (0.26 mmol) of cyclohexylamine in 10 ml of CH_2Cl_2. Purification as in the preceding procedure afforded [26] (0.36 g, 32%).

$IR(CH_2Cl_2)$: 2053 s, 2007 s

$^1H(CD_2Cl_2)$: 11.63 (br, NH), 5.25 (Cp), 3.49 (br); 1.56 (m) [Cy]

$^{13}C(CD_3CN)$: 234.5 (t, J_{CD} = 23.44, CD), 211.3 (CO), 88.8 (Cp), 69.8; 32.5; 25.3; 25.1 [Cy]

Synthesis of $\{Cp(CO)_2Fe[CH(NHPr^i)]\}PF_6$,[27] As in the preparation of [24], the reaction of i-propylamine (0.036 g, 0.62 mmol) and [4] (0.24 g, 0.62 mmol) in 10 ml of CH_2Cl_2 afforded [27] (0.074 g, 30%).

$IR(CH_2Cl_2)$: 2053 s, 2005 s

$^1H(CDCl_3)$: 10.85 (CH), 10.64 (NH), 5.28 (Cp), 3.89 (h, J_{HH} = 6.6, $NC\underline{H}Me_2$), 1.38 (d, J_{HH} = 6.6, $NCH\underline{Me}_2$)

^{13}(CD$_3$CN): 234.5 (CH), 211.5 (CO), 88.8 (Cp), 63.3 (N$\underline{C}$HMe$_2$)
21.8 (NCH$\underline{Me}_2$)

Synthesis of {Cp(CO)$_2$Fe[CH(NHBu^t)]}CF$_3$SO$_3$,[28] Analogous to the preparation of [25], the reaction of t-butylamine (0.045 g, 0.62 mmol) and [4] (0.24 g, 0.62 mmol) in CH$_2$Cl$_2$ produced a 0.15 g mixture of [28] and (NH$_3$Bu^t)CF$_3$SO$_3$ upon recrystallization from CH$_2$Cl$_2$-Et$_2$O at -20°C. The mixture was dissolved in 5 ml of CH$_2$Cl$_2$, and 100 µl of NaOH-saturated EtOH was added. The solution was allowed to react for 2 min and was then pumped to dryness. The resulting residue was extracted with hexane to give a golden solution after it had been filtered through a Celite-padded frit under N$_2$. The ether solution was treated with CF$_3$SO$_3$H until precipitation was completed (ca. 35 µl). The precipitate was recrystallized from CH$_2$Cl$_2$-Et$_2$O at -20°C affording analytically pure crystals of [28] (0.097 g, 38%).

Anal. Calcd.: C$_{13}$H$_{16}$O$_5$F$_3$SNFe; C: 37.96, N: 3.41, H: 3.89

Found: C: 37.55, N: 3.44, H: 4.00

IR(CH$_2$Cl$_2$): 2055 s, 2007 s

^{1}H(CDCl$_3$): 10.83 (CH), 10.63 (NH), 5.27 (Cp), 1.42 (Bu)

^{13}C(CD$_3$CN): 231.2 (CH), 212.5 (CO), 89.7 (Cp), 66.5 (NC),
29.0 (NC$\underline{Me}_3$)

Reaction of {Cp(CO)$_2$Fe[CH(SMe)(Pyr)]}CF$_3$SO$_3$,[21], with t-BuNH$_2$ A sample of t-BuNH$_2$ (12 µl, 0.12 mmol) was added to [21] (0.030 g, 0.064 mmol) in 5 ml of CH$_2$Cl$_2$; the resulting solution was stirred for 10 min. The solvent was then removed under reduced pressure, and the residue was recrystallized from CH$_2$Cl$_2$-Et$_2$O at -20°C to provide [28] (0.012 g, 47%).

Reaction of {Cp(CO)$_2$Fe[CH(SMe)(Pyr)]}CF$_3$SO$_3$ with NH$_3$ A 5 ml gas sample of NH$_3$ was bubbled slowly (ca. 30 sec) into a rapidly stirred 10 ml CH$_2$Cl$_2$ solution of [21] (0.030 g, 0.064 mmol); as soon as the addition of ammonia was completed, the solution was diluted with 10 ml of heptane. The solution volume was reduced to one-half by fast evaporation under reduced pressure. The remaining solvent was decanted, yielding a pale yellow precipitate. It was then recrystallized from CH$_2$Cl$_2$-Et$_2$O at -20°C to give {Cp(CO)$_2$Fe[CH(NH$_2$)]}CF$_3$SO$_3$,[29], (4 mg, 20%). It is quite stable to air and only soluble in very polar organic solvents, e.g., CH$_2$Cl$_2$, MeCN.

IR(CH$_2$Cl$_2$): 2056 s, 2010 s

^{1}H(CD$_3$CN): 11.51 (m, NH$_2$), 11.30 (m, CH), 5.33 (Cp)

Preparation of Cp(CO)$_2$Fe[CH(NCy)],[30] To a 2 ml CH$_2$Cl$_2$ solution of [25] (0.030 g, 0.069 mmol), 100 µl of NaOH-saturated EtOH was added; the light yellow solution turned gold at once. The solution was evaporated to dryness under reduced pressure; the remaining residue was extracted with hexane. The extract was then filtered through a Celite-padded frit under N_2 and pumped dry under vacuum, giving a thin yellow film of [30] (0.015 g, 78%). Compound [30] is very sensitive to air and decomposes at room temperature under N_2 when allowed to stand for a few hours to give $[Cp(CO)_2Fe]_2$ and cyclohexylisocyanide which was identified by its characteristic odor.

IR(hexane): 2030 s, 2021 s, 2013 s, 1982 sh, 1971 vs,
1963 s

$^1H(CDCl_3)$: 10.18 (d, J_{HH} = 1.79, CH), 10.15 (CH), 4.90;
4.85 [Cp], 2.91 (m); 1.58 (m) [Cy]

Like the NaOH-EtOH reaction, the reaction of [25] with 50% NaH-mineral oil also produced a 75% yield of [30] under similar conditions.

Preparation of $Cp(CO)_2Fe[CH(NPr^i)]$,[31] Analogous to the preparation of [30], the reaction of [27] (0.030 g, 0.076 mmol) and 100 µl of NaOH-saturated EtOH in 2 ml of CH_2Cl_2 produced [31] (0.013 g, 68%).

IR(hexane): 2028 sh, 2014 s, 1980 sh, 1971 s, 1963 s

$^1H(CDCl_3)$: 10.21; 10.16 [d, J_{HH} = 2.20, CH], 4.94; 4.91 [Cp]
3.20 (m); 1.17 (d, J_{HH} = 6.23); 1.22 (d, J_{HH} =
6.23) [i-Pr]

Synthesis of $Cp(CO)_2Fe[CH(NBu^t)]$,[32] Following the preparation of [30], [28] (0.030 g, 0.73 mmol) reacted with 100 µl of NaOH-EtOH to yield [32] (0.014 g, 76%).

IR(hexane): 2019 s, 1972 vs

$^1H(CDCl_3)$: 10.22 (CH), 4.84 (Cp), 1.10 (Me)

Reaction of $Cp(CO)_2Fe[CH(NCy)]$ with $MeOSO_2F$ Freshly prepared [30] (0.015 g, 0.052 mmol) using the NaOH-EtOH route was dissolved in 2 ml of Et_2O. The solution was stirred vigorously and 45 µl (0.50 mmol) of $MeOSO_2F$ was injected, a pale yellow precipitate formed. The solution was carefully decanted, leaving the precipitate which was then washed with Et_2O a few times and pumped to dryness in vacuo to furnish a E/Z mixture of $\{Cp(CO)_2Fe[CH(N(Me)Cy)]\}SO_3F$,[33], (0.010 g, 88%) with a 26:74 ratio.

$IR(CH_2Cl_2)$: 2049 s, 2003 s, 1998 sh

$^1H(CD_3CN)$: 11.03; 10.84 [CH], 5.32; 5.31; 5.30 [Cp],
3.8, 1.6 [m, Cy], 3.48 (d, J_{HH} = 0.74, NMe),
3.44 (d, J_{HH} = 1.10, NMe)

When 6 eqv. of $MeOSO_2F$ was used in the above reaction, the E/Z ratio was 83:17; it was 90:10 in the reaction with 3 eqv. of $MeOSO_2F$.

Reaction of $Cp(CO)_2Fe[CH(NPr^i)]$ with $MeOSO_2F$ Under the conditions described above, the reaction of [31] (0.013 g, 0.053 mmol) and $MeOSO_2F$ (25 µl, 0.30 mmol) gave a E/Z mixture of $\{Cp(CO)_2Fe[CH(N(Me)(Pr^i)]\}SO_3F$,[34] (0.013 g, 77%) with a 62:38 ratio. Likewise, [34] was isolated in 74% yield and contained a 95:5 E/Z ratio of isomeric products when three eqv. of $MeOSO_2F$ was employed in the reaction.

IR(CH_2Cl_2): 2044 s, 2000 s

$^1H(CD_3CN)$: 11.04; 10.83 [CH], 5.32; 5.30 [Cp], 4.20; 3.90 [h, J_{HH} = 6.60, N$\underline{C}$HMe$_2$], 3.45 (d, J_{HH} = 0.73, NMe), 3.42 (d, J_{HH} = 0.74, NMe), 1.36; 1.32 (d, J_{HH} = 6.60, NCH$\underline{Me}_2$

<u>Reaction of {Cp(CO)$_2$Fe[CH(NHCy)]}CF_3SO_3,[25], with H_2NR</u> A 5 mg (0.01 mmol) sample of [25] was dissolved in 1 ml of CH_2Cl_2; 5 µl (0.05 mmol) of $CyNH_2$ was injected. The mixture was stirred for half an hour. After that time, the IR spectrum of the solution showed that ∿75% of [25] had been consumed, and $Cp(CO)_2FeH$ (2010 s, 1958 vs) and NN'-dicyclohexylforamidinium (1712 vs) had formed. The solvent was pumped out and the remaining solid was found to contain $[Cp(CO)_2Fe]_2$ and the organic product; this solid was extracted with Et_2O, and its mass spec. was obtained.

MS of [CyNHCHNHCy]CF_3SO_3

m/e: 209 (M = CyNHCHNHCy), 208 (M-H), 110 (M-$CyNH_2$)

Under the same conditions, 5 eqv. of NH_2Me also converted 75% of [25] to $Cp(CO)_2FeH$ and a mixture of (RNHCHNHR')CF_3SO_3, (R = Cy, Me, R' = Cy, Me), in 20 min. The (MeNHCHNHCy)CF_3SO_3 compound was the major product on the basis of the mass spectrum.

MS of [CyNHCHNHMe]CF_3SO_3

m/e: 141 (M = CyNHCHNHMe), 140 (M-H), 110 (M-$MeNH_2$)

The reaction of t-$BuNH_2$ with [25] was noticeably slower, and 20 eqv. of the amine was needed to observe appreciable reaction.

Reaction of {Cp$(CO)_2$Fe[CD(NHCy)]}CF_3SO_3,[26], with NH_2Cy A 30 mg (0.068 mmol) sample of [26] reacted with 60 µl (0.30 mmol) of $CyNH_2$ in 5 ml of CH_2Cl_2. After 30 min of reaction, the solution was evaporated and the mixture was analyzed by MS; the spectrum demonstrated that the deuterium was incorporated into the foramidinium product. After MS study, the sample was allowed to react with n-BuLi in THF to afford CyNHCDNCy, whose NMR spectrum in CD_3CN showed no 7.31 δ resonance for the CHN_2 proton which was observed in the hydrogen analog.

MS for [CyNHCDNHCy]CF_3SO_3

m/e: 210 (M = CyNHCDNHCy), 209 (M-H), 111 (M-$CyNH_2$)

Decarbonylation of {Cp$(CO)_2$Fe[CH(NHCy)]}CF_3SO_3 Into a 5 ml solution of [25] (0.030 g, 0.068 mmol) was injected 670 µl of a 0.123 M acetonitrile solution of Me_3NO; the pale yellow solution turned yellow-red instantly. The solution was allowed to stir for an additional 10 min and was evaporated to dryness in vacuo. Extraction with CH_2Cl_2 and evaporation of the solvent gave {Cp(CO)(MeCN)Fe[CH(NHCy)]}CF_3SO_3, [36], (0.028, 93%).

A 0.10 g sample of [25] was added to a quartz tube equipped with a magnetic stir bar and a water cooling probe; then 35 ml of acetonitrile was added. The solution was irradiated with UV light at 254 nm for 2 hours at an ambient temperature which was maintained by running water through the cold finger; a brown solution was obtained. Evaporation and recrystallization from CH_2Cl_2-Et_2O-hexane at -20°C afforded golden cystals of [36] (0.086 g, 85%).

Anal. Calcd.: $C_{16}H_{21}O_4N_2SF_3Fe$; C: 42.67, H: 4.67, N: 6.22

Found: C: 43.28, H: 4.70, N: 6.08

IR(CH_2Cl_2): 1994

^1H($CDCl_3$): 11.84 (NH), 11.62 (CH), 4.76 (Cp), 3.56 (m); 1.88-1.26 (m) [Cy], 2,35 (Me)

^{13}C($CDCl_3$): 243.9 (CH), 216.1 (CO), 133.7 (CN), 83.7 (Cp), 69.1; 32.1; 24.8; 24.6 [Cy], 5.1 (Me)

Reaction of {Cp(CO)$_2$Fe[CH(SMe)]}CF_3SO_3 with ROH (R = Me, H) To a 5 ml CH_2Cl_2 solution of [4] (0.10 g, 0.26 mmol), 100 µl of doubly distilled-degassed H_2O was added; the solution was stirred for 10 min. During this time, MeSH liberation was evident by its odor and GC. The solvent was evaporated under reduced pressure. The resulting residue was extracted with benzene to give 28 mg (45%) of [7]. The remaining residue was found to contain 42 mg (46%) of [37]. The identical reaction was repeated and the crude mixture was analyzed by ^1H NMR. On the base of the integrated Cp resonance areas, the [7]:[37] ratio was 1:1.

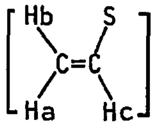
A 0.10 g (0.26 mmol) sample of [4] was suspended in 1 ml of CH_2Cl_2; 0.83 g (26 mmol) of dry MeOH was added. The mixture was stirred for 10 min and the gas phase above the solution was withdrawn by a gas-tight syringe and injected into the GC; the presence of CO, CH_4, MeSH and the solvent were established by comparing retention times with authentic samples. The solution was evaporated in vacuo, and the residue was dissolved in CD_3CN for ^1H NMR analysis. On the basis of the integrated Cp resonance areas, the relative concentrations of [37]:[7] were 60:40. The yield of this crude mixture was about 88%.

Reaction of $\{Cp(CO)_2Fe[CD(SMe)]\}CF_3SO_3$ with H_2O Following the procedure for the reaction of [4] and H_2O, $\{Cp(CO)_2Fe[CD(SMe)]\}CF_3SO_3$ was allowed to react with H_2O in CH_2Cl_2 for 10 min. After evaporation to dryness, the residue was extracted with benzene. A mass spectrum of this solution showed m/e fragments for $Cp(CO)_2FeCD_2SMe$ (m/e: 212 (M-CO), 184 (M-2CO)) which was the sole product.

Reaction of $[Cp(CO)_2FeCH(SMe)]CF_3SO_3$ with CH_2N_2 To a 10 ml CH_2Cl_2 solution containing [4] (0.17 g, 0.44 mmol), anhydrous CH_2N_2-Et_2O[55] was added dropwise until the evolution of N_2 ceased (ca. 1 ml). The resulting orange solution was allowed to stir for 45 min, and a yellow solution was obtained. The solvent was removed under reduced pressure, and the oily residue was then washed with Et_2O. Extraction of the oil with 10 ml of CH_2Cl_2, filtering the extract, and evaporating the solvent gave a yellow oil of $\{Cp(CO)_2Fe[SMe(CH{=}CH_2)]\}CF_3SO_3$, [38], (0.13 g, 76%). The oil was recrystallized from dichloromethane/ethanol/cyclohexane at room temperature for a few days, affording red needle crystals of [38] (0.02 g, 10%).

$IR(CH_2Cl_2)$: 2062 s, 2019 s

$^1H(CD_3CN)$:



6.31 (m, H_c); 5.81 (m, J_{HaHc} = 8.98, Ha); 5.71 (m, J_{HbHc} = 16.50, Hb), 5.38 (Cp), 2.47 (SMe)

$^{13}C(CD_2Cl_2)$: 208.4 (CO), 130.8 (=CH), 124.1 (H_2C=), 87.7 (Cp) 25.3 (SMe)

<u>Synthesis of $\{Cp(CO)(PPh_3)Fe[CH(SMe)]\}CF_3SO_3$, [41]</u> To 10 ml of a THF solution of $\{Cp(CO)(PPh_3)Fe[C(SMe)_2]\}PF_6$, [39], (0.10 g, 0.15 mmol), $(Et_3BH)Li$ (0.16 ml, 0.16 mmol) was added dropwise, and the mixture was allowed to react for 30 min. The solvent was then removed in vacuum, and the remaining residue was extracted with 20 ml of the mixture of hexane-diethylether (75:25) giving a yellow oil of $Cp(CO)(PPh_3)FeCH(SMe)_2$, [40], (0.048 g, 62%) upon evaporation. Complex [40] had its ν(CO) absorption at 1960 cm^{-1} in hexane. This oily [40] was then dissolved in 5 ml of Et_2O, and 50 μl of CF_3SO_3H was injected into the solution, providing a bright yellow solution and oil. The solution was decanted, and the yellow oil was established by IR and ^1H NMR spectrum to be [41] (0.041 g, 71%). The crude substance obtained

here was not readily recrystallized; it is slightly soluble in Et_2O and resists hydrolysis.

IR(CH_2Cl_2): 2006

$^1H(CD_3CN)$: 14.94 (CH), 7.4 (m, Ph), 4.84 (d, J_{PH} = 1.10, Cp), 2.99 (d, J_{PH} = 0.73, SMe)

Synthesis of $\{Cp(CO)(P(OPh)_3)Fe[CH(SMe)]\}CF_3SO_3$, [44] As in the reaction of [39], $\{Cp(CO)(P(OPh)_3)Fe[C(SMe)_2]\}PF_6$, [42] (0.10 g, 0.13 mmol) reacted with $(Et_3BH)Li$ (0.15 ml, 0.15 mmol) to give a yellow oil of $Cp(CO)(P(OPh)_3)Fe[CH(SMe)_2]$, [43], (0.056 g, 76%), which had a ν(CO) band at 1963 in hexane. The crude [43] further reacted with CF_3SO_3H (50 μl) in 5 ml of Et_2O to provide a yellow oil of [44] (0.047 g, 72%). Although it could not be recrystallized from CH_2Cl_2-Et_2O, spectral characterization indicated that it was quite pure. Like [41], [44] is moisture-stable.

IR(CH_2Cl_2): 2011

$^1H(CD_3CN)$: 14.92 (CH), 7.27 (m, Ph), 4.79 (d, J_{PH} = 1.10), 2.96 (SMe)

$^{13}C(CD_3CN)$: 320.6 (d, J_{PC} = 33.21, CH), 212.2 (d, J_{PC} = 39.07, CO), 150.5 (d, J_{PC} = 9.7); 130.7; 126.5; 121.0 (d, J_{PC} = 5.85) [Ph], 34.6 (SMe)

Preparation of $\{Cp(CO)(P(OPh)_3)Fe[CH(NEt_2)]\}CF_3SO_3$,[45] A freshly prepared sample of [44] (0.094 g, 0.14 mmol) was taken up in 10 ml of CH_2Cl_2; Et_2NH (27 µl, 0.28 mmol) was added. After the addition of amine, 5 ml of heptane was added to the solution, and the solution volume was slowly reduced to 1/3 its original size; a pale yellow precipitate formed. The remaining solvent was carefully decanted, and the precipitate was recrystallized from CH_2Cl_2-Et_2O at -20°C to afford bright yellow crystals of [45] (0.054 g, 56%).

Anal. Calcd.: $C_{30}H_{31}NO_7F_3PSFe$; C: 51.95, H: 4.47, N: 2.02

Found: C: 51.61, 4.41, 1.87

IR(CH_2Cl_2): 1981

$^1H(CD_3COCD_3)$: 11.36 (d, J_{PH} = 5.13, CH), 7.41 (m, Ph), 4.82 (d, J_{PH} = 1.10, Cp), 4.11 (q, J_{HH} = 7.33, NCH_2), 3.89 (q, J_{HH} = 7.33, NCH_2), 1.44 (t, J_{HH} = 7.33, $NCH_2\underline{Me}$), 1.30 (t, J_{HH} = 7.33, NCH_2Me)

$^{13}C(CD_3CN)$: 239.0 (d, J_{PC} = 39.07, CH), 216.6 (d, J_{PC} = 41.02, CO), 151.5 (d, J_{PC} = 9.77); 131.4; 127.1; 121.9 (d, 3.82) [Ph], 86.6 (Cp), 60.1; 52.1 [NCH_2], 14.8; 13.9 [$NCH_2\underline{Me}$]

RESULTS AND DISCUSSION

Synthesis of $Cp(CO)_2Fe[CH(SMe)_2]$

The preparation of [2] was previously reported by McCormick and Angelici,[27] accomplished simply by reacting $\{Cp(CO)_2Fe[C(SMe)_2]\}PF_6$,[1], with $LiAlH_4$ in THF (Eqn. 25).

$$\underset{[1]}{\{Cp(CO)_2Fe[C(SMe)_2]\}PF_6} + LiAlH_4 \longrightarrow \underset{[2]}{Cp(CO)_2Fe[CH(SMe)_2]} \qquad (25)$$

Although this reaction proceeds smoothly and the yield reaches 85%, it is limited to small scale. Attempts to extend reaction 25 to larger scales were uniformally unsuccessful, and the major identifiable product is $[Cp(CO)_2Fe]_2$,[3]. Thus, alternative procedures for synthesizing [2] were sought. Bodnar and Cutler[32] demonstrated that $[Et_3BH]Li$ is capable of donating hydride to $Cp(CO)_2Fe[C(Me)(OMe)]^+$ under mild conditions to furnish the ether product (Eqn. 26).

$$Cp(CO)(L)Fe[C(Me)(OMe)]^+ + [Et_3BH]Li \searrow Cp(CO)(L)Fe[CH(Me)(OMe)] \qquad (26)$$

$L = CO, PPh_3, P(OPh)_3$

As anticipated, [1] is readily transformed to [2] in the presence of the borohydride at room temperature in a respectable 85% yield, and the reaction can easily be increased to a several gram scale (Eqn. 27).

$$\underset{[1]}{\{Cp(CO)_2Fe[C(SMe)_2]\}PF_6} + [Et_3BH]Li \longrightarrow \underset{[2]}{Cp(CO)_2Fe[CH(SMe)_2]} \tag{27}$$

To our surprise, the mild hydride donating agent, $Li[(t\text{-}OBu)_3AlH]$ also works well. However, [2] prepared by this method is often contaminated with a small amount of a white inert substance which is probably an aluminum-containing material (Eqn. 28).

$$\begin{array}{l} \underset{[1]}{\{Cp(CO)_2Fe[C(SMe)_2]\}PF_6} + Li[(t\text{-}OBu)_3AlH] \\ \qquad\qquad\qquad\qquad\qquad\searrow \\ \qquad\qquad\qquad\qquad\qquad\qquad \underset{[2]}{Cp(CO)_2Fe[CH(SMe)_2]} \end{array} \tag{28}$$

Nevertheless, the aluminum hydride is easier to handle and more cost effective than the borohydride, and the resulting [2] from Equation 28 is suitable for further studies.

Compound [2] is a bright yellow, air-sensitive material. It is readily dissolved in most organic solvents, and displays two strong $\nu(CO)$ absorptions (2019, 1975 cm^{-1}) in hexane.

Attempted Preparation of [2]

Although [2] has been successfully prepared via the previously described methods, the overall procedure is nevertheless laborious. To improve accessibility to [2], a more direct synthetic method was desired. The reaction of $[Cp(CO)_2Fe]Na$ and $[HC(SMe)_2]PF_6$,[59] (Eqn. 29), was attempted.

$$Na[Cp(CO)_2Fe] + [HC(SMe)_2]PF_6 \longrightarrow \underset{[3]}{[Cp(CO)_2Fe]_2} \qquad (29)$$

Instead of [2], [3] is the sole identifiable organometallic product. The formation of [3] is presumed to occur by oxidation of the anion, credited to its low oxidation potential.[70] That conclusion was also reached by Hartshorn et al.[14] who attempted the synthesis of $\{Cp(CO)_2Fe[CH(NMe_2)]\}^+$ from $(Me_2NCH_2)Cl$ and the organometallic anion. With a less reducing anion, $[Mn(CO)_5]^-$, however, approximately 5% of $(CO)_5Mn[CH(SMe)_2]$ is obtained (Eqn. 30). Although the complex has not been fully characterized, its ^1H NMR spectrum is consistent with the formulation.

$$[(CO)_5Mn]Na + [HC(SMe)_2]PF_6 \longrightarrow (CO)_5Mn[CH(SMe)_2] + NaPF_6 \atop {+ \atop Mn_2(CO)_{10}} \qquad (30)$$

Synthesis of
$\{Cp(CO)_2Fe[CH(SMe)]\}X$, ($X = CF_3SO_3$, BF_4)

Complex [2] is very sensitive to acid and readily gives the carbene, $\{Cp(CO)_2Fe[CH(SMe)]\}CF_3SO_4$,[4], and $\{Cp(CO)_2Fe[CH(SMe)]\}BF_4$,[5], with the liberation of MeSH, upon reaction with CF_3SO_3H and HBF_4-Et_2O, respectively in diethylether (Eqn. 31). The yields for these reactions are good.

$$Cp(CO)_2Fe[CH(SMe)_2] \xrightarrow{HX} \{Cp(CO)_2Fe[CH(SMe)]\}X + MeSH \qquad (31)$$

[2]

	X	%
[4]	CF_3SO_3	74
[5]	BF_4	75

Compounds [4] and [5] are bright yellow powders which are stable to O_2 but decompose upon exposure to moisture and gradually decompose under N_2 to an indentified dark brown substance upon exposure to light for several days. These compounds can not be isolated without being contaminated by an appreciable amount of $Cp(CO)_3Fe^+$,[37]. [4] and [5] are sparingly soluble in CH_2Cl_2 and dissolve readily in polar, THF and CH_3CN, and protic, CF_3SO_3H, solvents.

Infrared spectra of [4] and [5] are similar, exhibiting two strong ν(CO) absorptions in CH_2Cl_2: 2067, 2026; 2067, 2028 cm^{-1}, respectively. These bands are an average of 17 cm^{-1} lower than those in $\{Cp(CO)_2Fe[CH(OMe)]\}^+$,[46],[24] which suggests the [CH(OMe)] moiety has a lower σ donor/π acceptor ratio than the sulfur analog. The ^1H NMR spectrum of [4] in CD_2Cl_2 displays a broad singlet at 14.8 δ, which is characteristic of a carbene hydrogen. In triflic acid, that resonance is shifted to 15.8 δ which is nearly 3 PPM downfield from the analogous proton in [46]. This indicates an increase in cationic character on the α hydrogen of the carbene ligand going from methoxide to thiomethoxide which is in line with the trend observed in the $\{(PPh_3)_2(CO)(L)Os[CH(XMe)]\}^+$ [19] and $\{Cp(PPh_3)(NO)Re[CH(XMe)\}^+$ [23,26], (X = O, S), series.

Synthesis of
$\{Cp(CO)_2Fe[CH(SMe)]\}PF_6$

Owing to the poor crystallizabilities and stabilities of [4] and [5], the hexafluorophosphate analog was sought. Anion metathesis of [4] and [5] with $(NH_4)PF_6$ and KPF_6 only resulted in decomposition; thus, an alternative scheme was needed. The aforementioned, trityl cation is capable of abstracting an α hydride from organometallic ethers, MCHROR'[24]; to a lesser extent, methoxide can sometimes be removed by it.[45] Although, thiomethoxide cleavage from $HC(SMe)_3$ is facilitated by $(Ph_3C)BF_4$,[59] (Eqn. 32), the analogous reaction is unknown in organometallic chemistry.

$$HC(SMe)_3 + (Ph_3C)BF_4 \longrightarrow Ph_3CSMe + [HC(SMe)_2]PF_6 \qquad (32)$$

Table 2. IR[a] and ^1H NMR[b] data for $\{Cp(CO)_2Fe[CH(SMe)]\}X$

X	$\nu(CO)\,cm^{-1}$	CH	Cp	SMe
CF_3SO_3, [4]	2067 s , 2026 s	14.86(br)[c]	5.11	3.00
BF_4, [5]	2067 s , 2028 s			
PF_6, [6]	2069 s , 2029 s	15.24(br)	5.15	3.12

[a] Solvent is CH_2Cl_2.

[b] Solvent is CD_2Cl_2.

[c] 15.79 in CF_3SO_3H.

As hoped, $(CPh_3)PF_6$ readily reacts with [2] at -78°C affording a golden powder of [6] (75%), (Eqn. 33).

$$\underset{[2]}{Cp(CO)_2Fe[CH(SMe)_2]} + (Ph_3C)PF_6 \longrightarrow \underset{\substack{[6]\\+\\Ph_3CSMe}}{\{Cp(CO)_2Fe[CH(SMe)]\}PF_6} \qquad (33)$$

Compound [6] is significantly less soluble in organic solvents than [4] and [5], and it is recrystallized from CH_2Cl_2/Et_2O at -20°C to yield golden platelets of [6] which occlude diethylether. Nevertheless, [6] shares similar spectral characteristics with [4] and [5] which are summarized in Table 2.

Direct Attempts to Prepare [6]

In light of the unsuccessful preparation of [2] in Equation 28, attention was diverted into developing a direct method for preparing [6] by avoiding [2]. Cutler[24] has shown that [46] can be prepared in a single step simply by reacting $Cp(CO)_2FeCH_2OMe$,[47], with trityl (Eqn. 34).

$$\underset{[47]}{Cp(CO)_2FeCH_2OMe} + (Ph_3C)PF_6 \longrightarrow \underset{[46]}{\{Cp(CO)_2Fe[CH(OMe)]\}PF_6} + HCPh_3 \qquad (34)$$

When similar conditions are employed with $Cp(CO)_2FeCH_2SMe$,[7],[63] [6] is the only identifiable organometallic product (vide infra), but is obtained in only approximately 5% yield (Eqn. 35).

$$\underset{[7]}{\mathrm{Cp(CO)_2FeCH_2SMe}} + \mathrm{[Ph_3C]PF_6} \longrightarrow \underset{[6]}{\mathrm{\{Cp(CO)_2Fe[CH(SMe)]\}PF_6}} + \text{''}\mathrm{Cp(CO)_2FeCH_2}\text{''} \qquad (35)$$

The ineffectiveness of reaction 35 probably stems from the fact that the α-hydrogen in [7] is less labile than in its oxyl counterpart. That assumption is supported by the hydride transfer reactions of $\mathrm{Cp(PPh_3)(NO)ReCH_2^+}$ and $\mathrm{Cp(PPh_3)(NO)ReCH_2XMe}$ (X = S, O). In this system, the thiomethoxyl complex reacts with the methylidene complex[26] at 83°C during 8 hours whereas the methoxylether compound[23] transfers its hydride to the methylidene compound at -70°C (Eqn. 36).

$$\mathrm{Cp(PPh_3)(NO)ReCH_2^+} + \mathrm{Cp(PPh_3)(NO)ReCH_2XMe} \longrightarrow \mathrm{Cp(PPh_3)(NO)ReCH_3} + \mathrm{\{Cp(PPh_3)(NO)Re[CH(XMe)]\}^+} \qquad (36)$$

$$X = O,\ S$$

Perhaps, the slower rate of α-hydride removal from $\mathrm{MCH_2SMe}$ compounds as compared to $\mathrm{MCH_2OMe}$, results in an increase in the tendency of the trityl cation to abstract $\mathrm{MeS^-}$ rather than $\mathrm{H^-}$, giving the methylidene complex or the methylidene-$\mathrm{MeSCPh_3}$ adduct[71] (Eqn. 35). Since the decomposition product in Equation 35 has not been characterized, the presence of the methylidene complex or the adduct has not been verified.

Reaction of [4], [5] with Tertiary Phosphines and Phosphites

As mentioned previously, the C_{carb} of metal carbene complexes is frequently the site of nucleophilic attack. For instance, the transient complexes, $(CO)_5W[CH(Ph)]$[43] and $Cp(CO)_2Fe[CH(Me)]^+$ [32] readily react with PPh_3 giving the stable phosphine adducts, $(CO)_5W[CH(Ph)(PPh_3)]$ and $Cp(CO)_2Fe[CH(Me)(PPh_3)]^+$, respectively. When a CH_2Cl_2 suspension of [5] is treated with PPh_3, the gradual dissolution of the insoluble complex is apparent. The infrared spectrum of the solution shows that [5] had been completely consumed (ca. 30 min) as indicated by the absence of its ν(CO) bands. Upon recrystallization, the resulting material affords air-stable yellow crystals of $\{Cp(CO)_2Fe[CH(SMe)(PPh_3)]\}BF_4$, [9a] in 86% yield. [9a] exhibits two strong ν(CO) absorptions (2027, 1975 cm^{-1}) which are an average of 45 cm^{-1} lower than those in [5] (Table 2). This shift to lower energy indicates an increase of metal to CO π-backbonding. The electron density at the metal which facilitates greater backbonding is contributed by the phosphine's lone electron-pair. By comparison, it should be noted that the ν(CO) bands of [9a] are about 15 cm^{-1} higher than those found in [2]; this indicates that the positive charge is delocalized onto the iron, which reduces the degree of d-P π-backbonding from the metal to the carbonyls.

Similarly, a variety of tertiary phosphines and phosphites; $MePPh_2$, $ClPPh_2$, $P(OPh)_3$ and $P(OCH_2)_3CMe$, react with [4] and [5] to furnish the corresponding adducts (Eqn. 37, Tables 3-4). The anion of these

Table 3. Selected IR and ^{1}H NMR data for the phosphine adducts, $Cp(CO)_2Fe[CH(SMe)L]^+$

Complex		IR(ν(CO), cm^{-1})^a	
$Cp(CO)_2Fe[CH(SMe)_2]^c$	[2]	2012 s	1960 s
$\{Cp(CO)_2Fe[CH(SMe)(PPh_2Me)]\}PF_6$	[8]	2021 s	1971 s
$\{Cp(CO)_2Fe[CH(SMe)(PPh_3)]\}BF_4$	[9a]	2027 s	1975 s
$\{Cp(CO)_2Fe[CH(SMe)(PPh_3)]\}PF_6$	[9b]	2027 s	1975 s
$\{Cp(CO)_2Fe[CH(SMe)(PClPh_2)]\}BF_4$	[10]	2030 s	1982 s
$\{Cp(CO)_2Fe[CH(SMe)(PCl_3)]\}BF_4$	[11]	2031 s	1982 s
$\{Cp(CO)_2Fe[CH(SMe)(P(OPh)_3)]\}PF_6$	[12]	2032 s	1986 s
$\{Cp(CO)_2Fe[CH(SMe)(P(OCH_2)_3CMe)]\}CF_3SO_3$	[13a]	2041 s	1992 s
$\{Cp(CO)_2Fe[CH(SMe)(P(OCH_2)_3CMe)]\}PF_6$	[13b]	2042 s	1992 s

[a] CH_2Cl_2,

[b] CD_3CN.

[c] In hexane (2018 s, 1968 s).

Cp	^{1}H NMR^b		Other
	CH	SMe	
5.16	3.75(d, J_{PH}=2.93)	1.36(d, J_{PH}=0.73)	7.7(m, Ph), 2.45(d, J_{PH}=12.46, PMe)
5.25	4.28(d, J_{PH}=1.46)	1.67(d, J_{PH}=0.74)	7.35(m, Ph)
5.21	4.16(d, J_{PH}=11.73)	1.65	7.7(m, Ph)
5.25	3.41(d, J_{PH}=7.33)	2.12(d, J_{PH}=1.71)	7.35(m, Ph)
5.13	2.67(d, J_{PH}=2.44)	2.22	4.74(d, J_{PH}=5.37, OCH_2), 0.94(CMe)

Table 4. ^{13}C NMR data for $Cp(CO)_2Fe[CH(SMe)L]^+$ in CD_3CN solvent

Complex	CO	Cp	SMe
[8]	214.5	89.3	22.5
[9b]	215.5(d, J_{PC}=5.86), 213.0	89.7	23.2
[10]	214.4(d, J_{PC}=5.86), 213.2	89.3	22.7
[12]	214.5, 213.6	88.1	20.5
[13b]	214.0(d, J_{PC}=3.66), 213.1	87.4	23.5

$^{a}CD_3COCD_3$

CH	Other
	134.7(d, J_{PC}=3.9); 133-130; 127.7; 126.6; 124.3; 123.2[Ph]
7.5(d, J_{PC}=25.4)	5.4(d, J_{PC}=11.72, PMe)
6.0(d, J_{PC}=25.39)	135.1(d, J_{PH}=7.81); 130.5(d, J_{PH}=11.72); 125.7; 122.0[Ph]
12.7(d, J_{PC}=15.62)	136.3; 134.0; 133.6; 126.5; 122.7[Ph]
10.8(d, J_{PC}=130.86)^{a}	150.7(d, J_{PC}=13.68); 131.7; 128.3(d, J_{PC}=3.90); 120.6[Ph]
-5.1(d, J_{PC}=101.32)	80.7(d, J_{PC}=6.1, OCH_2), 36.3(d, J_{PC}=34.2, $\underline{C}$Me), 13.0(C$\underline{Me}$)

compounds can be readily metathesized with PF_6^- to give a more managable product. Astonishingly, the weak Lewis acid, PCl_3, also gives the corresponding adduct

$$\underset{[4]}{\{Cp(CO)_2Fe[CH(SMe)]\}X} \xrightarrow{L} \{Cp(CO)_2Fe[CH(SMe)(L)]\}X \tag{37}$$

$X = CF_3SO_3,\ BF_4$

$L = PPh_3,\ MePPh_2,\ ClPPh_2,\ PCl_3,\ P(OPh)_3,\ P(OCH_2)_3CMe$

in solution when reacted with [5], but it could not be isolated in pure form without undergoing some decomposition. [4] fails to produce stable adducts with CH_3CN, THF, Me_2S, or $AsPh_3$.

Spectral Properties of the $Cp(CO)_2Fe[CH(SMe)(L)]^+$ Complexes

Uniformally, the ^1H NMR resonance of the methine hydrogen of these adducts (Table 3) is shifted upfield, as much as 12 PPM, from the parent carbene complex, which is in the range of a saturated iron alkyl complex, such as [2].[27] Invariably, the methine carbon in these complexes occurs as a doublet in the ^{13}C NMR spectrum due to coupling with the phosphorous (^{31}P $I = \frac{1}{2}$); the chemical shift of the methine carbon is in the range of -5 to 12 PPM, as compared with -23.3 PPM. observed in $[Cp(CO)_2FeCH_2PPh_3]BF_4$.[72]

In the carbonyl region (Table 4), the majority of these adducts display three-line patterns for the CO groups as exemplified by [13b]

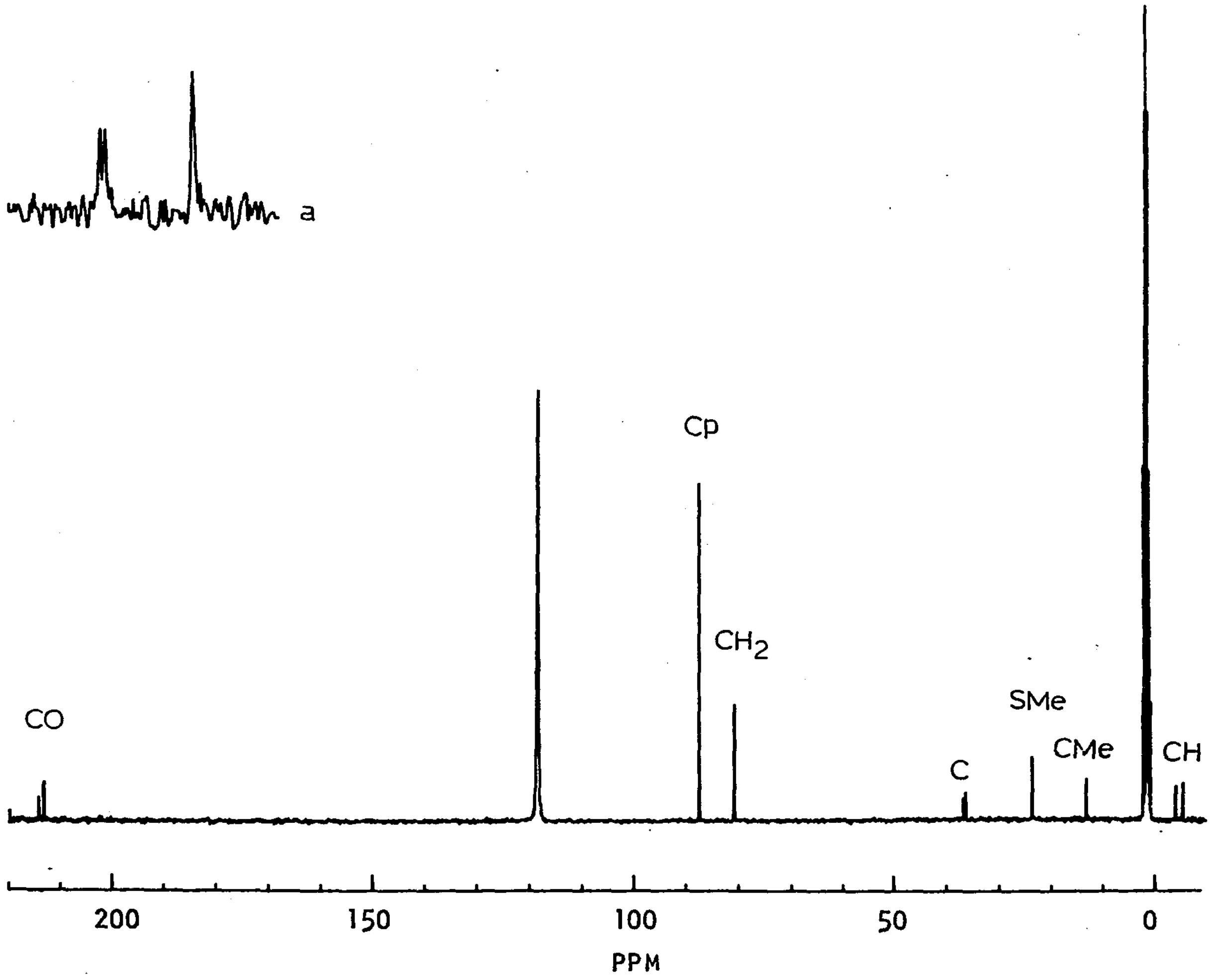


Figure 2. ^{13}C NMR spectrum of $\{Cp(CO)_2Fe[CH(SMe)P(OCH_2)_3CMe]\}PF_6$,[13b], in CD_3CN.^{a} Expansion of the carbonyl region

in Figure 2. This phenomenon can be explained by diastereotopism, which has been cited in $Cp(CO)_2Fe[CH(OMe)(Me)]$.[49] As a consequence of the nucleophilic attack by phosphorous on the C_{carb}, the resulting methine carbon becomes an optically active center, the complex can exist in several rotomeric forms with the staggered rotomers, whose Newman projections are shown in Figure 3, being the most likely structures for each enantiomer.

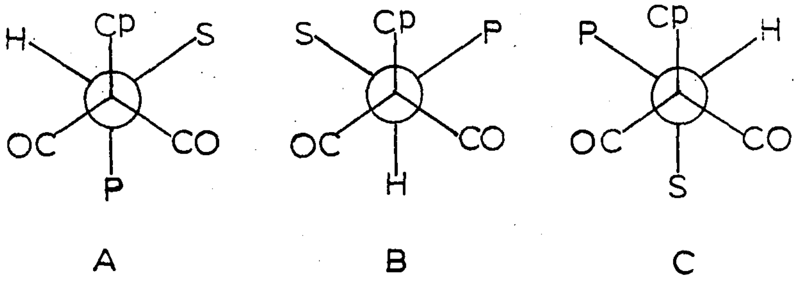


Figure 3. Newman projections for $Cp(CO)_2FeCHPS$

In all of the rotomers in Figure 3, the carbonyls are clearly chemically and magnetically non-equivalent with respect to the phosphorus; thus, the CO groups should have different chemical shifts and coupling constants with the P. Presumably, rotation about the Fe-C bond is rapid relative to the NMR time scale even at the ambient probe temperature at which the data in Table 4 were obtained. Consequently, the carbonyl pattern is the average of the various rotomers and occurs as a doublet and singlet, arising from different J_{PC} values. The chiral-methine carbon also induces diastereotopism in PPh_2Me adduct, [8], whose ^{13}C spectrum shows two sets of phenyl carbon resonances, though, its carbonyl signals are observed to be coincident.

X-Ray Structure of [13b]

To ensure that the ylide moiety, $[CH(SMe)(PR_3)]$, was bonded to the iron through the methine carbon rather than the sulfur, an X-ray crystal determination was undertaken on [13b]. As illustrated in the ORTEP drawing of the organometallic cation portion (Figure 4), the iron remains connected to the formerly carbene carbon, C1. The overall molecular configuration of the cation is a three-legged piano-stool structure where the carbonyls and C1 are the legs. The angles between the legs average 91.6° (Table 5) which is slightly greater than in a regular octahedral complex (90°). To our surprise, a Newman projection through the C1-Fe bond of the organometallic cation reveals that the complex adopts the most sterically hindered staggered rotomer, that in which both bulky groups, S and P, are adjacent to the Cp (Figure 5). It is not clear why this is the case; presumably, it is preferred due to favorable packing in the lattice.

In general, Fe-C single bond distances in $Cp(CO)_2Fe-R$ complexes[73-78] are in the range of 2.06-2.11 Å. In the case of [13b], the Fe-C1 bond length is 2.08 Å (Table 6) which is longer than the partial double bond observed in $Cp(CO)_2Fe[CH_2(SMe_2)]^+$ (2.036)[71] and is in close accord with that (2.11 Å) of the single bond complex, $Cp(CO)_2Fe[C(SMe)_3]$.[73] The Fe-CO (1.78 average) and FeC-O (1.14 average) distances in [13b] are longer and shorter, respectively, relative to the corresponding distances (1.76, 1.15) in $Cp(CO)_2Fe[C(SMe)_3]$, although the differences in bond distances are within experimental error. However, the ν(CO)

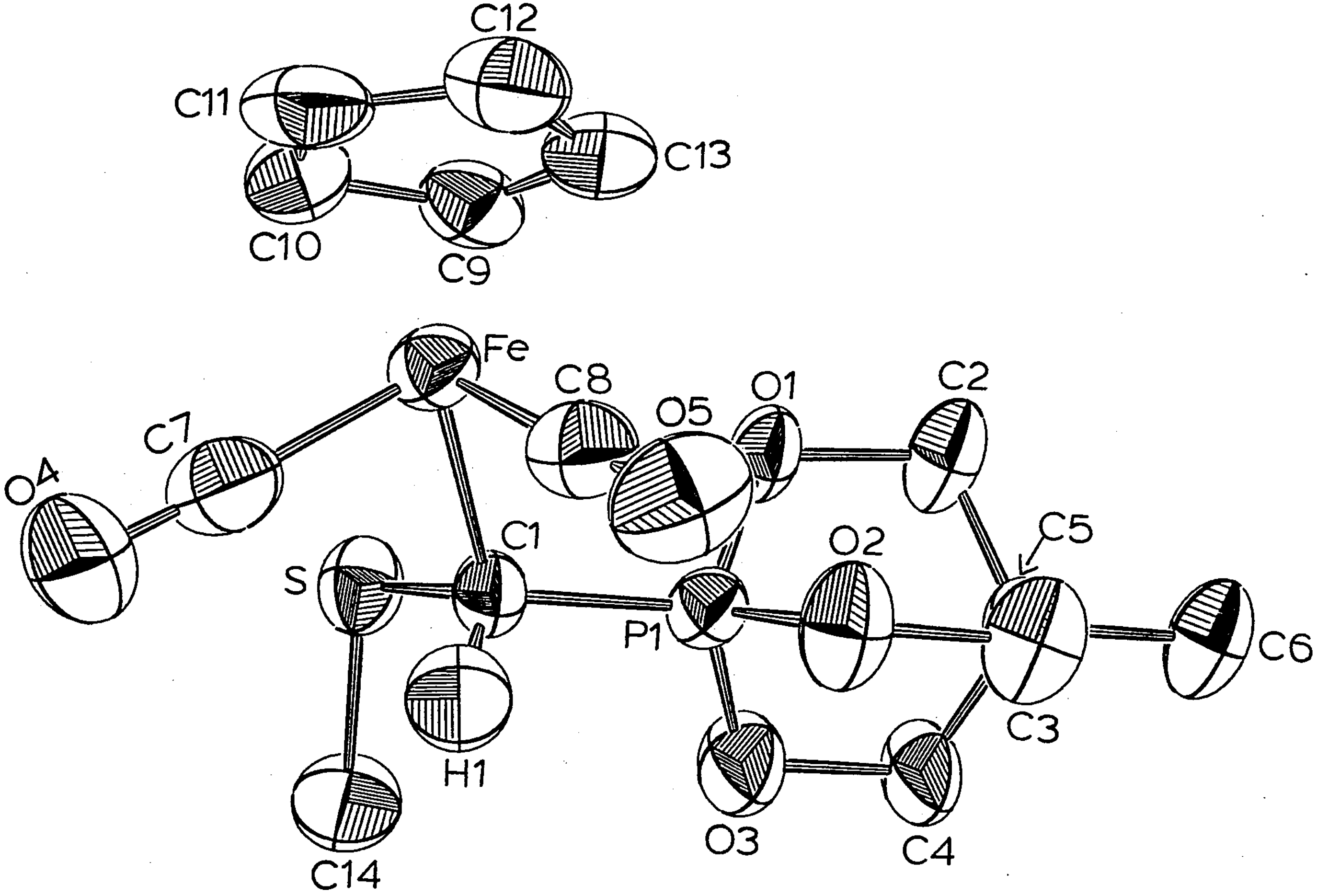
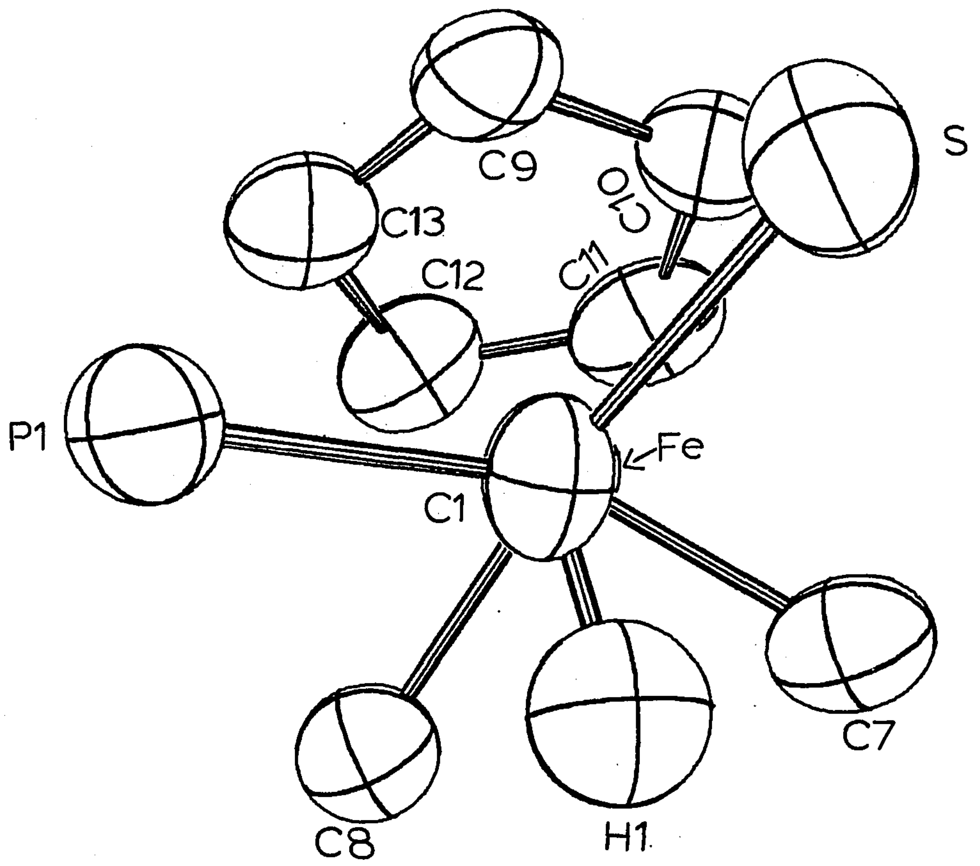


Figure 4. An ORTEP drawing of $Cp(CO)_2FeCHSMeP(OCH_2)_3CMe^+$



Torsion angles (deg)	
C_7-Fe-C_1-H_1	43.42
C_7-Fe-C_1-P_1	157.37
C_7-Fe-C_1-S	77.18
C_8-Fe-C_1-S	171.52
C_8-Fe-C_1-P_1	63.03
C_8-Fe-C_1-H_1	50.91

Figure 5. A Newman projection of the $CpC_2FeCHSP$ core viewing through the C_1-Fe bond

Table 5. Bond angles (deg) and their standard deviations (in parentheses) for $\{Cp(CO)_2Fe[CH(SMe)(P(OCH_2)_3CMe)]\}PF_6$

$Fe-C_7-O_4$	176.7(1.1)	$P_1-O_3-C_4$	112.7(6)
$Fe-C_8-O_5$	175.7(1.0)	$O_1-P_1-O_2$	106.7(4)
C_8-Fe-C_7	94.5(5)	$O_2-P_1-O_3$	105.2(4)
C_1-Fe-C_7	87.5(4)	$O_3-P_1-O_1$	104.8(4)
C_1-Fe-C_8	92.9(4)	$O_1-C_2-C_5$	107.3(8)
$Fe-C_1-H_1$	97.2(6)	$O_2-C_3-C_5$	107.8(8)
$Fe-C_1-S$	110.9(4)	$O_3-C_4-C_5$	109.0(9)
$Fe-C_1-P_1$	112.8(4)	$C_2-C_5-C_3$	108.4(8)
H_1-C_1-S	115.3(6)	$C_3-C_5-C_4$	108.6(9)
$H_1-C_1-P_1$	108.8(6)	$C_4-C_5-C_2$	112.3(9)
$S-C_1-P_1$	111.14(5)	$C_2-C_5-C_6$	110.1(9)
$C_{14}-S-C_1$	103.0(5)	$C_3-C_5-C_6$	107.5(8)
$C_1-P_1-O_1$	113.6(4)	$C_4-C_5-C_6$	110.0(9)
$C_1-P_1-O_3$	113.4(4)	$C_9-C_{10}-C_{11}$	109.3(1.0)
$C_1-P_1-O_2$	112.5(4)	$C_{10}-C_{11}-C_{12}$	108.7(1.0)
$P_1-O_1-C_2$	114.9(6)	$C_{11}-C_{12}-C_{13}$	104.5(9)
$P_1-O_2-C_3$	114.9(6)	$C_{12}-C_{13}-C_9$	108.5(1.1)
$C_{13}-C_9-C_{10}$	109.0(1.0)	$F_4-P_2-F_5$	175.9(9)
$F_1-P_2-F_2$	178.2(6)	$F_3-P_2-F_6$	172.8(9)
$F_2-P_2-F_3$	88.4(5)	$F_3-P_2-F_4$	83.5(7)
$F_5-P_2-F_6$	94.8(1.0)	$F_6-P_2-F_1$	89.6(7)

Table 6. Interatomic distances (Å) and their estimated standard deviations (in parentheses) for $\{Cp(CO)_2Fe[CH(SMe)(P(OCH_2)_3CMe)]\}PF_6$

Fe-C_1	2.085(9)	O_1-C_2	1.49(1)
Fe-C_7	1.78(1)	O_2-C_3	1.48(1)
Fe-C_8	1.78(1)	O_3-C_4	1.53(1)
Fe-C_9	2.13(1)	C_2-C_5	1.54(1)
Fe-C_{10}	2.11(1)	C_3-C_5	1.57(1)
Fe-C_{11}	2.08(1)	C_4-C_5	1.51(1)
Fe-C_{12}	2.12(1)	C_5-C_6	1.55(1)
Fe-C_{13}	2.16(1)	C_9-C_{10}	1.41(1)
C_7-O_4	1.13(1)	C_{10}-C_{11}	1.37(1)
C_8-O_5	1.14(1)	C_{11}-C_{12}	1.47(2)
C_1-S	1.809(9)	C_{12}-C_{13}	1.46(2)
C_1-H_1	1.054(9)	C_{13}-C_9	1.39(1)
C_1-P_1	1.732(9)	P_2-F_1	1.60(1)
S-C_{14}	1.82(1)	P_2-F_2	1.593(9)
P_1-O_1	1.551(6)	P_2-F_3	1.55(1)
P_1-O_2	1.547(7)	P_2-F_4	1.62(1)
P_1-O_3	1.544(7)	P_2-F_5	1.47(1)
		P_2-F_6	1.52(1)

absorptions of [13b] (2042, 1992 cm^{-1}) are noticeably higher energy than those of $Cp(CO)_2Fe[C(SMe)_3]$ (2013, 1964 cm^{-1}). Thus, on the basis of the X-ray results together with IR data, it appears there is less d-p π-backbonding to the CO groups in [13b]. The C1-S bond (1.809) is found to be in good agreement with a typical C-S single bond distance observed in $Cp(CO)_2Fe[C(SMe)_3]$ (1.809) and compares favorably with the values obtained from microwave studies of MeSH (1.819),[79] and Me_2S (1.802).[80]

The P1-C1 bond distance (1.732 Å) is in close accord with those in the terminal carbene phosphine adducts: $Me_3AuCH_2PPh_3$ (1.755 Å)[81], $(CO)_3Ni[CH(Me)PCy_3]$[82] (1.745 Å), trans $[Pt(CH_2PEt_3)I(PEt_3)_2]^+$ (1.77 Å)[83] and $\{(1,5-C_8H_{12})Pd[CH(SiMe_3)PPhMe_2](SiMe_3)(Cl)\}^+$ (1.780 Å)[84]; but is noticeably longer than those in the ylides, $(CO)_5W[SMe(C(SMe)PPh_2Me)]$ (1.704)[85] and $Cp_2ClZr[CH(PPh_3)]$ (1.716).[86] Thus, the P1-C1 bond may be considered a single bond.

Thermal Decomposition of [9a] and [13b]

Recently, in the course of studying the electrophilicity of [1] toward tertiary phosphines, Angelici and Matachek[87] observed the formation of $\{Cp(CO)_2Fe[C(SMe)_2PEt_3]\}PF_6$ when the carbene reacted with PEt_3 at -78°C (Eqn. 38).

$$\underset{[1]}{\{Cp(CO)_2Fe[C(SMe)_2]\}PF_6} + PEt_3 \xrightarrow[CH_2Cl_2]{-78^\circ C} \{Cp(CO)_2Fe[C(SMe)_2PEt_3]\}PF_6$$

$$\Big\downarrow 0^\circ C \qquad\qquad (38)$$

$$[Cp(CO)_2Fe(PEt_3)]PF_6 + (MeS)_2C\underset{?}{=}C(SMe)_2$$

This triethylphosphine adduct was described as having spectral properties similar to those of the compound in Tables 3-4. However, it was not isolated due to its inherent instability and decomposed to $[Cp(CO)_2Fe(PEt_3)]PF_6$ upon warming to 0°, and the remaining carbene fragment may have dimerized to give the tetrathiomethyoxyl ethylene.

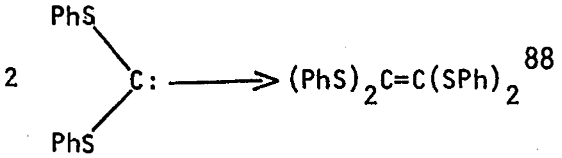
To evaluate the generality of this degradation reaction, the thermal stabilities of the 3^oPR_3 adducts, [9a] and [13b] were investigated. In contrast to the PEt_3 adduct, both complexes remain unaltered in refluxing CH_2Cl_2 and THF for two hours and maintain their structural integrities even when heated at 100°C in the solid state under an N_2 atmosphere for 15 min. When solid [9a] and [13b] are heated for 2 min at 200 and 180°C, respectively, decomposition occurs, affording $[Cp(CO)_2FePPh_3]BF_4$ (88%) and $[Cp(CO)_2FeP(OCH_2)_3CMe]PF_6$ (65%), respectively (Eqn. 39).

$$\{Cp(CO)_2Fe[CH(SMe)L]\}^+ \xrightarrow[\Delta]{} Cp(CO)_2L^+ + \text{cis and trans } (MeS)CH{=}CH(SMe)$$

$$+ HC(SMe)_3 + Cp_2Fe \qquad\qquad (39)$$

$L = PPh_3,\ P(OCH_2)_3CMe$

Both organometallic products were identified by comparing their spectral data with authentic samples synthesized from the reaction of $[Cp(CO)_2FeTHF]^+$ and L.[69] The organic products separated from the pyrolysis reaction of [9a] were identified by their GC-MS spectra to be cis and trans 1,2 bis(methylthio)ethylene in about equal proportions, trithiomethoxyl methane, and ferrocene. Undoubtedly, the olefins are derived from the coupling of "CH(SMe)" fragments; whether this coupling involves free carbene or coordinated carbene ligand is unknown, but certain thioalkoxyl carbenes have been shown to produce olefins under the proper conditions (Eqn. 40), and carbene complexes are also known to release the carbene as an olefin-product (Eqn. 41-43).



$$2\,(PhS)_2C: \longrightarrow (PhS)_2C{=}C(SPh)_2{}^{88} \qquad (40)$$

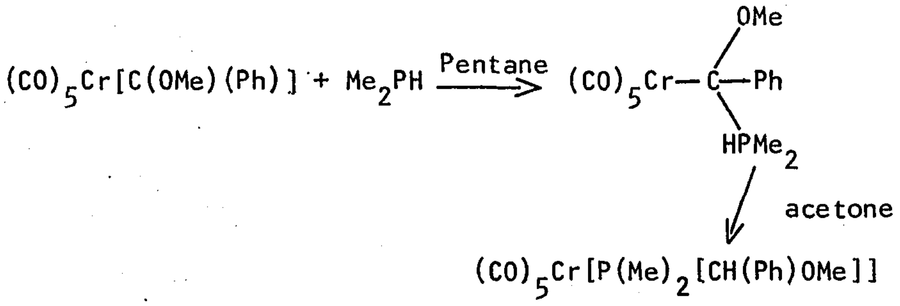
$$2\{Cp(CO)_2Fe[CHPh]\}^+ \longrightarrow (Ph)CH{=}CH(Ph)^{45} \qquad (41)$$

$$(CO)_5W[C(Ph)OMe] + Ph_3P{=}CH_2 \longrightarrow W(CO)_5PPh_3 + (Ph)(MeO)C{=}CH_2{}^{89} \qquad (42)$$

$$Cl_2PPh_3PtCH_2PPh_3 \xrightarrow{h\nu} Cl_2Pt(PPh_3)_2 + \text{"}CH_2\text{"}^{90} \qquad (43)$$

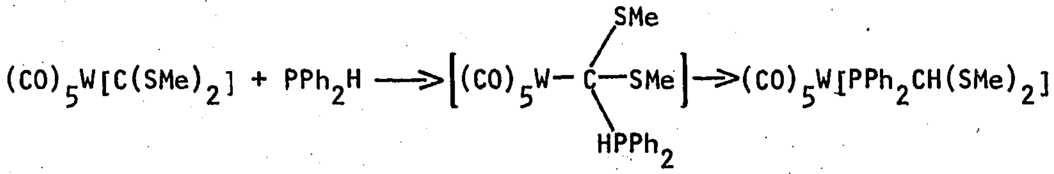
Reaction of [4]
with Secondary Phosphines

The reaction between secondary phosphines and transition metal carbene complexes is similar to those of tertiary phosphines, but with a slight variation. Kreissel et al.[91] observed that Me_2PH readily reacted with $(CO)_5Cr[C(OMe)(Ph)]$ to give $(CO)_5Cr[C(OMe)(Ph)PMe_2H]$. Upon stirring the adduct in acetone, rearrangement occurred affording a phosphine coordinated complex (Eqn. 44).



$$(CO)_5Cr[C(OMe)(Ph)] + Me_2PH \xrightarrow{Pentane} (CO)_5Cr{-}C(OMe)(Ph)(HPMe_2) \xrightarrow{acetone} (CO)_5Cr[P(Me)_2[CH(Ph)OMe]] \qquad (44)$$

More recently, Pickering et al.[85] observed a similar rearrangement in the reaction of $(CO)_5W[C(SMe)_2]$ and Ph_2PH. In that case, the phosphine complex was isolated and the phosphine adduct was presumed to be an intermediate, although there was no spectroscopic evidence for it (Eqn. 45).



$$(CO)_5W[C(SMe)_2] + PPh_2H \longrightarrow \left[(CO)_5W{-}C(SMe)(SMe)(HPPh_2)\right] \longrightarrow (CO)_5W[PPh_2CH(SMe)_2] \qquad (45)$$

Table 7. Selected IR and ^{1}H NMR data for the primary and secondary phosphine adducts, $Cp(CO)_2Fe[CH(SMe)L]^+$ and their derivative

Complex		IR((CO), cm^{-1})^a	
$\{Cp(CO)_2Fe[CH(SMe)(PPh_2H)]\}CF_3SO_3$	[14]	2033 s	1980 s
$\{Cp(CO)_2Fe[CH(SMe)(PCy_2H)]\}CF_3SO_3$	[15]	2025 s	1975 s
$\{Cp(CO)_2Fe[CH(SMe)(PPhH_2)]\}CF_3SO_3$	[16]	2036 s	1987 s
$\{Cp(CO)_2Fe[CH(SMe)(PCyH_2)]\}PF_6$	[17]	2036 s	1986 s
$\{Cp(CO)_2Fe(PPh_2CH_2SMe)\}CF_3SO_3$	[18]	2057 s	2012 s
$\{Cp(CO)_2Fe(PCy_2CH_2SMe)]\}CF_3SO_3$	[19]	2049 s	2005 s
$Cp(CO)_2Fe[CH(SMe)PPh_2]$	[20]	2008 s	1958 s

$^a CH_2Cl_2$.

$^b CD_3CN$.

$^c CDCl_3$.

$^d CD_3NO_2$.

$^e C_6D_6$.

^{1}H NMR Cp	CH	SMe
5.14[b]	3.46(dd, J_{PH}=1.47, J_{HH}=10.63)	1.59(d, J_{PH}=0.73)
5.16[b]	3.18(dd, J_{PH}=1.47, J_{HH}=2.93)	2.21(d, J_{PH}=1.10)
5.18[b]	3.06(dd, J_{PH}=1.28, J_{HH}=9.9)	1.79
5.15[c]	2.87(dm, J_{PH}=7.7)	2.29
5.38(d, J_{PH}=1.46)[d]		1.99(d, J_{PH}=1.46)
5.41(d, J_{PH}=1.47)[b]		2.32(d, J_{PH}=1.84)
4.36[e]	3.50(d, J_{PH}=4.39)	1.56

Table 7. continued

Other
7.22(m, Ph) 7.45(dd, J_{PH}=501.31, J_{HH}=10.63, PH)
1.83(m, Cy), 5.78(dm, J_{PH}=439, PH)
7.25(dm, J_{PH}=482.02); 6.98(dm, J_{PH}=502.18)[PH], 7.7(m, Ph)
1.90-1.4.(m, Cy), 6.16(dm, J_{PH}=470.84); 5.83(dm, J_{PH}=472.29)[PH]
3.82(d, J_{PH}=6.1, SCH_2), 7.7(m, Ph)
3.21(d, J_{PH}=9.53, SCH_2), 1.83(m, Cy)
7.91-7.1(m, Ph)

Table 8. ^{13}C NMR data for the primary and secondary phosphine adducts, $Cp(CO)_2Fe[CH(SMe)L]^+$ and their derivatives

Complex	CO	Cp	SMe
[14][a]	214.9(d, J_{PC}=5.86), 213.8	88.5	23.3
[15][b]	216.2(br), 215.0	89.2	23.3
[16][d]	213.3(br), 212.3[e]	87.6	22.2
[17][b]	214.2(d, J_{PC}=5.86), 213.8	87.6	22.4

[a] CD_3NO_2.

[b] CD_3CN.

[c] $CDCl_3$.

[d] CD_3COCD_3.

[e] CD_2Cl_2.

CH	Other
5.6(d, J_{PC}=21.49)	135-130(Ph)
-1.3(d, J_{PC}=19.53)[c]	34-26(Cy)
1.5(d, J_{PC}=11.72)	135-130(Ph)
-4.3(d, J_{PC}=19.53)	31.8(d, J_{PH}=37.11); 28.3; 26.5; 25.9[Cy]

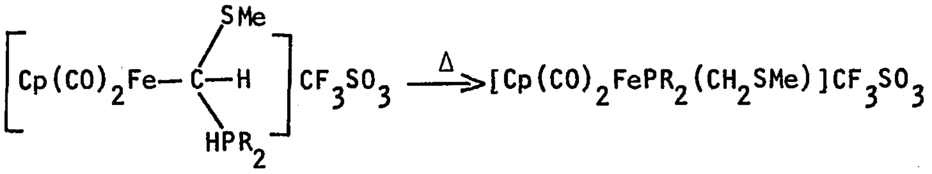
The addition of $HPPh_2$ or $HPCy_2$ to a dichloromethane solution of [4] at room temperature, results in the isolation of air-stable phosphine adducts in fair yields, $\{Cp(CO)_2Fe[CH(SMe)PPh_2H]\}CF_3SO_3$,[14], and $\{Cp(CO)_2Fe[CH(SMe)PCy_2H]\}CF_3SO_3$,[15], respectively (Eqn. 46).

$$\underset{[4]}{\{Cp(CO)_2Fe[CH(SMe)]\}CF_3SO_3} + R_2PH \longrightarrow \{Cp(CO)_2Fe[CH(SMe)PR_2H]\}CF_3SO_3 \qquad (46)$$

	R	%
[14]	Ph	62
[15]	Cy	38

The J_{PH} coupling constants for [14] and [15] are 501 and 439 Hz, respectively, and are consistent with the hydrogen atom being bound to the phosphorus.[92] Both complexes have spectral characteristics (Tables 7-8) similar to those of 3° phosphine adducts.

In contrast to $(CO)_5Cr[C(OMe)(Ph)(PMe_2H)]$,[14] is stable in acetone for a period of 12 hours, and shows no noticeable decomposition in refluxing CH_2Cl_2 and THF for 2 hours. However, it undergoes hydrogen migration when heated at 168°C in the solid state to yield $\{Cp(CO)_2Fe[PPh_2(CH_2SMe)]\}CF_3SO_3$,[18] (Eqn. 47). Much of the material obtained from the pyrolysis reaction is insoluble in common organic solvents and is believed to be a decomposition product of [14]. Likewise [15] is converted into $\{Cp(CO)_2Fe[PCy_2(CH_2SMe)\}CF_3SO_3$,[19], at elevated temperatures (Eqn. 47).



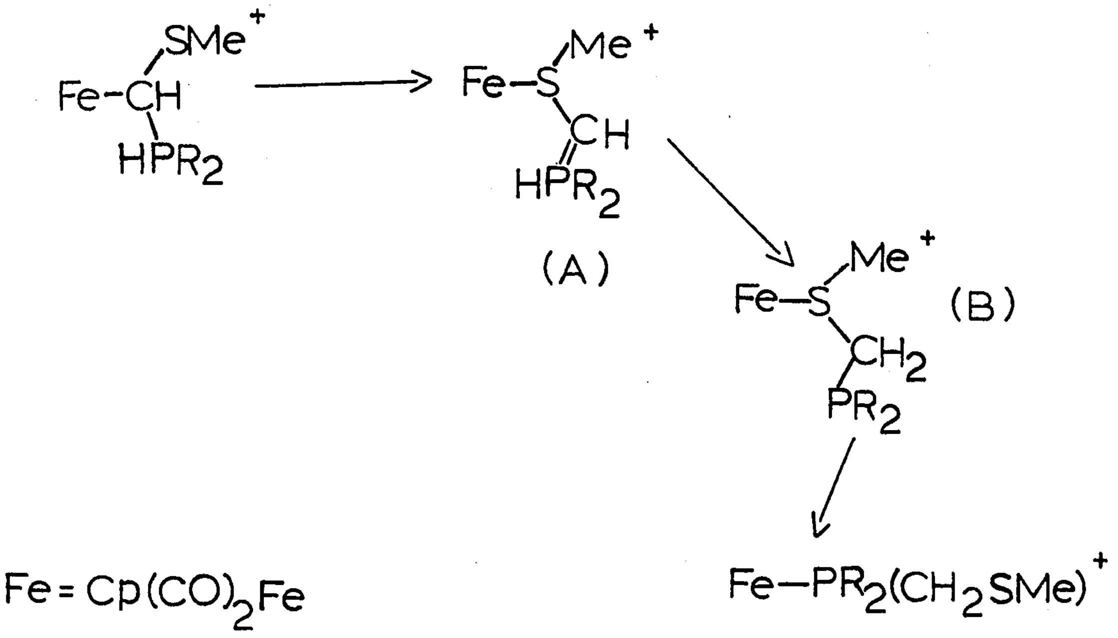
$$\left[Cp(CO)_2Fe-\overset{SMe}{\underset{HPR_2}{C}}-H\right]CF_3SO_3 \xrightarrow{\Delta} [Cp(CO)_2FePR_2(CH_2SMe)]CF_3SO_3 \tag{47}$$

	R	°C	%
[18]	Ph	168	20
[19]	Cy	200	20

IR spectra of these products show two strong ν(CO) bands in the regions where $Cp(CO)_2FePR_3^+$ complexes absorb[68] (Table 7). In the proton NMR spectrum, the PH signal is no longer present and a new resonance appears with a J_{PCH} (<10 Hz) coupling constant, which is consistent with the expected value (0.5-20 Hz)[92] for phosphines of the type R_2PCH_2R'.

A possible mechanism for reaction 47 is one that suggested for reaction 45.[93] Thus, the thioether group migrates to the iron and coordinates by lone pair donation from the sulfur giving a phosphorane complex (Scheme 1). Subsequent proton migration from the P to the C atom followed by phosphine displacement of the sulfur furnishes the observed product.

In an effort to determine the validity of Scheme 1, thermolysis of [14] was carried out at lower temperatures, in the hope of detecting the presence of the postulated intermediate sulfur-coordinated complexes. However, at 150-160°, no reaction takes place (vide infra). Thus, the sulfur coordinated intermediates must be short-lived at


Fe-CH(SMe)(HPR2)+
Fe-S(Me)(CH=HPR2)+
(A)
Fe-S(Me)(CH2PR2)+
(B)
Fe-PR2(CH2SMe)+
Fe = Cp(CO)2Fe

Scheme 1

168°, which is the minimum reaction temperature. Conceivably, the rearrangement reaction could proceed by an entirely different mechanism, in which sulfur-bound complexes are not involved.

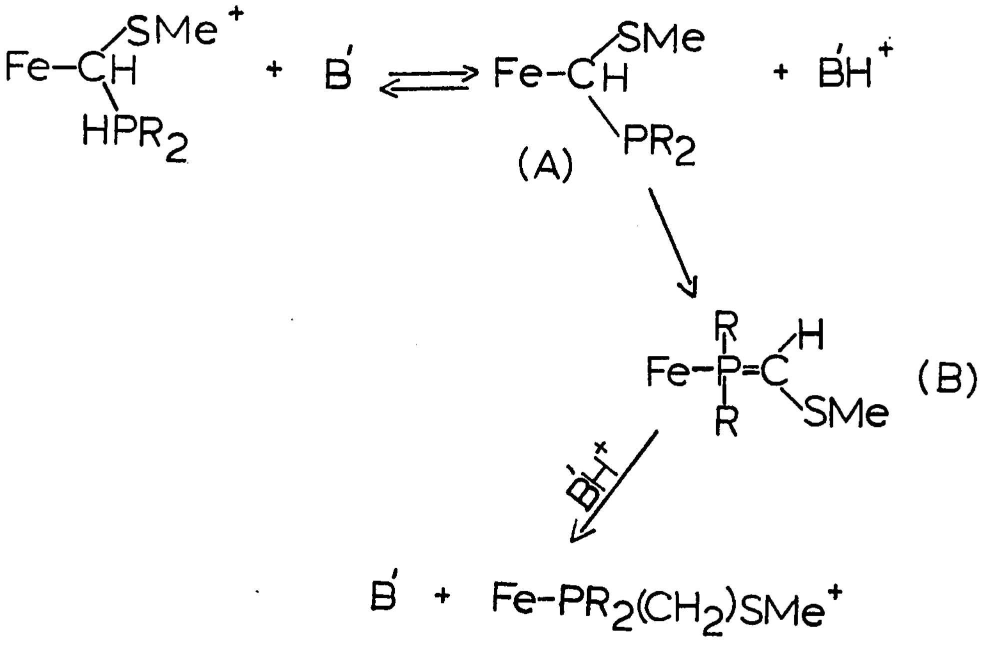
Alternatively, reaction 47 could be base catalyzed, where removal of the phosphonium hydrogen of the adduct is the initial step. The base involved in the deprotonation perhaps is PHR_2 which is derived from decomposition of the adduct (Scheme 2). Following attack on the iron by the resulting phosphine, reprotonation of the ylide with the conjugate acid or a H^+ donor, such as the adduct, would give the observed product.

In the course of these investigations, [14] was found to be deprotonated by n-BuLi in THF or Et_3N in CH_2Cl_2 to yield mainly $Cp(CO)_2Fe[CH(SMe)PPh_2]$,[20], and 5-12% of the rearranged complex, [18]. However, when 1/3 eqv. of base is used, a mixture consisting of [14], [18] and [20] results and [20] is only a minor product (Eqn. 48).

$$\underset{[14]}{\{Cp(CO)_2Fe[CH(SMe)(PPh_2H]\}CF_3SO_3} \underset{HO_3SCF_3}{\overset{base}{\rightleftarrows}} \tag{48}$$

$$\underset{[18]}{\{Cp(CO)_2Fe[PPh_2CH_2SMe]\}CF_3SO_3} + \underset{[20]}{Cp(CO)_2Fe[CH(SMe)PPh_2]}$$

base: η-BuLi/THF; Et_3N/CH_2Cl_2



Fe = Cp$(CO)_2$Fe

B'=base

Scheme 2

These experiments suggest the rearrangement of [14] to [18] is probably base influenced and the reaction is not catalytic, at least under the conditions in Equation 48.

Under pyrolytic conditions, the base involved in inducing the rearrangement reaction could be PR_2H which is generated by dissociation from the adduct $Cp(CO)_2Fe[CH(SMe)L]^+$. Indeed, a 5:1 mixture of neat [15]:PCy_2H gives [19] and a monocarbonyl complex, based on the single $\nu(CO)$ band (1965 cm^{-1}) and apparent liberation of CO during the reaction, (vide infra), at a considerably lower temperature (150°C) (Eqn. 49). However, a 5:1 mixture of [14]/Ph_2PH produces mostly a CO substituted product at 100°C.

$$\{Cp(CO)_2Fe[CH(SMe)PCy_2H]\}CF_3SO_3 \xrightarrow{150°} NR \qquad (49)$$

[15]

$$\xrightarrow[150°C]{\text{5 eqv. } PCy_2H} \{Cp(CO)_2Fe[PCy_2(CH_2SMe)]\}CF_3SO_3$$

[19]

Evidently, the Et_3N, n-BuLi and PCy_2H bases assist the rearrangement reaction; thus, Scheme 2 could be a viable alternative mechanism and deserves special attention in future work.

Preparation of [20]

The phosphonium proton in [14] is readily removed by n-BuLi at -78°C to give [20] predominantly; the reaction may be reversed by adding CF_3SO_3H (Eqn. 48). An Et_2O solution of [20] decomposes slowly in air. Attempts to crystallize [20] from Et_2O/pentane at -78°C only resulted in decomposition. In several instances, an Et_2O extract consisting of [20] decomposed to [18] and a deep-red unidentified material, when filtered through a frit under an N_2 atmosphere. This decomposition reaction is not well-understood and seldom reproducible. A closer examination of reaction 48 reveals that it also provides a small amount of [18] (5%). When the reaction is carried out at room temperature, the yield of [18] increases to 10%. Similarly, Et_3N reacts with [14] in CH_2Cl_2 at ambient temperature to produce [20] and 10% of [18] (Eqn. 48).

Complex [20] can be methylated (Eqn. 50) with $MeOSO_2F$ to furnish $\{Cp(CO)_2Fe[CH(SMe)(PPh_2Me)]\}SO_3F$ whose spectral properties are very similar to those of [8] which was synthesized by an independent route (Eqn. 37). Upon metathesis with $[NH_4]PF_6$ in acetone, it is converted to [8] and the overall yield is 82%.

$$\begin{tikzcd} \underset{[20]}{\mathrm{Cp(CO)_2Fe[CH(SMe)(PPh_2)]}} \arrow[r, "\mathrm{MeOSO_2F}"] & \mathrm{\{Cp(CO)_2Fe[CH(SMe)(PPh_2Me)]\}SO_3F} \arrow[d, "\mathrm{[NH_4]PF_6}"] \\ & \mathrm{[8]} \end{tikzcd} \qquad (50)$$

Attempts to obtain a phosphino carbene complex, $Cp(CO)_2Fe[CH(PPh_2)]^+$, by reacting [20] with $AgBF_4$ in the hope that Ag^+ ion would abstract MeS^- from the organometallic complex only led to an unisoluble material with ν(CO) absorptions (2027, 1976 cm^{-1}) which are probably not those of the expected product. Addition of anhydrous $[Ph_3C]BF_4$ to a CH_2Cl_2 solution of [20] at room temperature produces no apparent reaction.

Reaction of [4] with Primary Phosphines

Analogous to the reaction of secondary phosphines, $PhPH_2$ and $CyPH_2$ also react with [4] to give $\{Cp(CO)_2Fe[CH(SMe)(PPhH_2)]\}CF_3SO_3$, [16] and $\{Cp(CO)_2Fe[CH(SMe)(PCyH_2)]\}PF_6$, [17], (after metathesis with KPF_6 in CH_3CN) respectively (Eqn. 51). The ^{31}P NMR spectrum of [17] displays a deceptive triplet and the J_{PH} coupling constant (470 Hz) is consistent with the formulation in which both hydrogen atoms remain on the phosphorus.[92] Moreover, the phosphonium hydrogens of [16] and [17] are shown by ^1H NMR to be diastereotopic, because of the adjacent chiral methine carbon which was illustrated in Figure 3 earlier. IR and ^{13}C NMR spectra of these complexes are similar to those of the 2° phosphine adducts; these spectral data are summarized in Tables 7-8.

$$\underset{[4]}{\{Cp(CO)_2Fe[CH(SMe)]\}CF_3SO_3} \xrightarrow[2)\ KPF_6]{1)\ PRH_2} \{Cp(CO)_2Fe[CH(SMe)(PH_2R)]\}X \qquad (51)$$

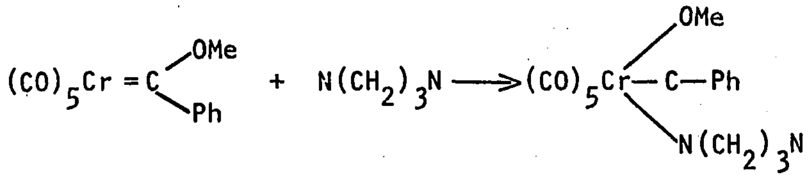
	R	X	%
[16]	Ph	CF_3SO_3	58
[17]	Cy	PF_6	52

Like their secondary phosphine analogs, [16] and [17] seem to rearrange at 160°C in the solid state based on IR spectra (2058, 2015;

2058, 2012 cm^{-1}, respectively) of the reaction mixture. However, ^1H NMR spectra of these reaction products indicate them to be mixtures, and they have not yet been positively identified.

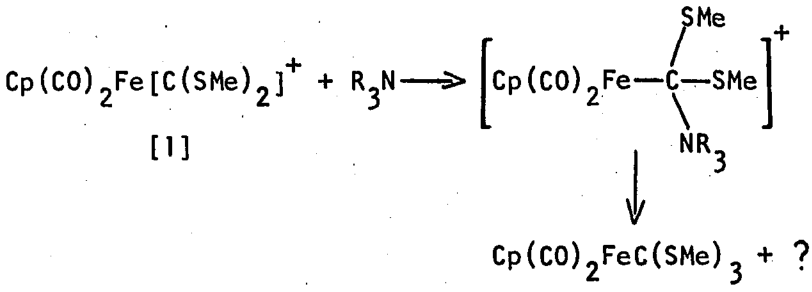
Reaction of [4] with Pyridine

Much attention has been paid to the reactivity of carbene complexes with 3° phosphines and phosphites; the analogous reactions with tertiary amines are seldom reported. Kreissel et al.[94] reported the preparation of a nitrogen adduct by reacting $(CO)_5Cr[C(OMe)Ph]$ and Dabco (Eqn. 52). A similar reaction was also observed between quinuclidine and $(CO)_5W[C(OMe)Ph]$.[95] Recently, Tam et al.[23] obtained $Cp(PPh_3)(NO)Re[CH_2Pyr]^+$ from the reaction of the methylidene complex with pyridine.



$$(CO)_5Cr{=}C(OMe)(Ph) + N(CH_2)_3N \longrightarrow (CO)_5Cr{-}C(OMe)(Ph)(N(CH_2)_3N) \qquad (52)$$

McCormick et al.[73] observed the disproportionation of [1] when it was treated with a variety of tertiary amines; an amino adduct was proposed as the key intermediate (Eqn. 53).

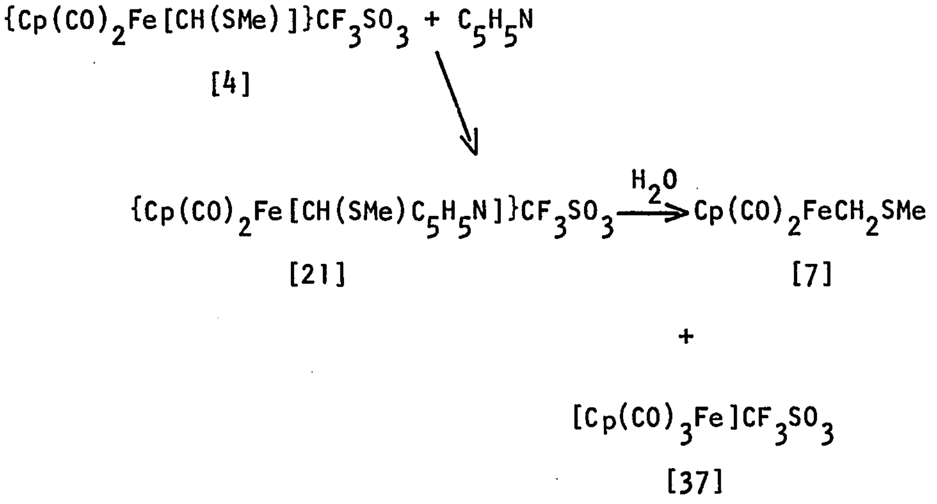


$$\underset{[1]}{Cp(CO)_2Fe[C(SMe)_2]^+} + R_3N \longrightarrow \left[Cp(CO)_2Fe{-}C(SMe)(SMe)(NR_3)\right]^+ \qquad (53)$$

$$\downarrow$$

$$Cp(CO)_2FeC(SMe)_3 + ?$$

Although, [4] does not appear to react with Dabco, at least to an appreciable extent, it smoothly reacts with pyridine to afford a bright-yellow solid upon recrystallization. Spectral data suggest that this modestly moisture-sensitive material is $\{Cp(CO)_2Fe[CH(SMe)(Pyr)]\}CF_3SO_3$, [21] (Eqn. 54). Compound [21] is hydrolyzed in wet organic solvent to [7] and [37]. The pathway which leads to the formation of these products is probably similar to that for the reaction of [4] and H_2O; a more detailed discussion is deferred to a later section.



$$\underset{[4]}{\{Cp(CO)_2Fe[CH(SMe)]\}CF_3SO_3} + C_5H_5N \longrightarrow \underset{[21]}{\{Cp(CO)_2Fe[CH(SMe)C_5H_5N]\}CF_3SO_3} \xrightarrow{H_2O} \underset{[7]}{Cp(CO)_2FeCH_2SMe} + \underset{[37]}{[Cp(CO)_3Fe]CF_3SO_3} \qquad (54)$$

As in reaction 53, [21] decomposes slowly at room temperature in the solid state or dried solvents to give mainly [2]. Since the process is rather slow, [21] may be stored indefinitely under an N_2 atmosphere at -20°C.

The infrared spectrum (Table 9) of [21] in CH_2Cl_2 displays two strong ν(CO) absorptions (2022, 1974 cm^{-1}) which are in the region characteristic of the PR_3 adducts (Table 3). The methine, FeCH, proton resonance is at 6.5 δ (Table 9) which is noticeably more deshielded than the corresponding signal in the PR_3 adducts (Table 3). The same trend is also observed in the ^{13}C NMR spectrum (Table 10) where the FeCH carbon is found at 64.5 PPM, which is at least 51 PPM downfield from those of the phosphine and phosphite adducts (Table 4). These observations suggest that [21] is more electrophilic and should be more susceptible to nucleophilic attack than the phosphorus analogs. That notion is supported by the reaction of [21] with H_2O (Eqn. 54), whereas [8] and [13b] tolerate H_2O.

Chemical Reactivity of [21]

Besides reacting with water, [21] also reacts smoothly with various organic nucleophiles which have proven to be effective in reactions with the parent compound, [4]; however, the reactions with [21] are slower than those with [4]. [21] reacts with 2 eqv. of diethylamine and t-butylamine to afford $\{Cp(CO)_2Fe[CH(NEt_2)]\}CF_3SO_3$,[23], and $\{Cp(CO)_2Fe[CH(NHBu^t)]\}CF_3SO_3$,[28], respectively (Eqn. 55, Tables 9-10). Frequently, these reactions produce slightly higher yields of the desired products and lesser amounts of [2] (10%). In contrast, [2] is one of the major products (25-35%) in the reactions of [4] and amines under similar conditions. The advantages of [21] are also seen in the reaction with NH_3 which gives $\{Cp(CO)_2Fe[CH(NH_2)]\}CF_3SO_3$,[29],

Table 9. Selected IR and ^1H NMR data for pyridine adduct and secondary amino carbene complexes

Complex		IR^a (ν(CO), cm^{-1})	
$\{Cp(CO)_2Fe[CH(SMe)(C_5H_5N)]\}CF_3SO_3$	[21]	2022s	1974 s
$\{Cp(CO)_2Fe[CH(NMe_2)]\}PF_6$	[22]	2049 s	2005 s
$\{Cp(CO)_2Fe[CH(NEt_2)]\}CF_3SO_3$	[23]	2048 s	2004 s
$\{Cp(CO)_2Fe[CH(NHMe)]\}PF_6$	[24]	2055 s	2007 s
$\{Cp(CO)_2Fe[CH(NHCy)]\}CF_3SO_3$	[25]	2054 s	2004 s
$\{Cp(CO)_2Fe[CD(NHCy)]\}CF_3SO_3$	[26]	2053 s	2007 s
$\{Cp(CO)_2Fe[CH(NHPr^i)]\}PF_6$	[27]	2053 s	2005 s
$\{Cp(CO)_2Fe[CH(NHBu^t)]\}CF_3SO_3$	[28]	2055 s	2007 s
$\{Cp(CO)_2Fe[CH(NH_2)]\}CF_3SO_3$	[29]	2056 s	2010 s
$\{Cp(CO)(MeCN)Fe[CH(NHCy)]\}CF_3SO_3$	[36]	1994	

[a] CH_2Cl_2 solution.
[b] $CDCl_3$ solution.
[c] CD_3CN solution.
[d] CD_3COCD_3 solution.
[e] CD_2Cl_2 solution.
*Exchanges with D_2O.

Cp	CH	NH*	Other
5.10[b]	6.42		9.31 (d, J_{HH}=5.49); 8.30 (t, J_{HH}=6.96); 7.92 (t, J_{HH}=6.60) [Pyr], 1.92 (SMe)
5.30[c]	10.79		1.94 (d, J_{HH}=2.6); 1.89 (d, J_{HH}=2.2) [NMe]
5.59[d]	11.30		3.99 (q, J_{HH}=7.3); 3.96 (q, J_{HH}=7.3) [NCH_2] 1.47 (t, J_{HH}=7.3); 1.36 (t, J_{HH}=7.3) [$NCH_2\underline{Me}$]
5.29[c]	10.69	10.90	3.33 (d, J_{HH}=3.3, NMe)
5.25[e]	10.76	10.55	3.52 (br); 1.56 (m) [Cy]
5.25[e]		11.63 (br)	3.49 (br); 1.56 (m) [Cy]
5.28[b]	10.85	10.64	3.89 (h, J_{HH}=6.6, $NC\underline{H}Me_2$), 1.38 (d, J_{HH}= 6.6, $NCH\underline{Me}_2$)
5.27[b]	10.83	10.63	1.42 (t-Bu)
5.33[c]	11.30 (m)	11.51 (m)	
4.76[b]	11.62	11.84	3.56 (m); 1.88-1.26 (m) [Cy], 2.35 (MeCN)

Table 10. ^{13}C NMR data for the pyridine adduct and secondary amino carbene complexes in CD_3CN

Complex	Carbene	CO	Cp	Others
[21][a]		213.6	87.2	19.8 (SMe), 143.0; 141.9; 128.2 [Pyr]
		213.2		64.5 (CH)
[22]	234.9	211.8	88.8	55.9; 47.7 [NMe]
[23]	232.4	211.7	88.9	58.8; 53.2 [$N\underline{C}H_2$] 14.4; 13.2 $NCH_2\underline{Me}$
[24]	238.6	211.2	88.6	45.8 (NMe)
[25]	235.1	211.3	88.8	69.9; 32.5; 25.3; 25.1 [Cy]
[26]	234.5 (t, 23.44)[b]	211.3	88.8	69.8; 32.5; 25.3; 25.1 [Cy]
[27]	234.5	211.5	88.8	63.3 ($N\underline{CH}Me_2$), 21.8 ($NCH\underline{Me}_2$)
[28]	231.2	212.5	89.7	66.5 ($N\underline{C}Me_3$), 29.0 ($NC\underline{Me}_3$)
[36][a]	243.9	216.1	83.7	133.7 (CN), 69.1; 32.1; 24.8; 24.6 [Cy], 5.1 (Me)

[a] $CDCl_3$.

[b] J_{CD}.

that is more readily purified than that obtained from [4]. Compound [29] has been synthesized from [4] and NH_3, but only an oily product which could not be purified was obtained (Eqn. 55).

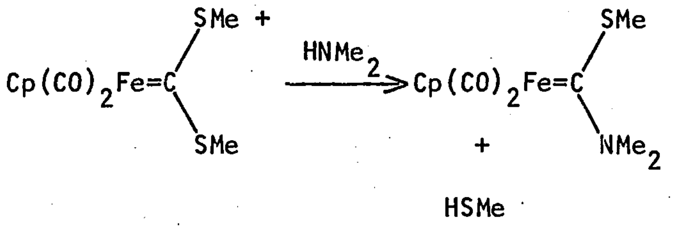
$$\underset{[21]}{\{Cp(CO)_2Fe[CH(SMe)C_5H_5N]\}CF_3SO_3} + NHRR' \longrightarrow \{Cp(CO)_2Fe[CH(NRR')]\}CF_3SO_3 \qquad (55)$$

	R	R'	%
[23]	Et	Et	32
[28]	t-Bu	H	47
[29]	H	H	20

Although, extensive chemical reactivity studies on [21] have not been undertaken, the success in Equations 54-55 suggest that [21] may be a useful and stable equivalent of [4].

Aminolysis of [4]

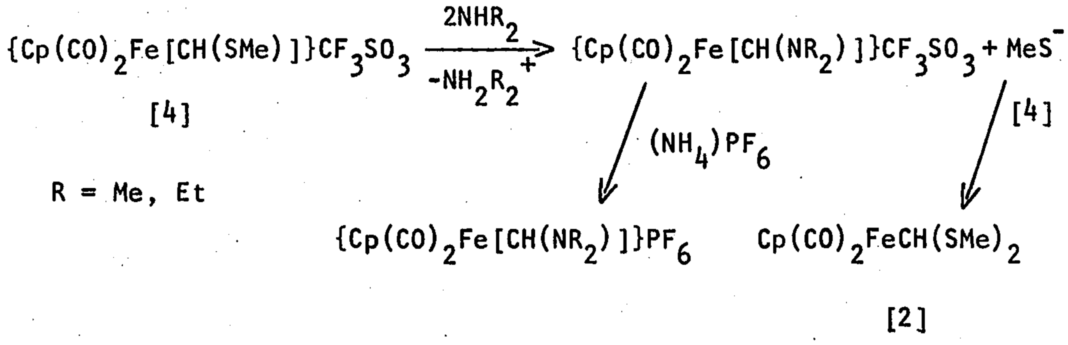
Reactions of amine nucleophiles with thioalkoxyl carbenes are known[19,96-98] to lead to the replacement of the thioalkoxyl group by an amino group, as illustrated in Equation 56. This reaction is undoubtedly facilitated by the good leaving ability of the thioalkoxyl group. The amino thiocarbene products are stabilized by strong p-p π-bonding between the nitrogen lone pair electrons and the C_{carb} Pz.



(56)

Secondary amines

When approximately one eqv. of Me_2NH is bubbled into a CH_2Cl_2 solution containing [4], an immediate color change is apparent. Upon evaporation of the solvent, a benzene extract and a CH_2Cl_2-soluble portion are obtained. The yellow air-sensitive benzene portion displays IR and ^1H spectra characteristic of [2]. The yield of [2] ranges from 20 to 35%, and is dependent upon the concentration of [4]. The formation of [2] is probably formed in a secondary reaction between [4] and MeS^- which is generated under the basic reaction conditions (Eqn. 57). An analogous reaction has been demonstrated[73] in a more sterically demanding and less electrophilic dithioalkoxyl carbene system, [1] (Eqn. 58).



(57)

$$\{Cp(CO)_2Fe[C(SMe)_2]\}PF_6 + NaSMe \longrightarrow Cp(CO)_2FeC(SMe)_3 + NaPF_6 \qquad (58)$$
$$[1]$$

The CH_2Cl_2 fraction is metathesized with $(NH_4)PF_6$/acetone and readily recrystallized from CH_2Cl_2/Et_2O to furnish pale yellow, air-stable crystals of $\{Cp(CO)_2Fe[CH(NMe_2)]\}PF_6$,[22], (30%). The yield of [22] is diminished sharply when more than one eqv. of Me_2NH is used. The predominate organometallic product when a 5:1 amine/carbene ratio is utilized is $[Cp(CO)_2Fe]_2$,[3]; the organic product in this case was found by its IR(ν(CN) = 1700 cm^{-1}) and NMR spectra[99] to be $[Me_2NCHNMe_2]CF_3SO_3$. Complex [3] is seemingly produced from the further reaction of [22] with excess amine; mechanistic aspects of this secondary reaction will be discussed in detail later.

Analogously, $\{Cp(CO)_2Fe[CH(NEt_2)]\}CF_3SO_3$,[23], may also be prepared, and the yields of [23] and [2] are comparable to those in the Me_2NH reaction (Eqn. 57). An excess of Et_2NH also decreases the yield of the desired complex, [23].

Spectral properties of [22] and [23] As mentioned previously, a lone-pair-bearing heteroatom (N, O, or S) is capable of p-p π-bonding to the empty P_z orbital of C_{carb}, resulting in a multiple-bond between the C_{carb} and the heteroatom. This results in restricted rotation around the C_{carb}-N bond in amino carbene complexes. This restricted rotation has been noted in the ^1H spectrum of $Cl_3(PEt_3)_2Rh[CH(NMe_2)]$[12], in which, two separate methyl signals were observed. These signals do not coalesce even at a temperature of 150°C.

In the ^{1}H NMR spectrum of [22] (Table 9), the methyl region shows two doublets. The doublets are assigned to two chemically and magnetically non-equivalent methyls (designated cis and trans in Figure 6) which are coupled differently to the carbene hydrogen.

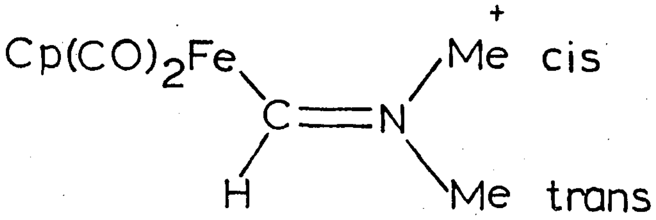


Figure 6. An illustration of [22]

Their non-equivalence is further supported by the ^{13}C spectrum (Table 10), in which, two distinct methyl carbon signals are observed. Collectively, these observations can be explained by assuming there is restricted rotation around the C_{carb}-N bond (Figure 6).

In the same way, ^{1}H and ^{13}C spectra of [23] exhibit two distinct ethyl groups; its ^{1}H spectrum is illustrated in Figure 7.

Primary amines

As shown in Equation 59, nucleophilic displacement of a thiomethoxyl group by a primary amine is a method for preparing $[Cl(PPh_3)_2(CO)_2Os(CH(NHMe))]^+$ from its thiomethoxyl carbene precursor[19]. Methylmercaptan was the other product.

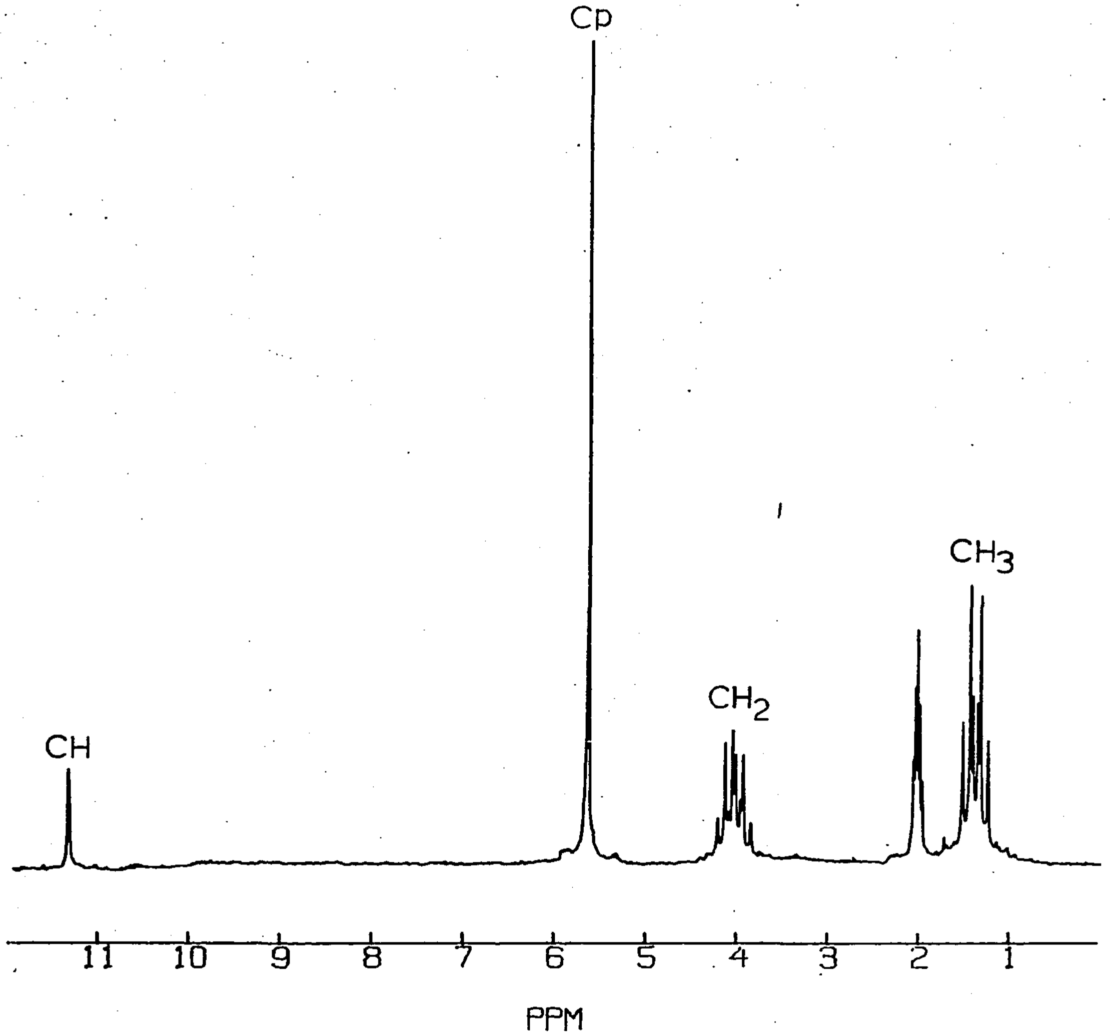


Figure 7. ^{1}H spectrum of $\{Cp(CO)_2Fe[CH(NEt_2)]\}CF_3SO_3$, [23], in d^6 acetone

$$\begin{array}{l} \text{trans } \{Cl(PPh_3)_2(CO)_2Os[CH(SMe)]\}SO_3F \\ \qquad\qquad \Big\downarrow H_2NMe \\ MeSH + \text{trans } \{Cl(PPh_3)_2(CO)_2Os[CH(NHMe)]\}SO_3F \end{array} \tag{59}$$

In the same way, we find that [4] reacts with a variety of amines, $MeNH_2$, $CyNH_2$, $i\text{-}PrNH_2$ and $t\text{-}BuNH_2$ giving the corresponding amino carbene complexes by displacing the thiomethoxide (Eqn. 60). Spectroscopic data for the amino carbene complexes are summarized in Tables 9 and 10.

$$\underset{[4]}{\{Cp(CO)_2Fe[CH(SMe)]\}CF_3SO_3} \xrightarrow{H_2NR} \{Cp(CO)_2Fe[CH(NHR)]\}CF_3SO_3 + \underset{[2]}{Cp(CO)_2CH(SMe)_2} \tag{60}$$

	R	% carbene
[24]	Me(PF_6^-)	28
[25]	Cy	35
[27]	i-Pr	30
[28]	t-Bu	38

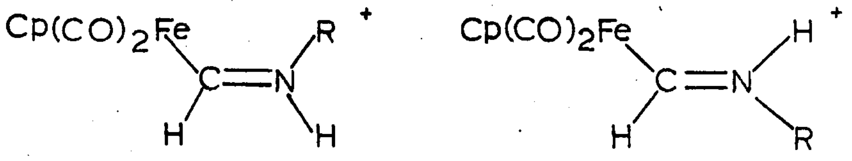
Although the reactions are virtually complete upon addition of one eqv. of the amine to [4], the yields of the amino carbenes are low (28-38%), and the yields of the side product , [2], are comparable (30-35%). Ironically, in an effort to improve the yields of the carbene complexes in Equation 60 by using a 2-5 fold excess of the amine to compete for the available [4] with MeS$^-$, lower or no yields of the desired amino carbene were obtained. In these cases, [2] and [3] are the other identified organometallic products (Eqn. 61).

$$\underset{[4]}{\{Cp(CO)_2Fe[CH(SMe)]\}CF_3SO_3} \xrightarrow{5\ \text{eqv.}\ NH_2Cy} \underset{[3]}{[Cp(CO)_2Fe]_2} + \underset{[2]}{Cp(CO)_2FeCH(SMe)_2} \qquad (61)$$

Spectral properties Infrared ν(CO) bands of these primary amino carbenes resemble those of [22] and [23] occurring as two strong absorptions in the regions of 2053-5 and 2004-7 cm^{-1}; they are an average of 20 cm^{-1} lower than those in [4] (Table 2). The carbene hydrogen is found in the general range 11.5-10 δ which is significantly more shielded, at least 3.5 PPM, than the thiomethoxyl analog, [4] (Table 2).

Although, ^{13}C data for [4] are not available for comparison, the C_{carb} resonance of a more stable and relatively electron-richer analog, $\{Cp(CO)(P(OPh)_3)Fe[CH(SMe)]\}CF_3SO_3$, [44], is found at least 90 PPM downfield from the C_{carb} resonance in these amino carbene complexes. In summary, the decreases in carbonyl stretching frequencies together with increases in shielding of the α-hydrogen of the carbene ligand are probably caused by greater p-p π-backbonding from X to the C_{carb} Pz orbital when X is N as compared to the situation when X = S.

Stereochemistry of primary amino secondary carbene complexes The amino carbene complexes prepared from primary amines may exist in either of two isomeric forms, that with the alkyl group syn to the $Cp(CO)_2Fe$ moiety and that with it anti (Figure 8). Restricted rotation around the C_{carb}-N bond would suggest that the isomers should interconvert sufficiently slow that both isomers could be observed in NMR spectra of the compounds. Both isomers were observed for the trans $[Cl(PEt_3)_2Pt(CH(NHR))]^+$ (R = p-tolyl)[11] carbene compound.



SYN ANTI

Figure 8. Syn and anti isomers of $Cp(CO)_2Fe[CH(NHR)]^+$

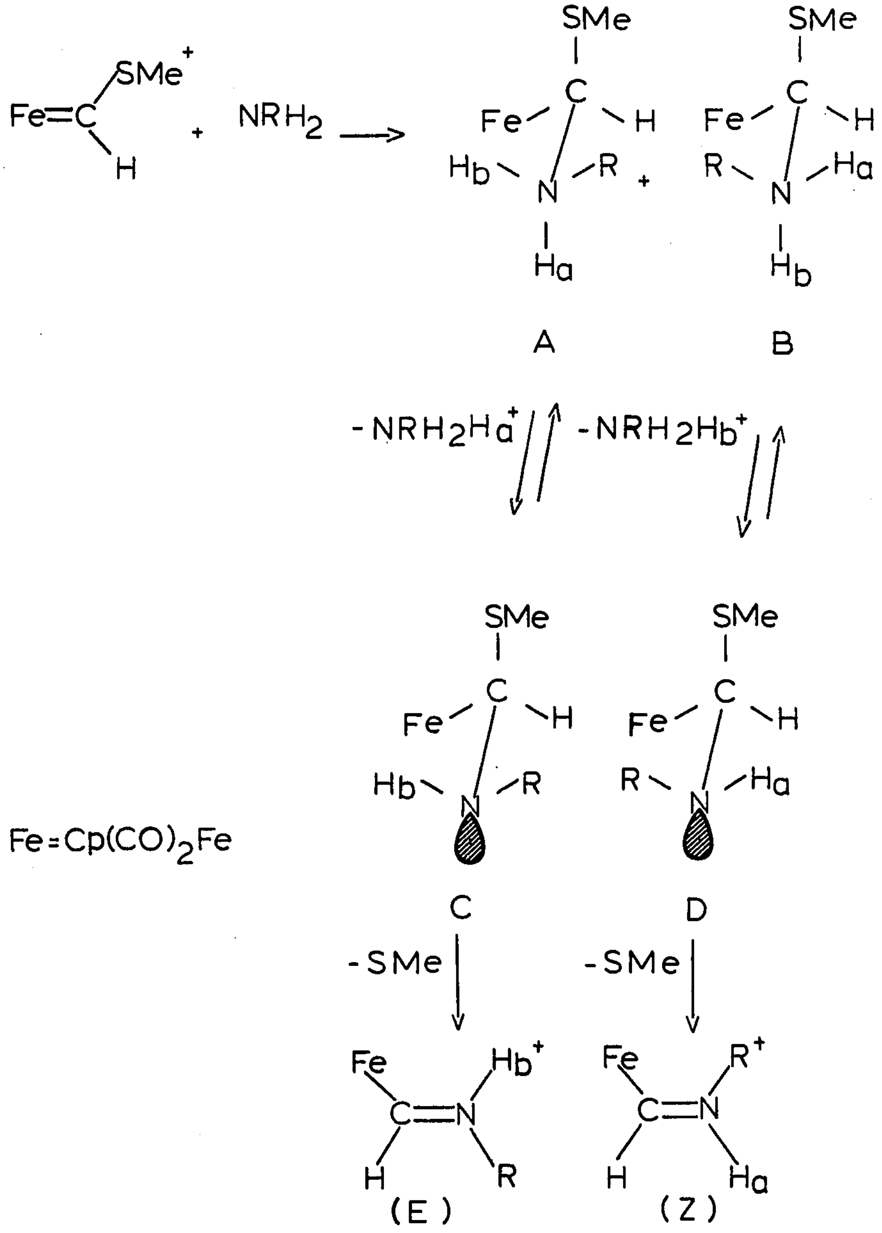
In contrast, ^{1}H and ^{13}C NMR spectra of [24]-[28] show the presence of only one isomer. Even with the sterically undemanding alkyl, [24], (R = Me), only one isomer is observed; a single doublet caused by coupling to the amino hydrogen is found. This doublet collapses to a singlet when D_2O is added to the solution.

Syn-anti structural assignments based on $^3J_{NHCH}$ coupling constants have been made in other primary amino carbene complexes[11]. Since the NH and CH resonances of these carbene complexes of iron are rather broad and unresolved, the $^3J_{NHCH}$ coupling constants are not computed. Based on steric arguments, the anti isomer is likely to be the more stable; indeed, the anti isomer is often the predominant species in other amino hydrido carbene complexes[11,19]. Thus, we believe that the anti isomer is probably the isomer which is observed in the NMR spectra of solutions of complexes [24]-[28].

One might speculate on mechanisms which would lead to that isomer only. By analogy with reactions of [4] with nucleophiles such as pyridine and phosphines, the primary amine probably first attacks the C_{carb} of [4] to give the adduct. Two of the possible rotomers of the adduct are shown as structures A and B in Scheme 3. In the presence of amine, one of the amino protons of A and B may be removed by a second mole of amine. Such a mechanism has been proposed[100] for a key step in the related reaction shown in Equation 62. This proton removal assists the elimination of MeS^- thus affording the amino carbene. This form of elimination is called an ElcB[101] mechanism.

$$(CO)_5W[C(SMe)_2] + H_2NR \longrightarrow (CO)_5WCNR + 2HSMe \qquad (62)$$

By and large, ElcB reactions proceed in an anti-periplanar fashion where the leaving group and the nucleophile achieve a dihedral angle of 180°. In that geometry, electron-electron repulsion between the incoming and leaving groups is minimized in the transition state. Removal of Ha by amine in A is preferred over Hb, owing to the fact that the former proton is more accessible to base. Thus, the neutral complex C is the predominate species. The lone pair of electrons on the nitrogen of C is now aligned anti-periplanar to the leaving group, MeS^-, which would facilitate MeS^- dissociation. This would lead to the anti complex. Similarly, if Hb in B were removed with base, the resulting D would



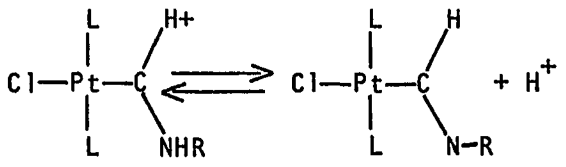
Scheme 3

ultimately yield the syn isomer. On steric grounds, structure B is likely to be present in lower concentration than A due to severe repulsion between the $Cp(CO)_2Fe$ and R moieties in rotomer B. Thus, structure A is favored, and the anti isomer would be predicted to be the major product in reaction 60, as observed.

The mechanistic arguments suggest that the anti isomer could be the sole kinetic product. However, it is also possible that an iminoyl formyl, $Cp(CO)_2Fe[CH{=}NR]$, is formed which isomerizes to the more thermodynamically stable anti product. In fact, studies of the alkylation of $Cp(CO)_2Fe[CH{=}NR]$ suggest that syn-anti interconversion in the iminoyl formyl complexes does occur. Thus, it is not possible to say whether stereospecific formation of the anti isomer of the amino carbene complex occurs for kinetic or thermodynamic reasons.

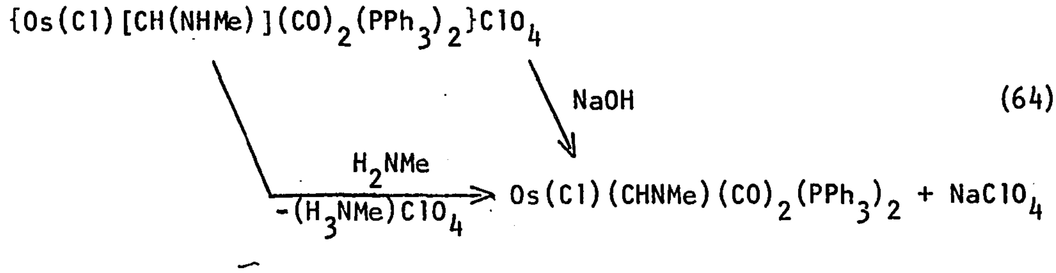
Reaction of $\{Cp(CO)_2Fe[CH(NHR)]\}X$ with Base

The amino proton of primary amino secondary carbene complexes has previously been found to undergo rapid exchange with D_2O[11,19]. At high temperature, $\{(Cl)(PEt_3)_2Pt[CH(NHR)]\}X$[11] was postulated to be in equilibrium with its iminoyl formyl (Eqn. 63).



(63)

Although the Pk_a of this equilibrium has not yet been determined, this equilibrium together with the D_2O exchange results clearly indicates the lability of the amino carbene proton. Indeed, amines[11,19] and sodium hydroxide[19] have been shown to be effective for the deprotonation reaction in Equation 64[19].



(64)

When [25] is allowed to react with a saturated NaOH-EtOH solution in CH_2Cl_2, the deprotonation reaction occurs immediately upon addition of the base to produce $Cp(CO)_2Fe(CHNCy)$,[30], in 78% yield. Likewise, [27] and [28] could also be deprotonated with the base, giving $Cp(CO)_2Fe(CHNPr^i)$ ([31], 68%) and $Cp(CO)_2Fe(CHNBu^t)$ ([32], 76%), respectively. These complexes [30]-[32], are vulnerable to air oxidization either in solution or solid; and revert to the trans isomer of the carbene complexes in the presence of 5 eqv. of CF_3SO_3H in Et_2O. When they are kept in an inert atmosphere at room temperature for a few hours, a small amount of decomposition is apparent; the products of this decomposition are [3], characterized by its IR spectrum, and the corresponding isocyanide (RNC), identified by its distinctive odor. Whether the isocyanide is derived from a retro-metal-hydride-insertion reaction of $Cp(CO)_2FeH$,[35], remains to be explored (Eqn. 65), though, the reverse reaction has been known for sometime[16,18] (Eqn. 66)[102].

$$\begin{tikzcd} \mathrm{Cp(CO)_2Fe(CHNR)} \arrow[r, "?"] & \mathrm{Cp(CO)_2FeH + RNC} \arrow[d, "{[35]}"] \\ \mathrm{R = Cy,\ i\text{-}Pr,\ t\text{-}Bu} & \begin{array}{c}\mathrm{[Cp(CO)_2Fe]_2} \\ \mathrm{[3]}\end{array} \end{tikzcd} \qquad (65)$$

$$\mathrm{(C_5Me_5)_2ZrH_2 + MeNC} \xrightarrow{-65^{\circ}C} \mathrm{(C_5Me_5)_2Zr(H)(CHNMe)} \qquad (66)$$

Spectral properties of [30]-[32]

The infrared spectrum of [32] in hexane exhibits two ν(CO) absorptions (2019, 1972 cm^{-1}), and its ^1H spectrum in $CDCl_3$ shows the CH resonance at a position upfield relative to [28], as expected for the removal of H^+ from the ligand (Tables 11, 12). More importantly, the ^1H NMR spectrum shows the presence of only one isomer. However, the IR spectra of [30] and [31] display six and five carbonyl stretching bands, respectively. The Cp resonance of [30] appears as a doublet while the CH occurs as a doublet and singlet in its ^1H NMR spectrum in $CDCl_3$. The ^1H spectrum of [31] exhibits the Cp and i-Pr groups as doublets, and the CH appears as a singlet and doublet (Figure 9a). The CH doublet in [31] is observed to collapse to a singlet when the methine resonance region of the i-Pr group is simultaneously irradiated in a homonuclear gated decoupled experiment (Figure 9b). Since two sets of CH and Cp

Table 11. Selected IR data for iminoyl formyl complexes and their carbene derivatives

Complex		ν(CO) cm^{-1}
$Cp(CO)_2Fe(CHNCy)^a$	[30]	2030 s, 2021 s, 2013 s, 1982 sh, 1971 vs, 1963 s
$Cp(CO)_2Fe(CHNPr^i)^a$	[31]	2028 sh, 2014 s, 1980 sh, 1971 s, 1963 s
$Cp(CO)_2Fe(CHNBu^t)^a$	[32]	2019 s, 1972 vs
$\{Cp(CO)_2Fe[CH(NMeCy)]\}SO_3F^b$	[33]	2049 s, 2003 s, 1998 sh
$\{Cp(CO)_2Fe[CH(NMePr^i)]\}SO_3F^b$	[34]	2044 s, 2000 s

[a] Hexane.

[b] CH_2Cl_2.

Table 12. ^{1}H NMR data for iminoyl formyl and carbene complexes (δ)

Complex		CH
[30][a]	Syn	10.15
	Anti	10.18 (d, $^4J_{HH}$ = 1.79)
[31][a]	Syn	10.21
	Anti	10.16 (d, $^4J_{HH}$ = 2.20)
[32][a]	Anti	10.22
[33][b]	Z	10.84
	E	11.03
[34][b]	Z	10.83
	E	11.04

[a] $CDCl_3$.
[b] CD_3CN.

Cp	Other
4.85	2.91 (m, Cy), 1.58 (m, Cy)
4.90	2.91 (m, Cy), 1.58 (m, Cy)
4.94	3.20 (m, $\underline{CH}Me_2$), 1.17 (d, J_{HH} = 6.23, Me)
4.91	3.20 (m, $\underline{CH}Me_2$), 1.22 (d, J_{HH} = 6.23, Me)
4.84	1.10 (Me)
5.33	3.44 (d, J_{HH} = 1.10, NMe), 3.8 (m); 1.6 (m) [Cy]
5.32, 5.31	3.48 (d, J_{HH} = 0.74, NMe) 3.8 (m); 1.6 (m) [Cy]
5.30	3.90 (h, J_{HH} = 6.60, $N\underline{CH}Me_2$), 3.42 (d, J_{HH} = 0.74, NMe), 1.36 (d, J_{HH} = 0.60, $NCH\underline{Me}_2$)
5.32	4.20 (h, J_{HH} = 6.60, $NC\underline{H}Me_2$), 3.45 (d, J_{HH} = 0.73 NMe), 1.32 (d, J_{HH} = 6.60, $NCH\underline{Me}_2$)

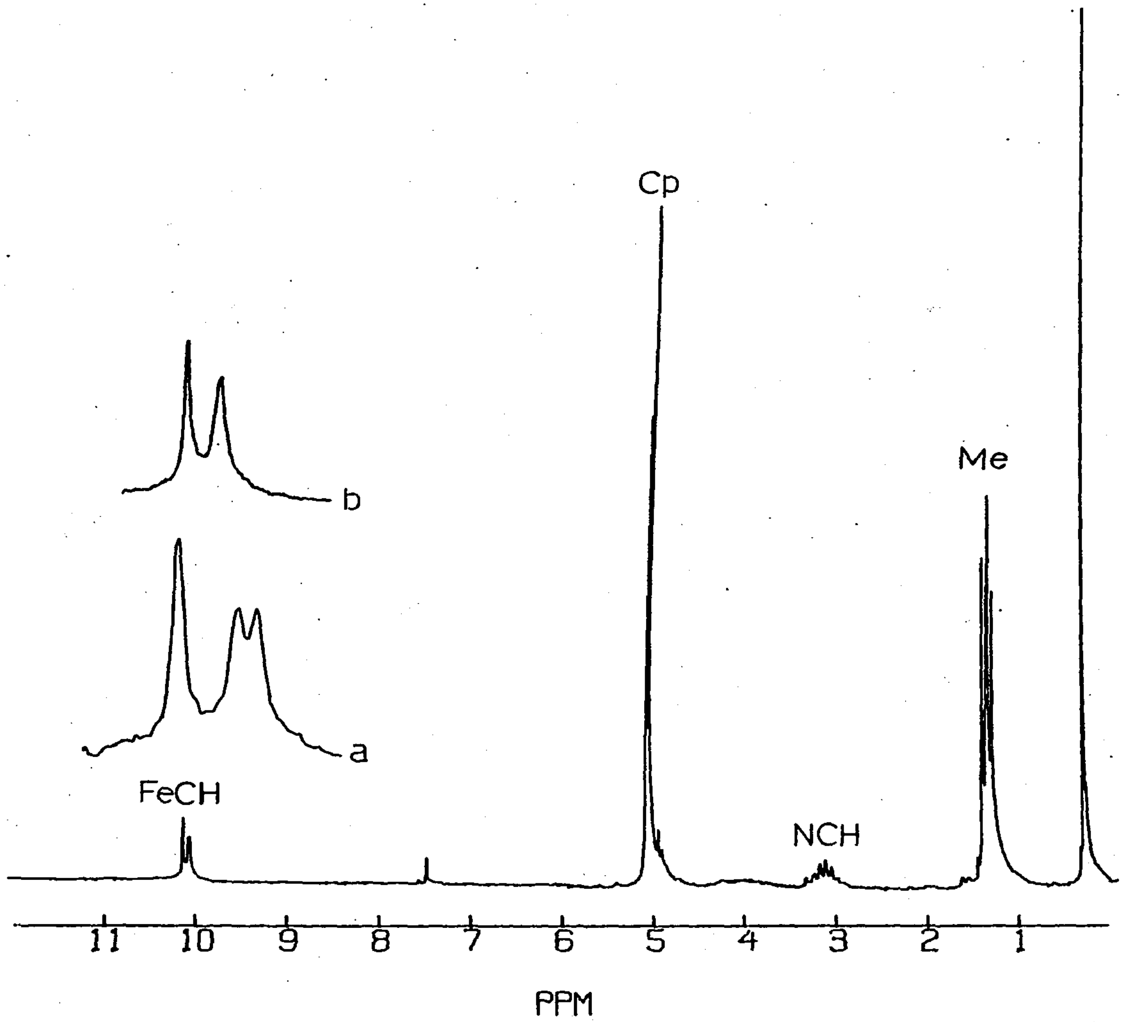


Figure 9. ^{1}H spectrum of Cp(CO)$_2$Fe[CH=NPr^i],[31], in CDCl$_3$ - TMS

a) Expansion of the FeCH region

b) The FeCH region after grated decoupling of the NCH resonances are evident, at least two isomers are present in solutions of [30] and [31]. However, it is not obvious why ν(CO) absorptions are so abundant relative to the ^1H signals, perhaps, two or more isomers are rapidly interconverting such that only their weighted-average spectrum is observed in the NMR, but their individual IR spectra are observed because of the shorter time scale for IR measurements.

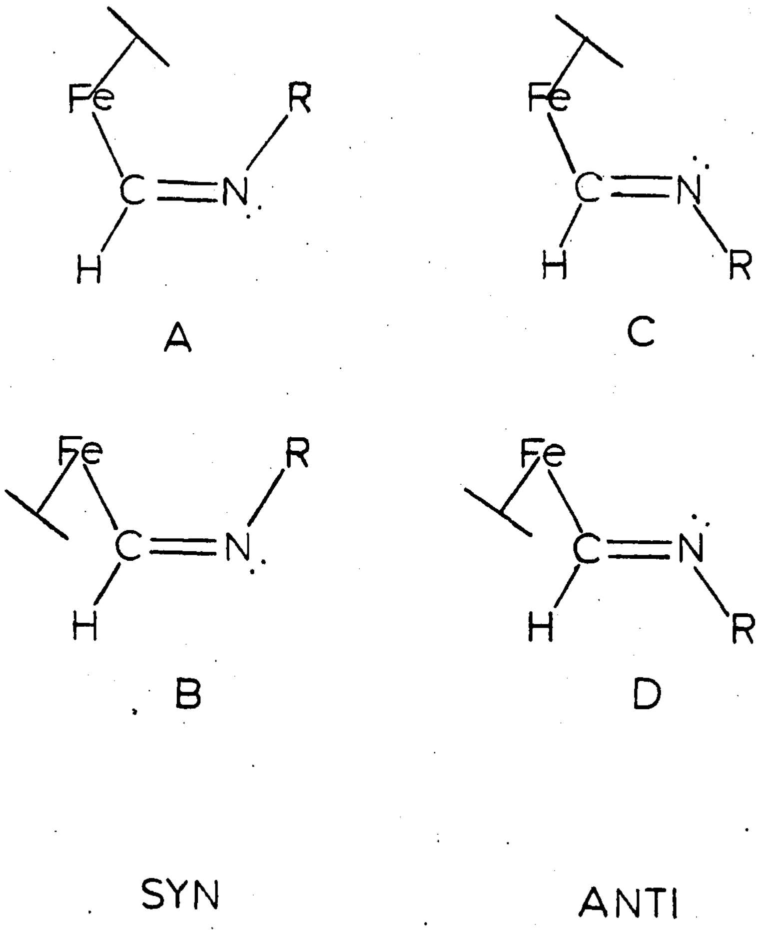


Figure 10. R = i-Pr, t-Bu; CO groups are omitted for clarity

As mentioned in the General Introduction section, on the basis of MO calculations on carbene complexes[103-105], the most favorable orientation of the carbene plane is perpendicular to the Cp plane (see Figure 3-A in General Introduction). In principle, there are four possible isomers for these iminoyl formyl complexes (Figure 10). We postulate that rotation around the Fe-C bond in the iminoyl formyl complexes is faster than the ^1H NMR time scale. Consequently, signals in the ^1H spectra of [30] and [31]could be the average of the syn (Figure 10-A, B) and anti (Figure 10-C, D) pairs.

Although a few other complexes have been reported to be mixtures of syn-anti isomers[18], structural assignments have proven to be difficult and ambiguous. Despite numerous studies of the structures of organic iminoyl formyls, reports of ^1H NMR studies, especially long-range coupling across the C=N double bond, $^4J_{CHNCH_2R}$, for the syn and anti isomers, are few in number. This is because most of the iminoyl formyls exist predominantly in the anti configuration[106]. It has been semi-empirically suggested that in allyl systems, $H_2C{=}C(CH_3)X$, $^4J_{CH_2=CCH_3}$ coupling of a cisoid is stronger than the transoid.[107] However, the ^1H NMR spectrum of N-methylmethylene imine, $H_2C{=}NCH_3$[108], was observed to exhibit an ABX_3 pattern with $^4J_{cis}$ identical to $^4J_{trans}$. Based on the allyic system, the iminoyl formyl hydrogen of [30] in the anti conformation must have a larger $^4J_{HH}$ than the syn counterpart; thus, the doublet is assigned to the isomer where the Cy is trans to the $Cp(CO)_2Fe$ moiety whereas the singlet is the syn isomer. Therefore, the anti:syn ratio is 52:48. Analogously, the anti:syn ratio for [31] is 58:42. It is interesting to note that the anti isomer, which is thermodynamically favored based on steric arguments, is the predominate conformer in both cases, [30] and [31]. Thus, it is conceivable that [32] may adopt only the anti conformation, due to the bulkiness of the t-Bu group. The trend in the anti to syn ratio for [30]-[32] is consistent with steric hindrance arguments which indicate the bulkiness of the R group decreases in the order: t-Bu > i-Pr > Cy. For [30], the anti:syn ratio is the approaching the statistical distribution (50:50); hence, the Cy group appears to exert little or no steric effect on the anti/syn ratio.

Interestingly, both isomers of [30] and [31] are obtained by deprotonation of their trans carbene precursors; thus, syn-anti isomerization must be occurring after removal of the amino proton of the carbene. That is, the iminoyl formyl complex can rapidly isomerize. This phenomenon was observed in $Cl(PEt_3)_2Pt(CHNR)$ using variable-temperature ^1H NMR techniques; however, the barrier of this interconversion for the syn-anti isomers was not determined[18]. An attempt was made to verify rapid isomerization in [31] by variable temperature ^1H NMR studies; it was found that within experimental error, the anti/syn isomeric ratio remains constant from ambient temperature to 50°C.

Evidence for syn-anti interconversion comes, however, from alkylation studies. When an Et_2O solution of [31] is quenched with a 6-fold excess of $MeOSO_2F$ at room temperature, two isomers, E and Z, of $\{Cp(CO)_2Fe[CH(NMePr^i)]\}SO_3F$, [34], are apparent in the ^1H spectrum of the solution. When only three eqv. of $MeOSO_2F$ is added under the same conditions, the E form increases to 95%. These experiments imply that one iminoyl formyl isomer of [31] (anti) is more susceptible to methylation; the less reactive isomer apparently converts to the more reactive form during the reaction. These alkylation reactions will be discussed in detail shortly.

Mechanistic discussion of the syn-anti interconversion in the iminoyl formyl complexes Theoretical calculations on mechanisms of the interconversion of isomers of imines have been performed. Two primary mechanisms, C-N bond rotation and planar inversion of nitrogen (lateral shift mechanism) have been proposed[109]. The rotational pathway requires bond breaking and charge separation in proceeding to the transition state (TS). Inversion involves a linear intermediate which loses its stereochemical integrity (Figure 11).

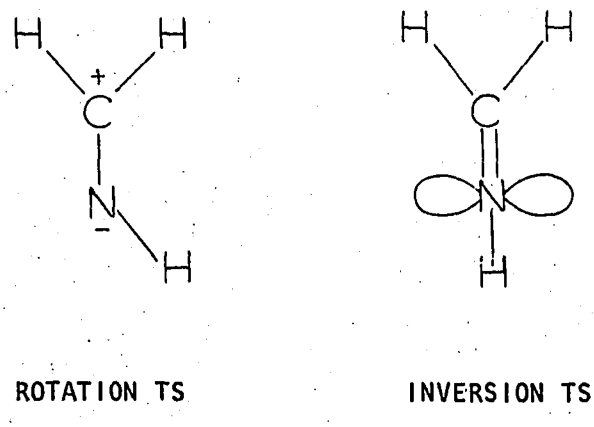
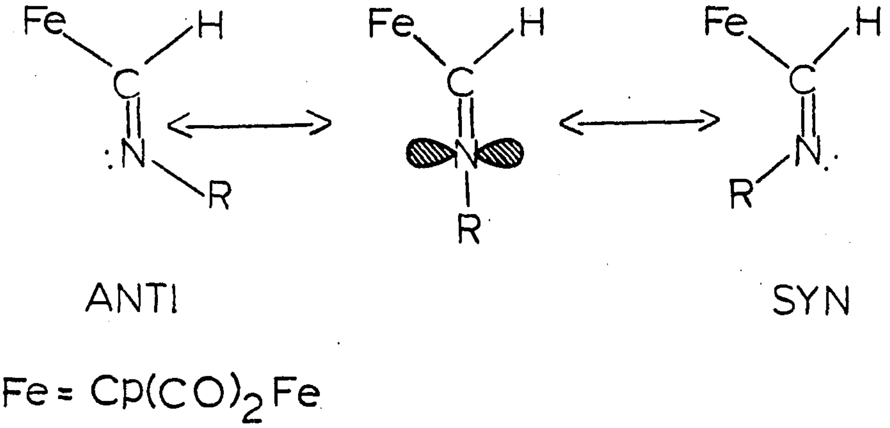


Figure 11. Interconversion transition states

SCF-LCAO-MO calculations for the simple methyleneimine ($H_2C{=}NH$) showed that the barrier for inversion (27.9 kcal/mol) is lower than that for rotation by a factor of 2 (57.5 kcal/mol). Therefore, the inversion pathway appears to be more favorable for the syn-anti topomerization for simple imines. When applied to the iminoyl formyl complexes, the lateral shift mechanism is as shown in Scheme 4.

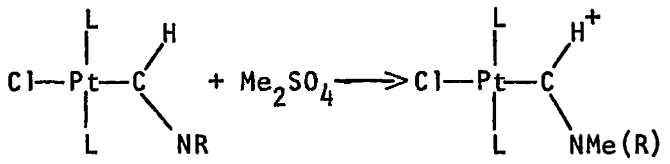


Scheme 4

This mechanism offers an explanation for the ready isomerization of iminoyl formyl complexes, [30] and [31], and the very slow isomerization of their carbene analogs. If a rotation mechanism were involved in the isomerization, one would expect the carbene complexes to isomerize more rapidly than the iminoyl formyls since the C-N bond of a carbene $(I)_2(CNtolyl)(PPh_3)(CO)Ru[CH(NMe(tolyl))]$[15] is known to be longer than its iminoyl formyl analog[21]. In the inversion mechanism, the C-N bond is not broken in the transition state; thus, the increase in the C-N bond strength in the iminoyl formyl complex is probably not an important factor in influencing the overall activation energy. It has also been demonstrated that Lewis acids and protic solvents are capable of retarding the syn-anti topomerization of organic imines[109]. This retardation was rationalized by noting that the lone pair electrons which are needed for the inversion process are bonded by the acid or proton. Thus, a protonated or alkylated iminoyl formyl complex, is unable to undergo the lateral shifting motion. The C-N bond rotation is the other viable alternative pathway for the syn-anti conversion, but as mentioned previously it has a higher energy barrier. Thus, one would expect, and it is observed, that the iminoyl formyl complexes, [30] and [31], are more fluxional than their carbene precursors, [25] and [27].

Methylation of the Iminoyl Formyl Complexes

The methylation of the nitrogen in iminoyl formyl complexes with MeI or (Me)X is facile, giving the corresponding dialkylamino carbene compounds[15,16]. The previously reported methylation of a platinum compound is illustrated in Equation 67.



(67)

L = PEt_3, R = p-tolyl

When an ether solution of [30] reacts with $MeOSO_2F$, a yellow precipitate is formed and the reaction is complete within 5 min; methyl iodide fails to produce a precipitate under similar conditions. IR and ^1H spectra (Tables 11, 12) of the methylated product show the isolated solid to be a mixture of isomeric carbene compounds, $\{Cp(CO)_2Fe[CH(NMe(Cy))]\}SO_3F$, [33], and the product ratio is dependent on the concentration of the methylating agent (Eqn. 68).

$$Cp(CO)_2Fe(CHNR) + MeOSO_2F \longrightarrow \underset{E/Z}{\{Cp(CO)_2Fe[CH(NMe(R))]\}SO_3F} \qquad (68)$$

R = Cy [33]
= i-Pr [34]

With a [30]:$MeOSO_2F$ ratio of 1:10, two carbene hydrogen (11.03, 10.84 δ) and three Cp ring proton (5.328, 5.316, 5.295 δ) resonances are observed. Integration of the three Cp absorptions shows the presence of three isomers in the ratio 74:10:16, respectively (Figure 12-A). When the iminoyl formyl:$MeOSO_2F$ ratio is reduced to 1:6, the Cp ring ratio changes to 17:34:39 (Figure 12-B). Finally, with a ratio of 1:3, the result is 10:71:19 (Figure 12-C) (Table 13).

In these experiments, the carbene hydrogen ratio varies from 26:74, 83.17 to 90:10, respectively (Figure 12). In principle, four products are possible in this reaction (Figure 13). However, it is clear that only three are obtained, and the CH(11.03 δ) and Cp(5.316, 5.295 δ) resonances belong to a pair of isomers whereas CH(10.84 δ) and

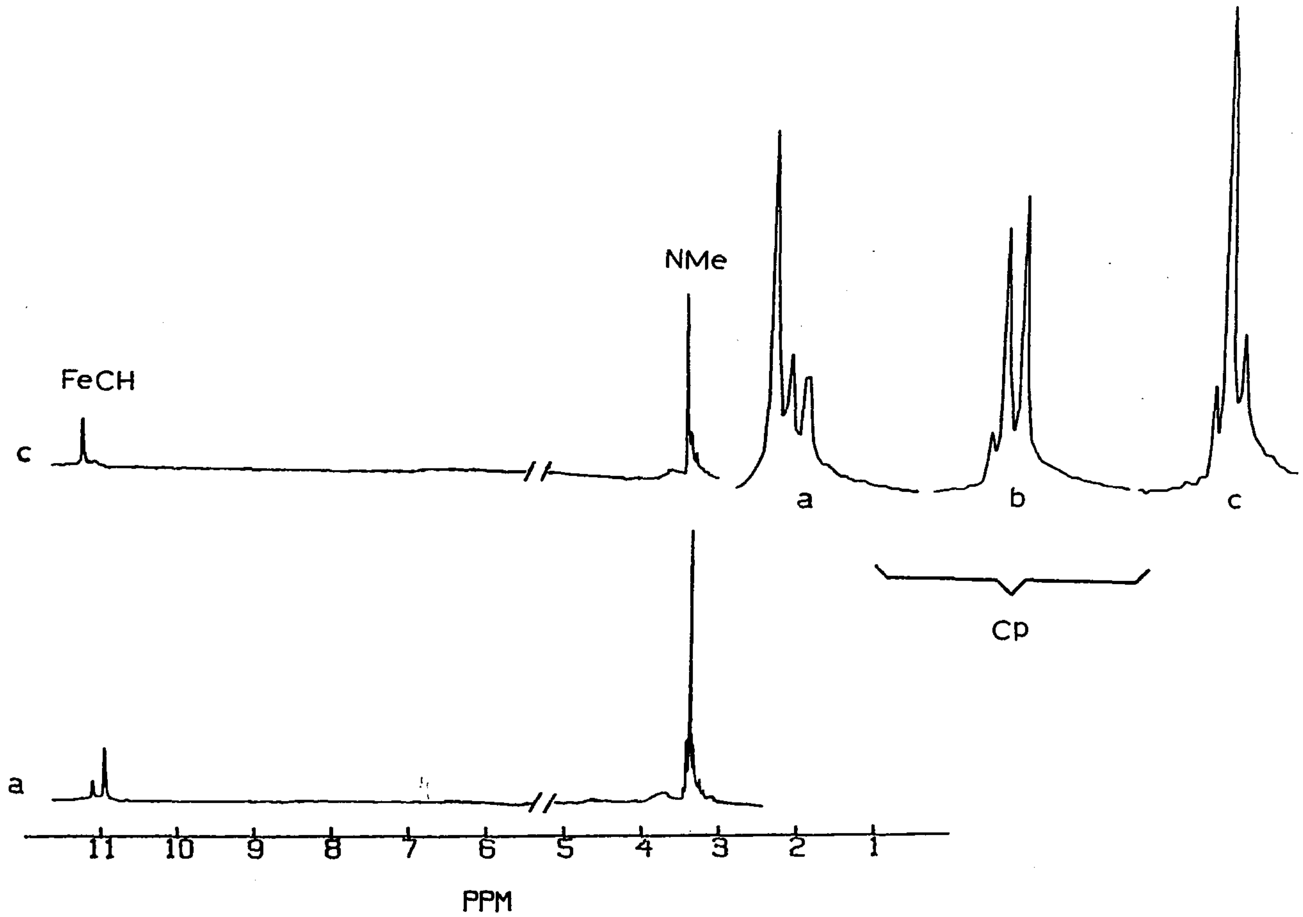
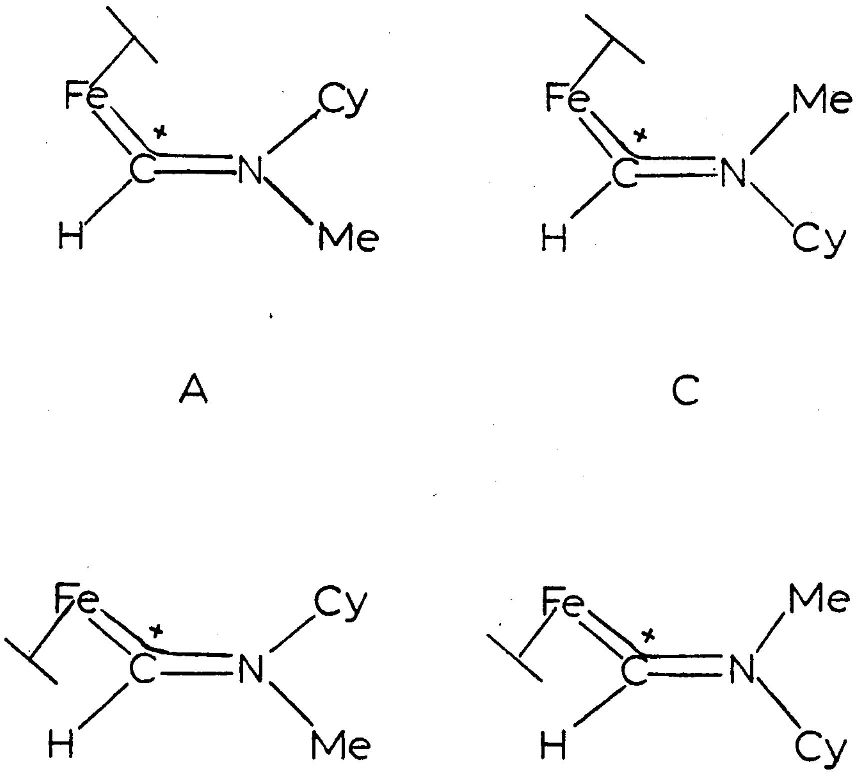


Figure 12. ^{1}H spectra of {Cp(CO)$_2$Fe[CH(NMeCy)]}SO$_3$F,[33]; Cy is omitted. [30]/MeOSO$_2$F ratio: a (1:10), b (1:6), c (1:3)

Cp(5.328 δ) belong to one isomer of the other possible isomeric pair.



A C

B D

(Z) (E)

Figure 13. CO groups are omitted for clarity

As mentioned previously, $^4J_{cis}$ hydrogen coupling constants in the allyic system are larger than $^4J_{trans}$. Thus, the lone isomer is assigned structure B in Figure 13 with $^4J_{CHNMe}$ 1.10 Hz. This assignment is preferred over structure A for steric reasons; since A is too sterically strained and should be the least favored isomer. Thus, when a solution of [30] is quenched with a large excess of $MeOSO_2F$, the product distribution presumably gives a better indication of the thermodynamic distribution of isomers of [30] than when a smaller amount of $MeOSO_2F$ is used. Little or no compound A is observed, as expected. For the remaining isomeric pair, Figure 13-C, D, the $^4J_{CHNMe}$ coupling constant is smaller (0.74 Hz) which is consistent with an E configuration. As the $MeOSO_2F$ concentration decreases, the ratio of the Cp ring areas of this pair (5.316, 5.295 δ) increases. This clearly suggests one of the anti isomers of [30] is more reactive toward the incoming methyl cation. Models also show that the nitrogen lone pair in structure D of Figure 10 is more accessible to Me^+ than it is in C; hence, structure D (5.316 δ) in Figure 13 is probably the predominant product at low $MeOSO_2F$ conditions. It is worth mentioning that structures C and D in Figure 10 are related by a Fe-C bond rotation and are produced in approximately equal amounts using the high $MeOSO_2F$ concentration as shown by the product distribution in Figure 12-A, B. The lowest Me^+ concentration (3-fold excess) gives structure D in Figure 13 almost stereospecifically (Figure 12-C). Therefore, Fe-C bond rotation interconverting structures 10-C and D must be occurring during the alkylation, and the rate must be faster than that of the alkylation of structure 10-D and faster still than the alkylation of structure 10-C at the lowest $MeOSO_2F$ concentration. These relative rates would give predominantly structure 13-D at low $MeOSO_2F$ concentrations. These results lend credence to our earlier assumption of relatively rapid Fe-C bond rotation in [30] which allows the interconversions of the two observed syn and anti isomers.

The E:Z product ratio of the carbene complex [33] also varies with the $MeOSO_2F$ concentration. Structures 10-C and D which give rise to the E isomers are evidently more reactive toward the alkylating agent than structure 10-B, although there is no obvious reason for these differences in rates. The changes in the E:Z product distribution undoubtedly reflect the ongoing isomerization between the syn and anti isomers of [30].

It is worth noting that although the anti:syn ratio of [30] is 52:48, it gives [33] with an E:Z ratio of 26:74 upon methylation with 10 eqv. of $MeOSO_2F$. Since the alkylation reaction was carried out in diethylether while the anti:syn ratio of [30] was determined in $CDCl_3$, the change in isomeric distribution may result from a different distribution of [30] in the different solvents. Such a change in isomeric distribution has been noted in the $Cl(PEt_3)_3Pt(CHNR)$ system[11]. Indeed, when the alkylation is carried out in $CHCl_3$ with a 10-fold excess of $MeOSO_2F$, the E:Z ratio becomes 68:32 (as compared with 26:74 in Et_2O). Interestingly, the major E isomeric product in the above reaction in $CHCl_3$ is structure 13-C (64%) which was found to be formed in only a slightly greater amount than 13-D when the alkylation was carried out with a 10-fold excess of $MeOSO_2F$ in ether solvent (Table 13). These results suggest that structure 10-C is sterically more favorable than D since the nitrogen lone electron pair is directed away from the electron rich CO groups.

Table 13. Methylation results for $Cp(CO)_2Fe[CH{=}NR]$

R	Complex/$MeOSO_2F$	Solvent	E/Z	Isomeric carbene products (%)[a]			
				A	B	C	D
Cy	1:10	Et_2O	26:74	0	74	16	10
Cy	1:10	$CHCl_3$	68:32	0	32	64	4
Cy	1:6	Et_2O	83:17	0	17	39	34
Cy	1:3	Et_2O	90:10	0	10	19	71
i-Pr	1:6	Et_2O	62:38	-	-	-	-
i-Pr	1:3	Et_2O	95:5	-	-	-	-

[a] These isomers are depicted in Figure 13.

When 6 eqv. of $MeOSO_2F$ react with [31] in Et_2O, a mixture of E and Z isomers of [34] (Eqn. 68) is obtained. However, only two isomeric carbene complexes are observed in the ^1H NMR spectrum of the product (Figure 14). Presumably, only one of each of the isomeric pairs exists in solution due to steric crowding. Since the $^4J_{CHNMe}$ of both isomers only differ by 0.01 Hz, which is within the resolution limits of the instrument, structural assignments based on these values are inappropriate. Following the assignments made for the isomers of [33], the

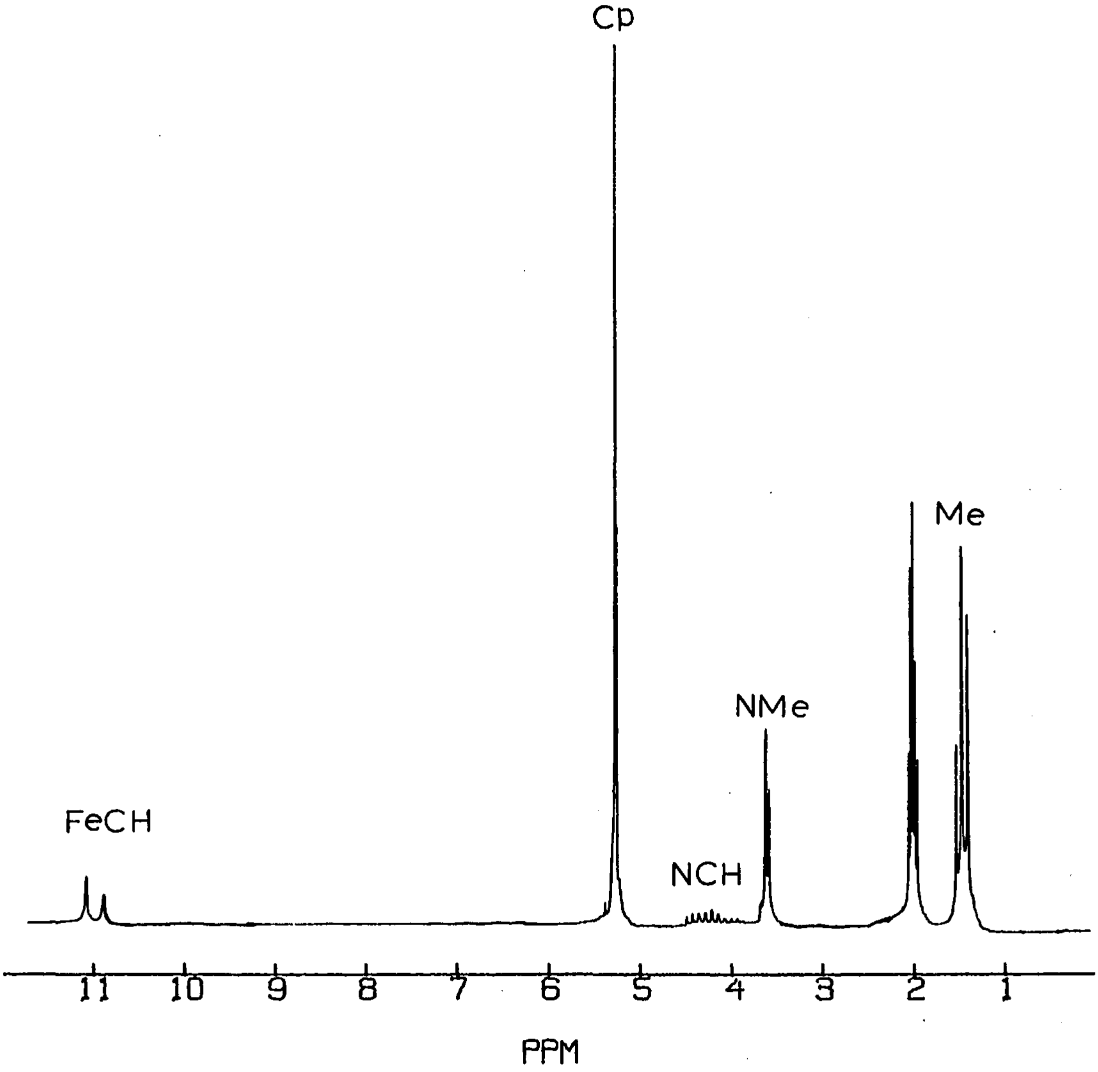


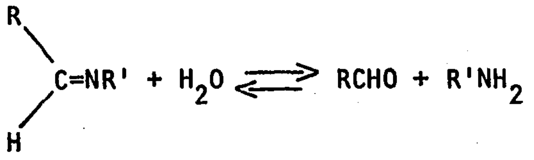
Figure 14. ^{1}H spectrum of $\{Cp(CO)_2Fe[CH(NMePr^i)]\}SO_3F$, [34], in CD_3CN with [31]/$MeOSO_2F$ ratio 1:6

carbene hydrogen of the E isomer of [34] appears at lower field than that in the Z isomer; thus, the E:Z ratio for [34] would be 62:38. The assignment is believed to be reliable since it is consistent with the trend observed in [33]; namely, the E isomer of [34] is the predominant product (95%) when 3 eqv. of $MeOSO_2F$ is used (Table 13).

In summary, [30] and [31] are believed to undergo syn-anti interconversion as well as Fe-C rotation at ambient temperature. Methylation of [30] and [31] gives up to three isomers of [33] and [34] depending upon the concentration of $MeOSO_2F$ and the relative rates of syn-anti interconversion and Fe-C bond rotation.

Hydrolysis of $Cp(CO)_2Fe[CH{=}NPr^i]$

Organic aldimines are known to hydrolyze to aldehydes and amines (Eqn. 69)[110]. An attempt to react [31] with water in CH_2Cl_2 at room temperature, in the hope of obtaining the metal formyl compound, resulted in isolation of the starting material (Eqn. 70). This clearly demonstrates the stability of [31]; more vigorous conditions for this reaction have not been explored.



$$\mathrm{R(H)C{=}NR' + H_2O \rightleftharpoons RCHO + R'NH_2} \qquad (69)$$

$$\underset{[31]}{\mathrm{Cp(CO)_2Fe[CH{=}NPr^i]}} + \mathrm{H_2O} \xrightarrow{\quad X \quad} \mathrm{Cp(CO)_2FeCHO + H_2NPr^i} \qquad (70)$$

Decarbonylation of [25]

Trimethylamineoxide has been used for the decarbonylation of metal carbonyl complexes[111-113]. The reaction is often rapid, and the conditions are milder than photolytic or thermolytic methods of removing CO (Eqn. 71)[113].

$$LMo(CO)_5 + L + Me_3NO \longrightarrow cis\text{-}L_2Mo(CO)_4 + CO_2 + NMe_3 \qquad (71)$$

A dichloromethane solution of [25] is titrated with $Me_3NO/MeCN$. The decarbonylation reaction is complete as soon as 1.2 eqv. of the amine oxide is introduced; $\{Cp(CO)(MeCN)Fe[CH(NHCy)]\}CF_3SO_3$,[36], is obtained (93%). The identical product,[36], is isolated (85%) from an acetonitrile solution of [25] after it is irradiated with 254 nm light for 2 hours (Eqn. 72).

$$\begin{tikzcd}
\{Cp(CO)_2Fe[CH(NHCy)]\}CF_3SO_3 \arrow[ddr, "Me_3NO/MeCN"] \arrow[ddr, bend right, "h\nu/MeCN"'] & \\
\text{[25]} & \\
& \{Cp(CO)(MeCN)Fe[CH(NHCy)]\}CF_3SO_3 \\
& \text{[36]}
\end{tikzcd} \qquad (72)$$

Compound [36] is an air-stable yellow crystalline material which has its $\nu(CO)$ band at 1994 cm^{-1}; the NH proton is much less labile than that in the parent compound, [25], and exchanges with D_2O in one hour (Tables 9, 10) in $CDCl_3$.

Reactions of $\{Cp(CO)_2Fe[CH(NHR)]\}CF_3SO_3$ with NH_2R'

As outlined earlier, the reaction of [4] with excess cyclohexylamine gives $[Cp(CO)_2Fe]_2$,[3], and $(CyNHCHNHCy)CF_3SO_3$. These products undoubtedly result from the reaction of the amine and [25] which is generated under the reaction conditions. This reaction was studied in greater detail (Eqn. 73).

$$\underset{[25]}{\{Cp(CO)_2Fe[CH(NHCy)]\}CF_3SO_3} + NH_2Cy \longrightarrow \underset{[35]}{Cp(CO)_2FeH} + (CyNHCHNHCy)CF_3SO_3 \qquad (73)$$

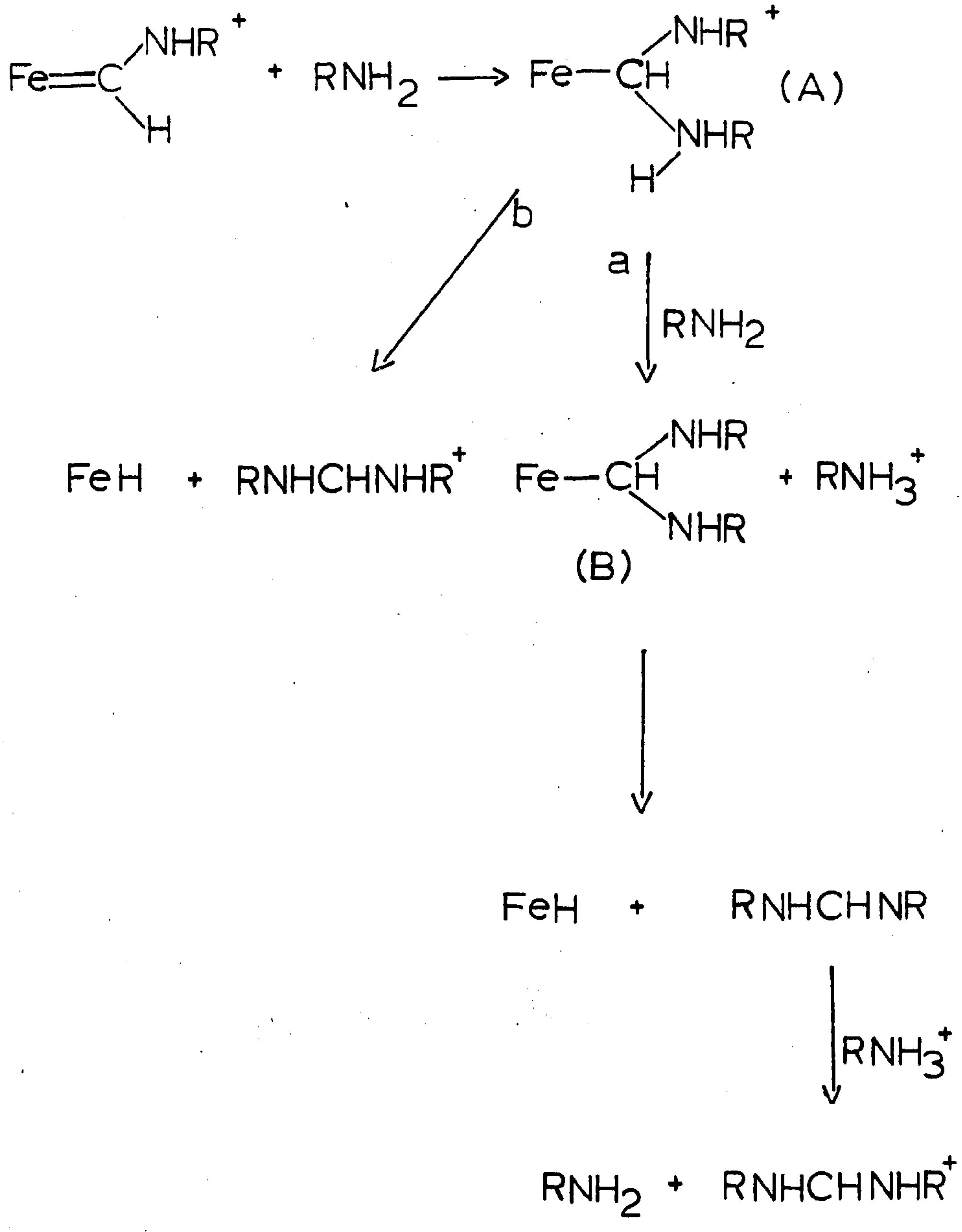
The reaction of 5 eqv. of $CyNH_2$ with 1 eqv. of [25] in CH_2Cl_2 solvent at room temperature was monitored by scanning the 2100-1600 cm^{-1} region at various time intervals. After 30 min of mixing, 75% of [25] was consumed. The presence of NN'-dicyclohexyl foramidinium ($\nu(CN)$ = 1712 cm^{-1}) and new $\nu(CO)$ absorptions (2011 s, 1952 vs) are evident; however, $[Cp(CO)_2Fe]_2$ is absent at this stage. The organometallic product is very volatile and is isolated along with the reaction solvent by vacuum distillation. This pale red, air-sensitive solution exhibits IR bands identical to those noted above; in hexane, these $\nu(CO)$ absorptions occur at 2020, 1965. This spectrum is identical to that of an authentic sample of $Cp(CO)_2FeH$ synthesized from $Cp(CO)_2FeCl$ and $Na(BH_4)$[114]. It is known that $Cp(CO)_2FeH$ decomposes to $[Cp(CO)_2Fe]_2$[114], which explains the origin of the dimer in reaction 61. The $\mathrm{(CyNHCHNHCy)CF_3SO_3}$ product is isolated as a white solid whose proton NMR and IR spectra are in accord with an authentic sample prepared from the reaction of cyclohexylamine and cyclohexylisocyanide (Eqn. 74)[115]. Interestingly, the foramidinium compound decomposes to its foramidine

$$\begin{tikzcd} \mathrm{CyNC} + \text{excess } \mathrm{CyNH_2} \arrow[r, "\mathrm{CuI}", "\mathrm{neat}"'] & \mathrm{CyN{=}CHNHCy} \arrow[d, "\mathrm{CF_3CO_3H}"] \\ & \mathrm{(CyNHCHNHCy)CF_3SO_3} \end{tikzcd} \qquad (74)$$

which is reprotonated under the mass spectrometry conditions to give $\mathrm{(CyNHCHNHCy)^+}$ with a parent peak at m/e 209[116-117].

The hydride complex $\mathrm{Cp(CO)_2FeH}$ is the sole organometallic product in reaction 73. Since the hydrogen in this complex could originate from the carbene hydrogen or the amine hydrogens, the carbene hydroggen was labeled with deuterium,[26], and this compound was allowed to react with 5 eqv. of $\mathrm{NH_2Cy}$ in $\mathrm{CH_2Cl_2}$. The crude organic product was analyzed by mass spec. and found to have a parent peak at m/e 210. This product also reacts with n-BuLi to give NN'-dicyclohexylforamidine, whose ^{1}H NMR spectrum shows no methine proton resonance. These results indicate that the carbene hydrogen is not transferred to the iron, thus, the hydrogen in $\mathrm{Cp(CO)_2FeH}$ is acquired from the amine.

Reaction 73 may occur by several possible mechanisms. One involves initial removal of the NH proton from $\mathrm{Cp(CO)_2Fe[CH(NHR)]^+}$; the resulting



Fe = $Cp(CO)_2Fe$

Scheme 5

$Cp(CO)_2Fe(CHNR)$ could then react with additional amine to form the products. Thus, the reaction of $Cp(CO)_2Fe(CHNR)$ with excess of RNH_2 was carried out. The proton was removed from [25] by treating it with a saturated NaOH/EtOH solution. The solvent was evaporated and the resulting iminoyl formyl complex, [30], was then allowed to react with 5 eqv. of $CyNH_2$ in CH_2Cl_2 at room temperature. IR spectra of the solution showed that no reaction had taken place after a period of a half hour. However, when 5 eqv. of CF_3SO_3H were introduced into the mixture, progressive growth of IR bands for $Cp(CO)_2FeH$ and the foramidinium ion occurred. Thus, removal of the NH proton inhibits the reaction, and the iminoyl formyl complex is an unlikely reaction intermediate leading to the products in Equation 73.

To summarize these and other pertinent results, we have proposed two pathways that may be involved in reaction 73. Initially, an amine attack upon the C_{carb} yields A in Scheme 5. Under excess amine reaction conditions, A is deprotonated to give B as illustrated by path a. Subsequent β-hydrogen elimination affords $Cp(CO)_2FeH$ and the foramidine, which is then reprotonated to give the observed cationic product. Alternatively, A may undergo a direct β-hydrogen elimination as depicted in path b, to furnish the observed products. Both paths a and b are indistinguishable based on our earlier experiments. However, in the reaction of [22] and Me_2NH, though much slower than reaction 73 under the same conditions, [3], [35] and $(Me_2NCHNMe_2)CF_3SO_3$ are produced after one hour of reaction. The organic product is identified by its

IR(ν(CN) 1700 cm^{-1}), and its ^{1}H NMR spectrum is the same as that reported for NN'-tetramethylforamidinium[99]. The fact that this reaction occurs suggests that path a is not the mechanism for reaction 73 since [22] lacks an NH proton for the necessary deprotonation step. In summary, path b in Scheme 5 is the more probable mechanism for reaction 73.

Other primary amines also react with [25] to give [35] and a mixture of foramidinium compounds. For instance, the reaction of NH_2Me with [25] produces NN'-methylcyclohexyl foramidinium, NN'-dimethyl foramidinium and a small amount of NN'-dicyclohexyl foramidinium ions. The relative yields and identifications were established by their mass spectra (Eqn. 75).

$$\begin{array}{ccc} \{Cp(CO)_2Fe[CH(NHCy)]\}CF_3SO_3 + H_2NMe & \longrightarrow & Cp(CO)_2FeH \\ [25] & & [35] \\ & & + \\ (CyNHCHNHCy)CF_3SO_3 & \xrightarrow{MeNH_2} & (RNHCHNHR')CF_3SO_3 \end{array} \qquad (75)$$

R	R'
Me	Cy
Cy	Cy
Me	Me

The NN'-dimethyl and NN'-dicyclohexyl foramidinium compounds are probably the product of alkyl exchange reactions of the NN'-methylcyclohexyl foramidinium and free amines. Indeed, NN'-dicyclohexyl foramidinium readily reacts with $MeHN_2$ in CH_2Cl_2 for ½ hour at room temperature to give all of the three products (Eqn. 75). The reactivity trend for the reaction of [25] and primary amines is inversely proportional to the steric hindrance of the amine. That is, methylamine reacts faster than cyclohexylamine which is still faster than t-butylamine. The importance of the size of the amine hints that some sort of nucleophilic attack mechanism is operating. These results certainly lend credence to our earlier assumption that amine attack on the C_{carb} of the amino carbene complexes is the initial, and perhaps rate-determining, step in these reactions (Scheme 5).

Synthesis of $\{Cp(CO)_2Fe[CH(NH_2)]\}CF_3SO_3$

Despite the large number of examples of nucleophilic substitution reactions in metal carbene ligands with alkylamines, the corresponding reaction with ammonia is rare[118-120]. Fischer et al. found that an acetonitrile solution saturated with NH_3 reacted with $Cr(CO)_5[C(OMe)Ph]$[118] to yield $Cr(CO)_5[C(Ph)NH_2]$. When $MeCN\text{-}NH_3$ is added dropwise to a CH_2Cl_2 solution of [4], an intractable oil showing $\nu(CO)$ absorptions at 2056 and 2010 cm^{-1} is obtained (Eqn. 76). The oil is presumed to be $\{Cp(CO)_2Fe[CH(NH_2)]\}CF_3SO_3$, [29]. By bubbling NH_3 gas directly into a CH_2Cl_2 solution of [4], a similar oily product is obtained. However, $\{Cp(CO)_2Fe[CH(SMe)pyr]\}CF_3SO_3$, [21], readily reacts with gaseous NH_3 to give [29]. Moreover, the product from this reaction can be recrystallized from $CH_2Cl_2\text{-}Et_2O$ to yield pale yellow, air-stable [29] in 20% yield (Eqn. 55). Its IR spectrum is identical to that obtained in the reaction of [4] with NH_3 noted above.

$(CO)_5Cr[C(Me)NH_2]$ has been shown by an ^1H variable temperature NMR study to have a substantial rotational barrier about the C-N bond[121]. Unfortunately, the ^1H spectrum of [29] displays an unresoluable and complex pattern in the NH and CH regions (Tables 9 and 10).

$$\underset{[4]}{\{Cp(CO)_2Fe[CH(SMe)]\}CF_3SO_3} + \xrightarrow[\text{or } NH_3]{MeCN\ -\ NH_3} \underset{[29]}{\{Cp(CO)_2Fe[CH(NH_2)]\}CF_3SO_3} + \underset{[2]}{Cp(CO)_2FeCH(SMe)_2} \qquad (76)$$

Reaction of $\{Cp(CO)_2Fe[CH(SMe)]\}CF_3SO_3$ with H_2O

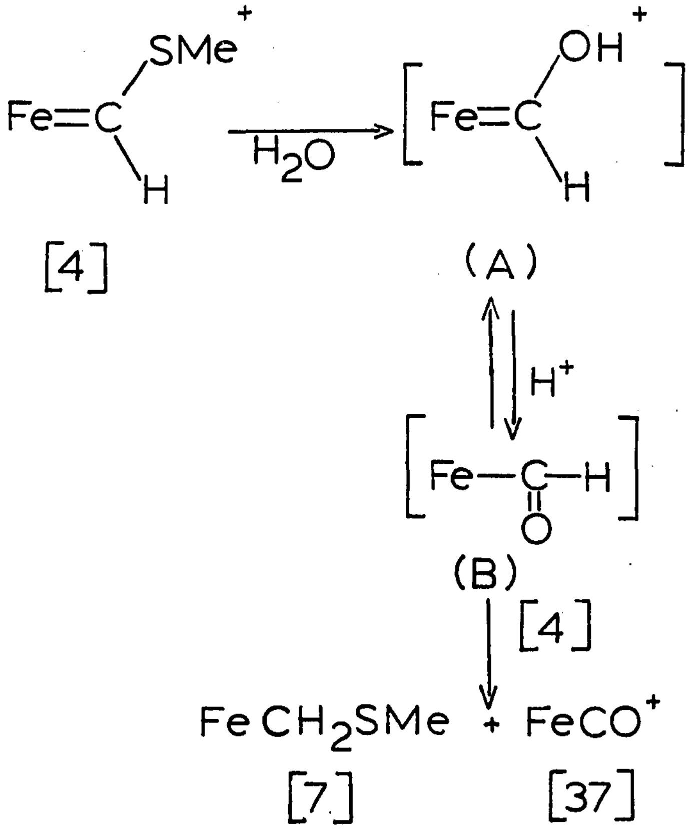
Compound [4] is very sensitive to moisture and decomposes in water on contact. Upon closer study, it was found that [4] reacts with doubly-distilled, degassed water producing $[Cp(CO)_3Fe]CF_3SO_3$,[37], and a previously[27] uncharacterized product, $Cp(CO)_2FeCH_2SMe$,[7], which is identified by comparing its IR and ^1H NMR spectra with those of an authentic sample synthesized by the reaction of $[Cp(CO)_2Fe]^-$ and $ClCH_2SMe$[63]. The product ratio of [37]:[7] is 1:1. Moreover, MeSH is identified by GC to be the major organic product in that reaction (Eqn. 77).

$$\begin{array}{ccc} \{Cp(CO)_2Fe[CH(SMe)]\}CF_3SO_3 & \xrightarrow{H_2O} & Cp(CO)_2FeCH_2SMe \\ {[4]} & & {[7]} \\ & & + \\ & & [Cp(CO)_3Fe]CF_3SO_3 \\ & & {[37]} \\ & & + \\ & & MeSH \end{array} \qquad (77)$$

In understanding the mechanism of reaction 77, it is necessary to know the origin of the additional H in product [7]. Conceivably, [7] is the product of [4] and a hydride donor, presumably, H_2O or a derivative of [4]. When deuterium labelled $Cp(CO)_2Fe[CD(SMe)]^+$ is used in the reaction with H_2O, only the di-deuterated $Cp(CO)_2FeCD_2SMe$ is formed. This was established from the mass spectrum of this product. Although the parent ion is missing, two intense peaks, m/e 212, 184 which correspond to $M^+ - CO$ and $M^+ - 2CO$, respectively, are characteristic of $Cp(CO)_2FeCD_2SMe$. Thus, the hydride in [7] stems from [4], not H_2O.

Mechanistic possibilities for reaction 77

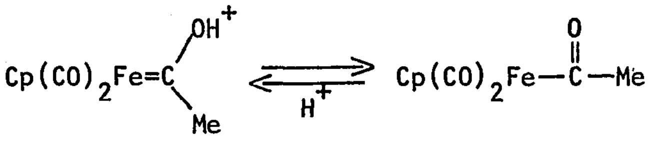
Nucleophilic attack by H_2O on the C_{carb} of [4] is likely to be the initial step in reaction 77 (Scheme 6). Subsequent loss of MeSH gives a hydroxy carbene. Although intermediate A in Scheme 6 has not been isolated nor observed in reaction 77, a similar hydroxy alkyl carbene, $Cp(CO)_2Fe[C(OH)(Me)]^+$ [122], has been synthesized and shown to be in equilibrium with its acyl analog (Eqn. 78). Moreover,



$Fe = Cp(CO)_2Fe$

Scheme 6

$Cp(NO)(PPh_3)ReCHO$[23] is reversibly protonated to its hydroxy carbene form, $Cp(NO)(PPh_3)Re[CH(OH)]^+$; thus, it is conceived that A could coexist with the formyl complex B. Collins and Roper[19] reported that H_2O reacted with $(PPh_3)_2(CO)_2(Cl)Os[CH(SMe)]^+$ to yield a stable formyl complex, $(PPh_3)_2(CO)_2(Cl)OsCHO$.



$$Cp(CO)_2Fe{=}C(OH^+)(Me) \underset{H^+}{\rightleftharpoons} Cp(CO)_2Fe{-}C({=}O){-}Me \qquad (78)$$

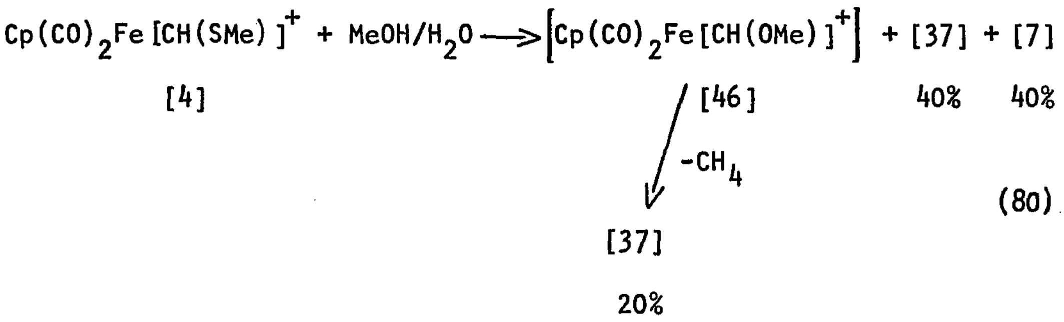
Although intermediate B was not detected by means of low temperature (-40°C) ^1H NMR in CD_2Cl_2, it might be expected to be unstable and rapidly react further. Metal formyls have been shown to be excellent hydride donors[2]. For instance[23], $Cp(NO)(PPh_3)ReCHO$ readily transfers its H^- to $Cp(NO)(PPh_3)ReCH_2^+$ to afford $Cp(NO)(PPh_3)ReCH_3$ and $Cp(NO)(PPh_3)ReCO^+$. Also, hydride transfer very similar to that in Scheme 6 has been postulated[24] in the reaction of $Cp(CO)_2Fe[CH(OMe)]^+$ and I^- (Eqn. 79). Thus, B (Scheme 6) probably transfers a hydride to

$$\begin{tikzcd}
\{Cp(CO)_2Fe[CH(OMe)]\}PF_6 \arrow[r, "I^-"] & {[Cp(CO)_2FeCHO]} \arrow[d, "{[46]}"] \\
{[46]} & Cp(CO)_2FeCH_2OMe \\
 & {[47]} \\
 & + \\
 & {[Cp(CO)_3Fe]PF_6}
\end{tikzcd} \qquad (79)$$

[4] to furnish the observed products. In that manner, the product ratio of [37]:[7] is expected to be 1:1, as observed.

Reaction of [4] with MeOH

In an effort to replace the MeS^- group in [4] with methoxide to form $Cp(CO)_2Fe[CH(OMe)]^+$, [4] reacted with MeOH. Instead of the expected product, [37] and [7] were obtained. The reaction is rapid when a 100-fold excess of methanol is used; the total yield of both products is 88%, and the [37]:[7] product ratio is approximately 60:40 (Eqn. 77). An examination of the gas phase of the reaction by GC reveals the presence of MeSH and CH_4, though, the latter was not positively verified by MS. When only 1-5 eqv. of MeOH is used for the reaction in CH_2Cl_2, no reaction is observed. Even when a 100-fold excess of $PhCH_2OH$ is allowed to react with [4], no reaction is observed. Thus, it is conceivable that H_2O is the primary reactant in the methanolysis reaction which then affords [37] and [7] (Eqn. 79), in spite of the careful drying of MeOH with Mg/I_2. The different product distribution of [37]:[7] in the methanolysis (60:40) vs hydrolysis (1:1) may result from a secondary reaction between [4] and MeOH, which gives [37] and CH_4 under the reaction conditions, possibly via [46] (Eqn. 80). Complex [46] was previously reported[24] and known to be stable in dry CH_3NO_2 and CH_2Cl_2, but it rapidly decomposed in wet solvents to $Cp(CO)_2FeCH_3$ and [37]. Its stability in MeOH was not mentioned, so it is not possible to draw any firm conclusions about the secondary reaction between [4] and MeOH (Eqn. 80).

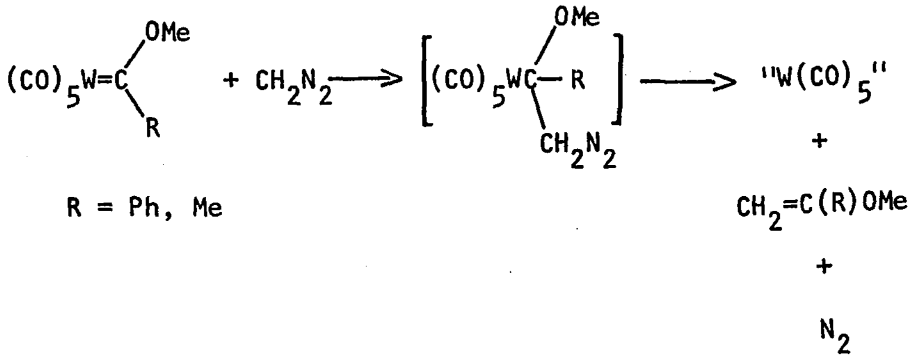


$$\underset{[4]}{Cp(CO)_2Fe[CH(SMe)]^+} + MeOH/H_2O \longrightarrow \left[\underset{[46]}{Cp(CO)_2Fe[CH(OMe)]^+}\right] \xrightarrow{-CH_4} \underset{20\%}{[37]} \quad + \underset{40\%}{[37]} + \underset{40\%}{[7]}$$

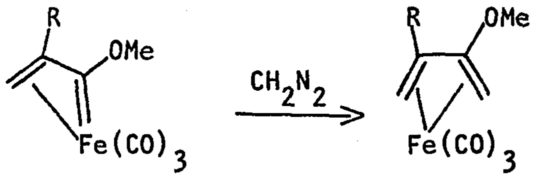
(80)

Reaction of
$\{Cp(CO)_2Fe[CH(SMe)]\}CF_3SO_3$ with CH_2N_2

Diazomethane has been shown to attack the C_{carb} of terminal carbene complexes to produce olefins[123] or an η^2-olefin complex[124]. The complex, $(CO)_5W[C(OMe)R]$ was found to react rapidly with CH_2N_2 to liberate free olefin and the $W(CO)_5$ moiety (Eqn. 81). It was postulated that the initial diazomethane attack was on the C_{carb}. Likewise, an iron complex reacted with CH_2N_2 to yield the corresponding η^4-diene complex[124]. (Eqn. 82). The slight variation in the latter reaction may be chiefly due to the stability of the iron diene product.



(81)



(82)

$$\underset{[4]}{\{Cp(CO)_2Fe[CH(SMe)]\}CF_3SO_3} \xrightarrow{CH_2N_2} \underset{[38]}{\{Cp(CO)_2Fe[S(Me)(CH=CH_2)]\}CF_3SO_3} + N_2 \qquad (83)$$

When CH_2N_2-Et_2O is added to a CH_2Cl_2 solution of [4], gas evolution (presumably N_2) is apparent; the yellow carbene solution turns deep orange, and two ν(CO) absorptions (2063, 2020 cm^{-1}) are noted. After 30 min of reaction, the solution changes to light orange with a slight shift in the ν(CO) bands (2062, 2019 cm^{-1}). After workup, 76% of $\{Cp(CO)_2Fe[SMe(CH=CH_2)]\}CF_3SO_3$, [38], is isolated; due to its reluctance to crystallize, only a small amount of needle-like red crystals (10%) were obtained (Eqn. 83); they have IR bands identical to those in the solution mixture. An ^1H NMR spectrum of [38] reveals that the vinyl protons display an ABX pattern and are shifted to lower field relative to those in the corresponding free olefin, $MeSCH=CH_2$[125]. In contrast to the tendency of olefins to form η^2-olefinic complexes of iron[126], the olefinic ligand in [38] is bonded to the iron through the sulfur[68,127,128]. This structural assignment is consistent with its ^{13}C spectrum which shows the vinyl carbons at 130.8 and 124.1 PPM which are characteristic of unsatuated carbons[129], whereas the corresponding carbons of η^2-olefinic complexes of iron often occur below 100 PPM[126].

Presumably, nucleophilic attack upon the C_{carb} of [4], elimination of N_2 producing the η^2-thiomethoxyl ethylene complex, then rearrangement to the S-adduct is the reaction sequence which leads to [38]. The existence of the η^2-olefin complex is uncertain since the deep orange transient species, which is most likely to be this postulated intermediate, has not been isolated nor fully characterized.

Synthesis of $\{Cp(CO)(L)Fe[CH(SMe)]\}CF_3SO_3$, $L = PPh_3$, $P(OPh)_3$

The replacement of a carbonyl ligand in an inherently unstable organometallic carbene complex with a better σ-donor ligand, such as a tertiary phosphine or phosphite, increases the stability of the resulting carbene derivative. Very often, the difference is remarkable. As mentioned earlier, [4] decomposes rapidly in a wet environment. Thus, we explored the possibility of synthesizing mono-substituted phosphine and phosphite derivatives of [4] in the hope that these complexes would be more manageable.

It has been shown that [1] is readily decarbonylated in acetonitrile under photolytic conditions[130], yielding a stable deep red complex, $\{Cp(CO)(MeCN)Fe[C(SMe)_2]\}PF_6$. The acetonitrile ligand in this complex may simply be replaced by PPh_3 or $P(OPh)_3$ to afford $\{Cp(CO)(PPh_3)Fe[C(SMe)_2]\}PF_6$, [39], and $\{Cp(CO)(P(OPh)_3)Fe[C(SMe)_2]\}PF_6$,

[42], respectively (Eqn. 84).

$$\begin{tikzcd}
\{Cp(CO)_2Fe[C(SMe)_2]\}PF_6 \arrow[r, "254\ nm", "MeCN"'] & \{Cp(CO)(MeCN)Fe[C(SMe)_2]\}PF_6 \arrow[d, "L"] \\
{[1]} & \{Cp(CO)(L)Fe[C(SMe)_2]\}PF_6
\end{tikzcd} \qquad (84)$$

	L
[39]	PPh_3
[42]	$P(OPh)_3$

However, when [4] is photolyzed with 254 nm UV light in acetonitrile for an hour, decomposition is apparent, and the decomposition product has not been characterized. An attempt to prepare $Cp(CO)(MeCN)Fe[CH(SMe)]^+$ using a milder decarbonylating agent, Me_3NO[111-113], which has been demonstrated to be effective in liberating a carbonyl ligand from [1] and [25], only led to an unisolable complex with ν(CO) bands at 2012, 1956 cm^{-1} in CH_2Cl_2.

Because of the unavailability of $\{Cp(CO)(MeCN)Fe[CH(SMe)]\}CF_3SO_3$, attention turned to [39] and [42] as precursors. Like [1], both complexes smoothly react with $(Et_3BH)Li$ to provide $Cp(CO)(PPh_3)FeCH(SMe)_2$, [40], (62%) and $Cp(CO)(P(OPh)_3)FeCH(SMe)_2$, [43], (76%) respectively. In contrast, $Li[Al(OBu^t)_3H]$ fails to react with either [39] or [42]. Complexes [40] and [43] are isolated as oily substances which are mildly susceptible to air oxidization; their IR data are summarized in Table 14. The addition of CF_3SO_3H to an Et_2O solution of [40], gives an oily $\{Cp(CO)(PPh_3)Fe[CH(SMe)]\}CF_3SO_3$, [41], (71%). Likewise,

Table 14. IR and ^1H NMR data for the $Cp(CO)LFe[CH(SMe)_2]$ complexes and their carbene derivatives

Complex		IR $\nu(CO)\,cm^{-1}$	Cp
$Cp(CO)PPh_3FeCH(SMe)_2$	[40]	1960[a]	
$Cp(CO)P(OPh)_3FeCH(SMe)_2$	[43]	1963[a]	
$\{Cp(CO)PPh_3Fe[CHSMe]\}CF_3SO_3$	[41]	2006[b]	4.84 (d, J_{PH}=1.10)[c]
$\{Cp(CO)P(OPh)_3Fe[CHSMe]\}CF_3SO_3$[d]	[44]	2011[b]	4.79 (d, J_{PH}=1.10)[c]
$\{Cp(CO)P(OPh)_3Fe[CH(NEt_2)]\}CF_3SO_3$[e]	[45]	1981[b]	4.82 (d, J_{PH}=1.10)[c]

---

[a] Hexane.

[b] CH_2Cl_2.

[c] CD_3CN.

[d] The C_{carb} resonates at 320.6 (d, J_{PC}=33.21) in ^{13}C NMR.

[e] The C_{carb} resonates at 239.0 (d, J_{PC}=39.07) in ^{13}C NMR.

^{1}H		
CH	SMe	Other
14.94	2.99 (d, J_{PH}=0.73)	7.4 (m, Ph)
14.92	2.96	7.27 (m, Ph)
11.36 (J_{PH}=5.13)		7.41 (m, Ph), 4.11; 3.89 [q, J_{HH}=7.33, NCH_2], 1.44; 1.30 [t, J_{HH}=7.33, NCH_2Me]

{Cp(CO)(P(OPh)$_3$)Fe[CH(SMe)]}CF$_3$SO$_3$,[44], forms [43]. As expected, [41] and [44] are more stable to moisture, though, they are reluctant to crystallize. They have been characterized by their IR and ^{1}H NMR spectra, which are summarized in Table 14.

Spectral properties

As does [4], both [41] and [44] exhibit low field proton resonances at 14.94 and 14.92 δ in CD$_3$CN, which are characteristic of carbene hydrogen atoms. Owing to the enhanced stability brought about by the presence of L, the ^{13}C spectrum of [44] could also be obtained. In it, the C_{carb} is found as a doublet at 320.5 PPM (J_{PC} = 33.21 Hz) in CD$_3$CN, which is approximately 46 PPM downfield from the only other ^{13}C resonances reported for a secondary thiomethoxyl carbene complex, {Cp(NO)(PPh$_3$)Re[CH(SMe)]}CF$_3$SO$_3$[26]. Interestingly, the spectrum also reveals the cyano carbon of acetonitrile, which is a singlet at 118.2 PPM in pure MeCN, as a broad peak centered at 132.2 PPM. The broadening and downfield shift of the CN carbon resonance suggests that there is a weak interaction between the nitrogen lone pair electrons of the acetonitrile and the electrophilic C_{carb} of [44]. To our knowledge, an acetonitrile metal carbene adduct complex has never been isolated; however, it was detected in the gas phase by ion cyclotron resonance spectroscopy. Stevans and Beauchamp[131] demonstrated that Cp(CO)FeCH$_2$NCMe$^+$ was the product when Cp(CO)$_2$FeCH$_2^+$, generated in stiu, reacted with MeCN in the gas phase (Eqn. 85).

$$\mathrm{Cp(CO)_2FeCH_2^+ + MeCN \longrightarrow Cp(CO)_2FeCH_2NCMe^+} \qquad (85)$$

Synthesis of $\{\mathrm{Cp(CO)(P(OPh)_3)Fe[CH(NEt_2)]}\}\mathrm{CF_3SO_3}$

As anticipated, [44] reacts smoothly with diethylamine to afford $\{\mathrm{Cp(CO)(P(OPh)_3)Fe[CH(NEt_2)]}\}\mathrm{CF_3SO_3}$, [45], in 56% yield (Eqn. 86). As in [23], [45] is a pale yellow, air-stable complex which shows two distinctive methylene and methyl groups in its ^1H and ^{13}C NMR spectra. The inequivalency of the ethyl groups in [45] indicate the importance of N to C_{carb} P-P π-backbonding in the complex. The pertinent spectral data for [45] are summarized in Table 14.

$$\begin{array}{l} \{\mathrm{Cp(CO)P(OPh)_3Fe[CH(SMe)]}\}\mathrm{CF_3SO_3} + \mathrm{HNEt_2} \\ \qquad\qquad [44] \qquad\qquad\qquad\qquad \searrow \\ \qquad\qquad\qquad\qquad \{\mathrm{Cp(CO)P(OPh)_3Fe[CH(NEt_2)]}\}\mathrm{CF_3SO_3} \\ \qquad\qquad\qquad\qquad\qquad\qquad [45] \end{array} \qquad (86)$$

REFERENCES

1. Brady, R. C.; Pettit, R. *J. Am. Chem. Soc.* 1981, *103*, 1287.
2. Gladysz, J. A. *Adv. Organomet. Chem.* 1982, *20*, 1.
3. Storch, H. H.; Golumbia, N.; Anderson, R. B. "The Fischer Tropsch and Related Synthesis"; Wiley: New York, 1951.
4. Master, C. *Adv. Organomet. Chem.* 1976, *17*, 61.
5. Muetterties, E. L.; Stein, *J. Chem. Rev.* 1979, *79*, 479.
6. Pruett, R. L. *Science* 1981, *211*, 11.
7. Schrock, R. R. *J. Am. Chem. Soc.* 1974, *96*, 6796.
8. Brookhart, M.; Tucker, J. R.; Flood, T. C.; Jensen, J. *J. Am. Chem. Soc.* 1980, *102*, 1203.
9. Kegley, S. E.; Brookhart, M.; Husk, G. R. *Organomet.* 1982, *1*, 760.
10. Fong, C. W.; Wilkinson, G. J. *J. Chem. Soc. Dalton Trans.* 1975, 1100.
11. Christian, D. F.; Clark, H. C.; Stepaniak, R. F. *J. Organomet. Chem.* 1976, *112*, 227.
12. Cetinkaya, B.; Lappert, M. F.; Mclaughlin, G. M.; Turner, K. *J. Chem. Soc. Dalton Trans.* 1974, 1591.
13. Cetinkaya, B.; Lappert, M. F.; Turner, K. J. *Chem. Soc. Chem. Comm.* 1972, 851.
14. Hartshorn, A. J.; Lappert, M. F.; Turner, K. *J. Chem. Soc. Dalton Trans.* 1978, 348.
15. Christian, D. F.; Clark, G. R.; Roper, W. R. *J. Organomet. Chem.* 1974, *81*, C7.
16. Christian, D. F.; Roper, W. R. *J. Organomet. Chem.* 1974, *80*, C35.
17. Treichel, P. M.; Stenson, J. P.; Benedict, J. J. *Inorg. Chem.* 1971, *10*, 1183.

18. Christian, D. F.; Clark, H. C.; Stepaniak, R. F. *J. Organomet. Chem.* 1976, *112*, 209.

19. Collins, T. J.; Roper, W. R. *J. Organomet. Chem.* 1978, *159*, 73.

20. Barefield, E. K.; Carrier, A. M.; Serpelak, D. J.; Van Deever, D. G. *Organomet.* 1982, *1*, 103.

21. Christian, D. F.; Clark, G. R.; Roper, W. R.; Water, J. M.; Whittle, K. R. *J. Chem. Soc. Chem. Commum.* 1972, 458.

22. Pombeiro, A. J. L.; Richards, R. L. *Trans. Met. Chem.* 1980, *5*, 55.

23. Tam, W.; Lin, G. Y.; Wong, W. K.; Kiel, W. A.; Wong, V. K.; Gladysz, J. A. *J. Am. Chem. Soc.* 1982, *104*, 141.

24. Cutler, A *J. Am. Chem. Soc.* 1979, *101*, 604.

25. Wolczanski, P. T.; Threlkel, R. W.; Bercaw, J. E. *J. Am. Chem. Soc.* 1979, *101*, 218.

26. McCormick, F. B.; Gladysz, J. A. *J. Organomet. Chem.* 1981, *218*, C57.

27. McCormick, F. B.; Angelici, R. J. *Inorg. Chem.* 1981, *20*, 1111.

28. Battioni, J. P.; Chottard, J. C.; Mansuy, D. *Inorg. Chem.* 1982, *21*, 2056.

29. Andersen, R. A.; Chistholm, M. H.; Gibson, J. F.; Reichert, W. W.; Rothwell, I. P.; Wilkinson, G. *Inorg. Chem.* 1981, *20*, 3934.

30. Ruppercht, G. A.; Messerle, L. W.; Fellmann, J. D.; Schrock, R. R. *J. Am. Chem. Soc.* 1980, *102*, 6236.

31. Schrock, R. R.; Messerle, L. W.; Wood, C. D.; Guggenberger, C. J. *J. Am. Chem. Soc.* 1978, *100*, 3793.

32. Bodnar, T.; Cutler, A. R. *J. Organomet. Chem.* 1981, *213*, C31.

33. Davison, A.; Selegue, J. P. *J. Am. Chem. Soc.* 1980, *102*, 2455.

34. Cutler, A.; Fish, R. W.; Fiering, W. P.; Rosemblum, M. *J. Am. Chem. Soc.* 1972, *94*, 4354.

35. Wood, C. D.; Mclain, S. J.; Schrock, R. R. *J. Am. Chem. Soc.* 1979, *101*, 4558.

36. Schrock, R. R.; Fellmann, J. D. *J. Am. Chem. Soc.* 1978, *100*, 3359.

37. Fellmann, J. D.; Ruppercht, G. A.; Wood, C. D.; Schrock, R. R. *J. Am. Chem. Soc.* 1978, *100*, 5964.

38. Wengrovius, J. H.; Schrock, R. R.; Churchill, M. R.; Missert, J. R.; Young, W. J. *J. Am. Chem. Soc.* 1980, *102*, 4515.

39. Sharp, P. R.; Schrock, R. R. *J. Organomet. Chem.* 1972, *171*, 43.

40. Schrock, R. R. *Acc. Chem. Res.* 1979, *12*, 98.

41. Caulton, K. G.; Marsella, J. A.; Folting, K.; Kuffman, J. C. *J. Am. Chem. Soc.* 1981, *103*, 5596.

42. Kiel, W. A.; Lin, G. Y.; Gladysz, J. A. *J. Am. Chem. Soc.* 1980, *102*, 3299.

43. Casey, C. P.; Polichnowski, S. W.; Schusterman, A. J.; Jones, C. R. *J. Am. Chem. Soc.* 1979, *101*, 7282.

44. Messerle, L. W.; Jennische, P.; Schrock, R. R.; Stucky, G. *J. Am. Chem. Soc.* 1980, *102*, 6744.

45. Brookhart, M.; Nelson, G. O. *J. Am. Chem. Soc.* 1977, *99*, 6099.

46. Fischer, E. O.; Frank, A. *Chem. Ber.* 1978, *111*, 3740.

47. Brown, F. J. *Prog. Inorg. Chem.* 1981, *27*, 1.

48. Fischer, E. O. *Pure Appl. Chem.* 1972, *30*, 353.

49. Brookhart, M; Tucker, J. R. *J. Am. Chem. Soc.* 1981, *103*, 979.

50. Brookhart, M.; Tucker, J. R.; Husk, G. R. *J. Organomet. Chem.* 1980, *193*, C23.

51. Johnson, C. D. "The Hammett Equation," Cambridge University Press: New York, 1973.

52. Mann, B. E.; Taylor, B. F. "^{13}C NMR for Organometallic Compounds," Academic Press: New York, 1981.

53. Butler, W. M.; Enemark, J. H. *J. Organomet. Chem.* 1973, *49*, 233.

54. Casey, C. P.; Burkhardt, T. J.; Bunnell, C. A.; Calabrese, J. C. J. Am. Chem. Soc. 1977, 99, 2127.

55. Fierser, L. F.; Fierser, M. "Reagants for Organic Synthesis," Wiley: New York, 1967; Vol. 1, p. 191, Procedure B.

56. Bardwell, F. G.; Pitt, B. M. J. Am. Chem. Soc. 1955, 77, 572.

57. Houben, J.; Schultz, K. M. L. Chem. Ber. 1911, 44, 3235.

58. Ugi, I.; Fetzer, U.; Eholzer, U.; Knupfer, H.; Offermann, K. Angew. Chemie Int. Ed. Eng. 1965, 4, 472.

59. Olofson, R. A.; Walinsky, S. W.; Marino, J. P.; Jernow, J. L. J. Am. Chem. Soc. 1968, 90, 6554.

60. Angelici, R. J. "Synthesis and Technique in Inorganic Chemistry," 2nd ed.; Saunders: Philadelphia; 1977; pp. 152-155.

61. Plotkin, J. S.; Shore, C. G. Inorg. Chem. 1981, 20, 284.

62. Gladysz, J. A.; Williams, G. M.; Tam, W.; Johnson, D. L. J. Organomet. Chem. 1977, 140, C1.

63. King, R. B.; Bisnette, M. B. Inorg. Chem. 1965, 4, 486.

64. Jacboson, R. A. J. Appl. Crystallogr. 1976. 9, 115.

65. Lapp, R. L.; Jacobson, R. A. "ALLS, A Generalized Crystallographic Least Squares Program," U.S.D.O.E. Report; Iowa State University and Ames Laboratory; Ames Laboratory, Ames, Iowa, 1979.

66. Gromer, D. T.; Waber, J. T. "International Table for X-Ray Crystallography," Kynock Press: Birmingham, England, 1974; Vol. IV, Table 2.2A, pp. 71-97.

67. Templeton, D. H. "International Tables for X-Ray Crystallography," Kynock Press: Birmingham, England; 1962, Vol. III, Table 3.3.2c, pp. 215-6.

68. Dombek, D. B.; Angelici, R. J. Inorg. Chim. Acta 1973, 7, 345.

69. Reger, D. L.; Coleman, C. J. Organomet. Chem. 1977, 131, 153.

70. Dessy, R. E.; Pohl, R. L.; King, R. B. J. Am. Chem. Soc. 1966. 88, 5121.

71. O'Connor, E. J.; Helquist, P. *J. Am. Chem. Soc.* 1982, *104*, 1869.

72. Reger, D. L.; Culbertson, E. C. *J. Organomet. Chem.* 1977, *131*, 297.

73. McCormick, F. B.; Angelici, R. J.; Pickering, R. A.; Wagner, R. E.; Jacobson, R. A. *Inorg. Chem.* 1981, *20*, 4108.

74. Bennett, M. J.; Cotton, F. A.; Davison, A.; Faller, J. W.; Lippard, S. J.; Morehouse, S. M. *J. Am. Chem. Soc.* 1966, *88*, 4371.

75. Churchill, M. R.; Ni Chang, S. W. Y. *J. Am. Chem. Soc.* 1973. *95*, 5931.

76. Pope, L.; Sommerville, P.; Laing, M.; Hindson, K. J.; Moss, J. R. *J. Organomet. Chem.* 1976, *112*, 309.

77. Grompper, R.; Bartmann, E.; Noth, H. *Chem. Ber.* 1979, *112*, 218.

78. Ariyaratue, J. K. P.; Bierrum, A. M.; Green, M. L. H.; Ishaq, M.; Prout, C. K.; Sqnwick, M. G. *J. Chem. Soc. A* 1969, 1309.

79. Kojima, T.; Nichikawa, T. J. *J. Phys. Soc. Jpn.* 1957, *12*, 680.

80. Pierce, L.; Hayaski, M. J. *J. Chem. Phys.* 1961, *35*, 479.

81. Stein, J.; Fackler, J. P., Jr.; Paparizos, C.; Chen, H. W. *J. Am. Chem. Soc.* 1981, *103*, 2192.

82. Bannett, B. C.; Kruger, C. *J. Cryst. Mol. Struct.* 1972, *2*, 271.

83. Kermode, N. J.; Lappert, M. F.; Skelton, B. W.; White, A. H.; Holton, J. *J. Organomet. Chem.* 1982, *228*, C71.

84. Buchanan, R. K.; Pierpont, C. G. *Inorg. Chem.* 1979, *12*, 3608.

85. Pickering, R. A.; Jacobson, R. A.; Angelici, R. J. *J. Am. Chem. Soc.* 1981, *103*, 817.

86. Baldwin, J. C.; Keder, N. L.; Strouse, C. E.; Kaska, W. C. *Z. Naturforsch.* 1980, *35B*, 1289.

87. Angelici, R. J.; Matachek, J. R. Unpublished results, Dept. of Chem., Iowa State University, Ames, IA.

88. Seebach, D.; Beck, A. L.; Stegmann, H. B. *Tetrahedron Lett.* 1970, 1933.

89. Casey, C. P.; Burkhardt, T. J. J. Am. Chem. Soc. 1972, 94, 6543.

90. Schuer, O. J.; Jungmann, H. Z. Naturforsch. 1981, 36B, 1663.

91. Kreissel, H.; Fischer, E. O.; Kreiter, C. G.; Fischer, H. Chem. Ber. 1973, 106, 1262.

92. Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. "Spectrometric Identification of Organic Compounds," 3rd ed.; Wiley: New York, 1974; p. 180.

93. Pickering, R. A.; Angelici, R. J. J. Organomet. Chem. 1982, 225, 253.

94. Kreissel, F. R.; Fischer, E. O.; Kreiter, C. G.; Weiss, K. Angew. Chimie Int. Ed. Eng. 1973, 12, 563.

95. Kreissel, F. R.; Fischer, E. O. Chem. Ber. 1974, 107, 183.

96. McCormick, F. B.; Angelici, R. J. Inorg. Chem. 1981, 20, 1118.

97. Pickering, R. A.; Angelici, R. J. Inorg. Chem. 1981, 20, 2977.

98. McCormick, F. B.; Angelici, R. J. Inorg. Chem. 1979, 18, 1231.

99. Ranft, J.; Dahne, S.; Helv. Chim. Acta 1964, 47, 1160.

100. Steinmetz, A. L.; Hershberger, S. S.; Angelici, R. J. Unpublished results, Dept. of Chemistry, Iowa State University, Ames, IA.

101. March, J. "Advanced Organic Chemistry," 2nd ed.; McGraw-Hill: New York; 1977; Chapter 17.

102. Wolczanski, P. T.; Bercaw, J. E. J. Am. Chem. Soc. 1979, 121, 6450.

103. Schilling, B. E. R.; Hoffman, R.; Lichtenberger, D. L. J. Am. Chem. Soc. 1979, 101, 582.

104. Schilling, B. E. R.; Hoffman, R.; Faller, J. W. J. Am. Chem. Soc. 1979, 101, 592.

105. Kastic, N. M.; Fenske, R. F. Organomet. 1982, 1, 974.

106. Patai, S. "The Chemistry of the Carbon-Nitrogen Double Bond," Wiley: New York, 1970; Chapter 9.

107. Lambert, J. B.; Shurvell, H. F.; Verbit, L.; Cooks, R. G.; Stout, G. H. "Organic Structural Analysis"; Macmillan: New York; 1976; p. 72.

108. Chang, C. F.; Fairless, B. J.; Willcott, M. R. J. Mol. Spectrosc. 1967, 22, 112.

109. Allinger, N. L.; Eliel, E. L. "Topics in Stereochemistry"; Wiley: New York: 1973; V. 7, pp. 329-358.

110. March, J. "Advanced Organic Chemistry," 2nd ed.; McGraw Hill: New York; 1977; p. 805.

111. Shro, Y.; Hazum, E. J. Chem. Soc. Chem. Commum. 1975, 829.

112. Gladysz, J. A.; Selover, J. C.; Strouse, C. E. J. Am. Chem. Soc. 1978, 100, 6766.

113. Blumer, D. J.; Barnett, K. W.; Brown, T. L. J. Organomet. Chem. 1979, 173, 71.

114. Green, M. L. H.; Street, C. N.; Wilkinson, G. Z. Naturforsch. 1959, 14B, 738.

115. Saegusa, T.; Ito, Y; Kabayashi, S.; Hirota, K.; Yoshioka, H. Tetrahedron Lett. 1966, 6121.

116. Hesse, M.; Leuzinger, F. Adv. Mass Spectrom. 1968, 4, 163.

117. Patai, S. "The Chemistry of Amidines and Imidate"; John Wiley and Son: New York; 1975; pp. 75-79.

118. Fischer, E. O.; Kollmeier, H. J. Chem. Ber. 1971, 104, 1339.

119. Klabunde, U.; Fischer, E. O. J. Am. Chem. Soc. 1967, 89, 7141.

120. Fischer, E. O.; Offhaus, K. Chem. Ber. 1969, 102, 2449.

121. Moser, E.; Fischer, E. O. Naturwissenchaften 1967, 54, 615.

122. Green, M. L. H.; Hurley, C. R. J. Organomet. Chem. 1967, 10, 188.

123. Casey, C. P.; Bertz, S. H.; Burkhardt, T. J. Tetrahedron Lett. 1973, 1421.

124. Mitsudo, T.; Watanabe, H.; Watanabe, K.; Watanabe, Y.; Takegami, Y. J. Organomet. Chem. 1981, 214, 87.

125. Ceccarelli, G.; Chiellini, E. *Org*. *Magn*. *Reson*. 1970, *2*, 409.

126. Faller, J. S.; Johnson, B. V. *J*. *Organomet*. *Chem*. 1975, *88*, 101.

127. Sawai, T.; Martin, J. P.; Butler, I. S.; Simkin, D. *J*. *Phys*. *(Paris)*, 1974, *35*, *Suppl*. *6*, 247.

128. William, W. E.; Lalor, F. J. *J*. *Chem*. *Soc*. 1973, 1329.

129. Kalabin, G. A.; Trofimov, B. A.; Bzhezovskii, V. M.; Kushnarev, D. F.; Amasova, S. V.; Gusmova, N. K.; Al'pert, M. L. *Izu*. *Akad*. *Nauk*. 1975, *24*, 501.

130. McCormick, F. B.; Angelici, R. J. *J*. *Organomet*. *Chem*. 1981, *205*, 79.

131. Stevans, A. E.; Beauchamp, J. L. *J*. *Am*. *Chem*. *Soc*. 1978, *100*, 2584.

APPENDIX I. FINAL POSITIONAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS (IN PARENTHESES)[a] FOR $\{Cp(CO)_2Fe[CH(SMe)P(OCH_2)_3CMe]\}PF_6$

Atom	X	Y	Z
Fe	0.2654(1)	0.3525(1)	0.2579(1)
S	0.1779(2)	0.3879(2)	0.0648(1)
P_1	0.4451(2)	0.3198(2)	0.1107(1)
O_1	0.4991(5)	0.4376(4)	0.1160(4)
O_2	0.5394(6)	0.2489(5)	0.1673(4)
O_3	0.4634(6)	0.2823(6)	0.0219(4)
O_4	0.0277(8)	0.2254(7)	0.2486(5)
O_5	0.4294(8)	0.1764(6)	0.3287(4)
C_1	0.2864(8)	0.3096(7)	0.1356(5)
C_2	0.6396(10)	0.4476(9)	0.1032(7)
C_3	0.6764(10)	0.2538(8)	0.1488(6)
C_4	0.6033(10)	0.2930(11)	0.0007(6)
C_5	0.6853(9)	0.3356(8)	0.0755(6)
C_6	0.8297(11)	0.3414(10)	0.0569(7)
C_7	0.1211(11)	0.2733(8)	0.2503(6)
C_8	0.3661(11)	0.2441(8)	0.2981(6)
C_9	0.2904(12)	0.5205(8)	0.2314(7)

---

[a] Positional parameters are listed in fractional unit cell coordinates; H_6 and H_{14} positions were not calculated.

Atom	X	Y	Z
C_{10}	0.1706(11)	0.5038(8)	0.2647(7)
C_{11}	0.1927(12)	0.4592(8)	0.3422(7)
C_{12}	0.3336(13)	0.4475(9)	0.3622(6)
C_{13}	0.3902(11)	0.4849(8)	0.2896(7)
C_{14}	0.1492(13)	0.2976(12)	0.9763(7)
P_2	0.2111(3)	0.9609(3)	0.1274(2)
F_1	0.1081(9)	0.0540(7)	0.1006(6)
F_2	0.3126(9)	0.8683(6)	0.1571(5)
F_3	0.2901(10)	0.0413(7)	0.1861(7)
F_4	0.1344(13)	0.9374(11)	0.2079(8)
F_5	0.2873(15)	-0.0130(16)	0.0583(8)
F_6	0.1252(16)	0.8784(10)	0.0795(12)
H_1	0.2625	0.2266	0.1406
H_{2a}	0.7026	0.4952	0.1413
H_{2b}	0.5804	0.4943	0.0622
H_{3a}	0.7318	0.1852	0.1506
H_{3b}	0.6682	0.2800	0.2094
H_{4a}	0.5952	0.3489	-0.0467
H_{4b}	0.6457	0.2250	-0.0206

Atom	X	Y	Z
H_9	0.3029	0.5536	0.1735
H_{10}	0.0791	0.5224	0.2352
H_{11}	0.1209	0.4373	0.3805
H_{12}	0.3821	0.4184	0.4171
H_{13}	0.4896	0.4855	0.2815

APPENDIX 2. THERMAL PARAMETERS (1 x 10^{-4}) AND THEIR ESTIMATED STANDARD DEVIATIONS (IN PARENTHESES) FOR $\{Cp(CO)_2Fe[CH(SMe)P(OCH_2)_3CMe]\}PF_6$

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Fe	88(1)	53(1)	35(0)	-2(1)	13(0)	-1(0)
S	90(2)	91(2)	38(1)	8(2)	5(1)	4(1)
P_1	79(2)	54(1)	31(1)	2(1)	10(1)	-1(1)
O_1	76(6)	51(4)	64(3)	-1(4)	26(4)	5(3)
O_2	91(7)	84(6)	56(3)	11(5)	13(4)	24(3)
O_3	88(8)	140(8)	49(3)	-6(6)	21(4)	-21(4)
O_4	145(11)	112(8)	77(4)	-45(8)	29(6)	-7(5)
O_5	183(12)	82(6)	49(3)	38(7)	4(5)	10(4)
C_1	62(9)	61(7)	37(4)	-9(6)	11(5)	-3(4)
C_2	89(12)	89(9)	63(6)	17(9)	27(7)	18(6)
C_3	101(12)	86(9)	46(5)	20(8)	17(6)	24(5)
C_4	88(12)	168(14)	46(5)	-10(11)	24(6)	-32(7)
C_5	72(10)	86(9)	40(4)	0(8)	14(5)	1(5)
C_6	99(12)	111(11)	67(6)	20(10)	34(7)	6(6)
C_7	123(13)	67(8)	50(5)	-4(9)	27(7)	-5(5)
C_8	128(14)	67(8)	40(5)	-3(9)	10(7)	-8(5)
C_9	151(15)	50(7)	52(5)	-19(9)	6(7)	-5(5)

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C_{10}	114(13)	58(8)	59(6)	13(8)	11(7)	-6(5)
C_{11}	156(16)	72(9)	51(6)	-16(9)	16(8)	-22(6)
C_{12}	171(17)	88(10)	41(5)	-19(10)	8(8)	-12(5)
C_{13}	123(13)	56(7)	61(6)	-6(8)	6(7)	-16(5)
C_{14}	154(17)	175(15)	47(5)	7(1)	-8(8)	-52(8)
P_2	138(4)	101(3)	61(2)	0(3)	1(2)	-9(2)
F_1	224(13)	172(10)	114(6)	36(9)	-13(7)	8(6)
F_2	233(13)	138(8)	93(5)	70(8)	6(6)	5(5)
F_3	270(16)	152(10)	156(8)	-3(10)	-83(10)	-48(7)
F_4	328(22)	318(18)	146(9)	54(17)	87(12)	95(11)
F_5	432(31)	560(32)	143(9)	220(27)	141(15)	193(15)
F_6	436(30)	173(13)	295(18)	40(15)	-189(20)	-111(12)

APPENDIX 3. STRUCTURAL FACTORS FOR $\{Cp(CO)_2Fe[CH(SMe)(P(OCH_2)_3CMe)]\}PF_6$

```
   L =-17
 H  K   FO   FC
 1 -4   69 -115
 1 -3   69  113
 3 -3  287 -320
 2 -2  203 -234
 3 -2  124 -143
 1 -1   45  -26
 2 -1   62 -102
 3 -1   79  136
-1  1  110  110
-2  2  132  153
-1  3  121 -171
 0  4   46   -5

   L =-16
 H  K   FO   FC
 2 -6   61  -60
 1 -5  171 -171
 2 -5   72 -169
 3 -5  206  226
 1 -4   69 -133
 4 -4   96 -160
 0 -3   63  -57
 1 -3   73   72
 2 -2   60   11
 5 -2   81  -72
 4 -1   76  -71
-3  0   88  118
 2  0  105 -117
 4  0  164  151
-2  1  182 -193
-2  2   64  -13
-1  2   58  -11
-1  3   88   74
-2  4   92   90
-1  4  152  156
-1  5  124 -146
 0  6   74   74

   L =-15
 H  K   FO   FC
 1 -7  104  109
 2 -7   77   87
 2 -6  121 -121
 0 -4  147  131
 3 -4  209 -219
 1 -2  143 -173
 3 -1   62   20
-2  3  372 -363
-1  3  305  296
-2  4   46  -19
-2  6   74  100
-1  7  120 -111

   L =-14
 H  K   FO   FC
 0 -8   73   77
 1 -8   92 -114

 2 -7   64   65
 3 -7   54  -39
 1 -6   60  -53
 2 -6  218  166
 4 -6  125 -106
 1 -5  280  299
 2 -5   53  -17
 0 -4  175   96
 2 -4  187 -189
 3 -4   82   99
 4 -4  210  183
 5 -3  107 -143
 1 -2   70  -46
 2 -2  126  -39
 3 -2   57  -96
 4 -2  195  187
 1 -1  119 -179
-3  0  120 -123
-2  0   90  -62
 3  0  262  306
 4  0  153 -158
 5  0   43  -22
-2  3   48   35
-1  3  136  131
-5  4   61 -113
-3  4  204  217
-2  4  144  -57
-1  4  228 -228
-1  5  146  126
-2  6   82   20
-1  7   47   -4
 0  7   72  -73
-1  8   52  -50

   L =-13
 H  K   FO   FC
 1 -9  156  171
 2 -9   54   57
 4 -8   98  109
 1 -7  161 -169
 2 -7   64 -110
 3 -7  274  256
 4 -7   57  -68
 1 -6   66   64
 3 -6   66  -62
 1 -5  118 -105
 3 -5  168 -186
 4 -5  115  131
 1 -4   70  -94
 3 -4   43  -22
 1 -3  218  229
 2 -3   86  -98
 3 -3   58  -62
 3 -2   83  107
 5 -2   63   73
 8 -2  159  214
 1 -1  263 -251
 2 -1   56   25
 3 -1  199  214

 4 -1   64  103
-2  1   69   74
-1  1   43  -40
-2  2  123 -116
-6  3  259  262
-4  3  254 -281
-2  3  221  212
-3  4  132 -141
-1  4  165 -179
-3  5  141 -154
-2  5  148  148
-1  6   85   84
-2  7  146 -180
-1  7  207  219
 0  7   94   99
-3  8  114 -120
-1  9   48  -53

   L =-12
 H  K   FO   FC
 1 -9  131  119
 2 -9  194  205
 3 -9  242 -248
 4 -9   60  -69
 1 -8   74  -54
 2 -8   60  -49
 3 -8  202 -204
 1 -7  143  155
 2 -7   63   50
 3 -7   43   16
 0 -6  118   95
 4 -6   72  -58
 0 -5   47   18
 1 -5  178 -188
 2 -5  130  149
 3 -5  261  247
 4 -5   71   73
 8 -5   69  -61
 1 -4   45   28
 1 -3  262  306
 2 -3   49   74
 3 -3  365 -393
 1 -2   53  -90
 2 -2  273  191
 4 -2   71  -54
 5 -2  117 -163
 2 -1   90  106
 5 -1  244  252
-4  0   67   68
-2  0   82   45
 5  0  224  234
 8  0   45   31
 9  0   48  -16
-7  1   38  -56
-2  1  334  337
 0  1  175  152
-2  2   94  -98
-5  3   45  -43
-1  4   73  105

-5  5   50  -59
-1  9  223  231
 0 10  102 -106

   L =-11
 H  K   FO   FC
 1-10   78   83
 2 -9   56  -50
 4 -9  122 -120
 2 -8  222  228
 3 -8   94  -89
 4 -8  252 -270
 0 -7   80  -70
 1 -7  152  156
 2 -7   77   79
 4 -7  101 -105
 7 -7  113 -136
 1 -6   45   34
 4 -6  265  266
 8 -6   48   20
 1 -5   74 -114
 7 -5  144 -169
 0 -4   45   67
 1 -4  326  324
 3 -4   84   94
 4 -4  102  -84
 9 -4  104 -121
 4 -3   99  -97
 8 -3  144 -147
 4 -2  141 -134
 5 -2   77 -134
 9 -1   44   14
-2  1  115 -167
-1  1  365 -316
-7  2   90  144
-5  2  195 -197
-1  2  263  257
-7  3   80  -92
-5  3  165 -179
-2  3  173  178
-7  4   42   27
-3  4  145 -199
-2  4  421  421
-4  5  149 -148
-1  5  238  206
-2  6  108  117
-1  6  328  356
-5  7   98 -112
-3  7  127  151
-2  7  141  144
-4  8  104  152
-1  8  108 -105
-1 10   66  -63

   L =-10
 H  K   FO   FC
 1-11   70   72
 2 -9   95  -94
 3 -9   76   98

 1 -8  125 -122
 3 -8   74   98
 4 -8   82   44
 7 -8  144 -143
 2 -7  135 -114
 3 -7  307  324
 8 -7   61  100
 2 -6  304  309
 4 -6  237 -233
 7 -6  120  112
 2 -5   55   46
 4 -5   74   62
 3 -4  216 -194
 4 -4  160  -35
 8 -4  126  133
 1 -3  184 -192
 2 -3  242 -237
 3 -3   41   51
 4 -2  211  207
 4 -1  200 -190
 9 -1  205 -216
-5  0  206 -222
-4  0  116 -128
-3  0  296 -356
-5  1   99  -92
-3  1  351  351
-2  1  274  260
-1  2  103  123
-1  4  383 -380
-5  5   42   28
 0  5   65  -53
-5  6   91  137
-3  6  208 -214
-2  6  376  375
 0  6  112 -120
-3  7   48  -75
-1  7  157 -149
-5  8   69   88
-3  8   58   96
-3  9   74  124
-1  9   51   25
-3 10  100   98

   L = -9
 H  K   FO   FC
 4-11   57  -58
 1-10   79   71
 2-10  119 -126
 4-10   66  -81
 4 -9   64   79
 3 -8   70  -89
 7 -8   96 -103
 2 -7   90  -76
 3 -7  255  237
 4 -7   41  -33
 7 -7  123  147
 2 -6  110 -104
 3 -6   54  -59
 4 -6   79   76

 9 -6   96  122
 1 -5   77  -79
 1 -4  100  110
 3 -4  243  245
 8 -4  224 -208
 9 -4  111  134
 2 -3  201  221
 4 -3   72  -81
 8 -3   41  -31
10 -3  147 -134
 1 -2  133  147
 3 -2   75  -42
 1 -1   49   59
 2 -1  115 -148
-7  1   72 -123
-9  2   48   48
-2  4   94 -124
-6  5   55  -91
-4  5   48  -45
-2  5   67  -76
-6  6   84 -107
-4  7   77  143
-1  7  153  166
-2  9   93  145
-1 10  108   93
-1 11   58  -54
 0 11   80  -91

   L = -8
 H  K   FO   FC
 1-12   54   36
 2-11   75  -98
 3-11  126  142
 4-11   85   82
 3-10   93   98
 4-10  224 -248
 1 -9  202  201
 3 -9  146 -164
 4 -9   61   77
 7 -9  216 -224
 2 -8  210 -198
 3 -8  337  330
 4 -8   69  -88
 7 -8   68   59
 8 -8  153  137
 1 -7  104 -124
 3 -7   51 -103
 4 -7   80  -88
 7 -7  120  150
 3 -6  281 -307
 4 -6  424  427
 8 -6   74   55
 2 -5   63  -60
 4 -5  105   66
 7 -5   71   95
 1 -4   69  129
 2 -4  239  237
 3 -4   69 -128
10 -4  110  124

 2 -3  335 -332
 8 -3   48   16
 9 -3   64  111
 5 -2  147  159
 0 -1   41  -22
 9  0  112  121
10  0  249 -239
-9  2   45   33
-5  2   86  124
-2  2  155  122
 0  2  349 -251
-7  3   97 -116
-3  3   30  -23
-4  4  106 -114
-2  4   90   21
-7  5  167  191
-6  6  196 -169
-1  8   77   77
-6  9  109 -117
-4  9   93  131
 0 11   60  -37

   L = -7
 H  K   FO   FC
 3-12   51   -8
 1-11   49  -17
 3-11  264  262
 4-11  159 -182
 3-10   46  -37
 4-10   47    6
 0 -9   51   16
 7 -8  102  -75
 8 -8  129 -127
 0 -7   38  -31
 2 -7   47   38
 4 -7   50   54
 7 -7   52  -70
 9 -7  131  126
 0 -6   38  -36
 7 -6   60  -40
 8 -6  130  153
 9 -6   66  -73
 3 -5  382  334
 8 -5  106  135
 9 -5   66   56
 2 -4  165 -156
 3 -4  176 -165
 9 -4   62   67
 3 -3  194  201
 8 -3   38   31
 1 -2  307  327
 8 -2  148 -178
 4 -1  120  174
-10  1   99  103
-2  1   82   18
-1  1  293 -264
-9  2   76  -74
-4  3   42   27
-3  3   63 -101
```

```
  0  3   61   63
 -2  4   77   70
 -1  5   75  -73
 -3  6  217 -227
 -2  6   44  -73
 -6  7  137  168
 -7  8   97  103
 -4  9   41  -25
 -3  9   59  -89
 -1  9  107   95
 -1 11   72   73
  0 11   88  -93

   L = -6
  H  K   FO   FC
  2-12  124  112
  3-12   67  -85
  3-11   67  -54
  1-10   92   88
  2-10   84  -69
  4-10  137  156
  7-10   88   63
  3 -9  442  467
  4 -9  204 -193
  7 -9   69   80
  3 -8   75   93
  7 -8   85   69
  8 -8   75  -70
  1 -7   76   84
  3 -7  166 -161
  9 -7   83 -113
  3 -6  158 -159
  4 -6   88  -53
  8 -6  112  -25
  2 -5   51   14
  3 -4  418 -425
 10 -4  102  -85
  4 -3  243  209
 10 -3   86  143
  3 -2  149  195
  5 -2   54   42
  9 -2  117   95
  4 -1   63  -85
  8 -1   84  -79
  9 -1   87 -102
  5  0  225 -262
 11  0  192 -187
 -9  1   71 -127
 -2  1   43  -33
 -9  2   47   -4
 -1  2   47   87
-10  3  105  104
 -6  3   94  114
 -3  4   98 -149
 -9  5  146  179
 -7  6   36  -17
 -8  7   53   79
 -5  7   62 -113
 -3  7   55   92

 -4  8   88  120
 -4  9   45  -61
 -5 10  137 -159
 -1 10  107 -114
 -1 11   73   93
 -1 12   72   82
  0 12   84  -61

   L = -5
  H  K   FO   FC
  0-13   55   -5
  2-12  135  139
  4-12  239 -248
  4-11   63   45
  0-10   50   58
  1-10   92   82
  7 -9  242 -250
  2 -8  212 -205
  3 -8  239  248
  4 -8  157  165
  7 -8  142  149
  8 -8  125  134
  2 -7   62  -41
  3 -6   58   81
  8 -6   67   26
 10 -6   58   98
  9 -4   49  -49
  2 -3   92  116
  4 -3  163 -159
  4 -2   43  -72
 10 -2  173 -186
 11 -2  156  159
  2 -1   56  -42
  5 -1  271 -311
  8 -1   65  -88
  9 -1   92 -156
 -9  1  156 -152
 -7  1   37   41
-10  2   57   17
 -9  2  186  209
 -8  2   39  -25
 -5  3  159 -202
 -7  4   38  -35
 -9  5   98  122
 -7  5   41  -52
 -7  6   41   56
 -6  6   43   37
 -8  7  167  181
  0  8   80  -70
 -6  9   46   26
 -4 10   47   73
 -1 12   61   39

   L = -4
  H  K   FO   FC
  3-12   66   68
  0-11   47  -13
  4-11  103 -106
  0-10   46  -25

  1-10   57   39
  3-10  129 -137
  4-10  334 -342
  7-10  154 -146
  0 -9   60  -68
  4 -9   41   19
  7 -9   83  -92
  2 -8  152   42
  7 -8  157  162
  8 -8  130   79
  1 -7  150  146
  4 -7   39   -7
  7 -7  221 -257
  9 -7   80 -120
  8 -6  252  277
  9 -6  221 -230
 10 -6   80   51
 10 -5  127  129
  3 -4  195  177
  9 -4  153  143
  2 -3   96 -108
  9 -3   47   28
 10 -3  110  -95
  4 -2   38  -38
 10 -1   67  -74
-10  1   84  -97
 -8  1   76  -78
-10  2  107  -67
 -7  2  305  368
-10  3   50  -15
 -8  3   49  -62
 -6  3  375  399
 -9  5   62  -48
 -5  5   36  -21
 -9  7  100  126
 -6  9  130 -143
 -3  9   65  -84
 -2 12   47  -38
 -1 12   80   72
  0 12   86   61
 -1 13  148 -152
  0 13   64   50

   L = -3
  H  K   FO   FC
  2-13   62  -47
  1-12   55   28
  3-12   50  -40
  4-12  148  151
  4-11  163  142
  4-10   86   92
  7-10   92 -117
  3 -9  408  410
  7 -9   73  -55
  8 -9   75  -64
  1 -8   53  -58
  3 -8   94  -72
  8 -8  201 -213
  9 -8  152  178

  4 -7  116  105
  7 -7   87  -96
  2 -6   89  -76
  4 -6  401  433
  9 -6   85  -55
 10 -6   59  -95
  3 -5   88 -113
  4 -5  128 -128
  7 -5  208  211
  8 -5   64  -69
 10 -5   97 -133
  8 -4  172  203
  9 -4  138 -146
 10 -4   61   92
  1 -3   63   88
  8 -3   47  -83
 10 -3   82   86
  2 -2  152  151
  9 -2   67   51
  5 -1   60  -63
  8 -1  149  156
  9 -1   64  108
 -8  1   60   48
-10  3   73  -72
 -9  4  267  285
 -7  4  122  141
 -5  4   35  -47
-10  5   63   43
 -7  5   53   58
 -8  7  183 -189
 -1  8   57   97
 -3 11   91 -140
 -1 12   76   56

   L = -2
  H  K   FO   FC
  1-13  135  138
  3-13   91  -86
  1-12   87 -101
  3-12   92   90
  4-12   76   26
  1-11  196  177
  3-10  106   94
  4-10  232  242
  2 -9   90  -70
  4 -9   55   55
  7 -9  209  196
  7 -8   78  -83
  8 -8   56  -49
  9 -8   49  -15
  1 -7   45  -63
  4 -7  203  198
  8 -7   95  -93
  9 -6  309  293
 10 -6  107   55
  4 -5   80   63
  8 -5   81  -94
  9 -5  210  202
 10 -5   83 -159

  3 -4   36   -7
 10 -4   65  -35
  2 -3  101  122
  8 -3   78  -98
 10 -3   50    6
 11 -3   48   30
  4 -2  442  387
  8 -2   52   53
  9 -2   39  -13
 10 -2   50   -8
  2 -1   55   66
 11 -1   96 -102
-11  0   70 -105
-10  0   67   89
-11  1   86  124
-10  1   55  -38
-10  2   71  -89
 -4  2  292  247
-10  3   70   79
 -9  3  314 -338
-10  5  118 -113
 -6  5  356 -382
 -9  6  133  153
 -1  6   84   83
 -6  7   55 -106
 -8  9   55  -56
 -5 10   36  -29
  0 11  147 -107
  0 12   88 -105
 -1 13   57   71
  0 13   69   83

   L = -1
  H  K   FO   FC
  3-13  114  117
  1-12  138 -138
  3-12   72  -85
  4-12   58  -80
  1-11  111  101
  2-11   88   68
  3-10   61   64
  4-10  118 -129
  7-10   71  -65
  0 -9   42  -12
  4 -9  153  179
  8 -9   70   53
  1 -8   74  126
  3 -8   95  111
  4 -8  452  430
  7 -8  158  165
  4 -7   42   26
  8 -7  121 -135
  4 -6   71  -76
  9 -6   91  115
  4 -5  102  111
  7 -5  183 -205
  8 -5   51   40
  9 -5  154 -150
 10 -5   97   99

  1 -4  257  241
  8 -4   56  -73
  9 -4  153  148
  8 -1  190 -181
  9 -1   65   76
-11  3  115  146
-10  3   93  109
 -8  4   65  -75
-10  5   86   84
 -9  5  135 -150
 -7  6  233  234
 -9  7  104  100
 -8  7  250  265
 -8  8   56  -69
 -5  8  188 -187
 -5 11   82  -96
 -3 12   42   29

   L =  0
  H  K   FO   FC
 -2-13   63   72
  4-12   75   -6
 -6-10   90  113
 -1-10  122  111
  7-10   49   28
  1 -9   82   71
  2 -9   39   19
  0 -8   52   37
  4 -8  132  -51
 -1 -7   47  -37
  4 -7   60   61
  9 -7   64   62
 -6 -5  162 -168
 -6 -3   85   73
 -4 -3   47   30
-10 -2  295  236
 -6 -2  260  269
  5 -2  106   94
  8 -2   76   61
-11  0  295  299
-10  0   99 -100
 -4  0  548  388
  1  0 1137-1244
  2  0 2044-1990
  3  0  726 -619
  5  0  492 -470
  7  0  497  506
  8  0  211 -185
  9  0  147 -171
-11  1   79 -101
  1  1  958 -961
  2  1  110 -107
  4  1  407  435
  5  1  854 -832
  6  1  373  409
  7  1   69   77
  8  1  271 -270
  9  1  212 -220
 10  1  210  193

-11  2   70 -106
 -9  2   91 -123
  1  2  748  840
  2  2 1336-1351
  3  2  193 -245
  4  2  216 -201
  7  2  496 -509
 -9  3   89  -99
  2  3  254  243
  3  3  445  471
  8  3  164 -141
 10  3  160  160
 11  3   68   69
  0  4  401  392
  1  4  409 -405
  2  4  757  756
  3  4  184  189
  4  4  356 -243
  5  4  139  136
  6  4  234  224
  7  4  299 -285
  9  4  236  253
 10  4   92   93
-10  5  135  153
  1  5  563  617
  2  5  313 -296
  3  5  601 -622
  4  5  469 -478
  5  5  737  761
  7  5  161 -149
  8  5   58   76
  9  5  115  111
-10  6   93 -105
  0  6  458  539
  1  6  304 -317
  2  6  611 -643
  3  6  221  211
  4  6  371  356
  5  6   37  -57
  6  6  504 -490
  7  6  453  442
  8  6   92 -107
  9  6   78  -86
  2  7  507  552
  3  7  444 -404
  5  7  423 -429
  6  7  539  513
 -9  8  157 -146
  1  8  302  328
  2  8  387 -423
  3  8  138  154
  6  8   70  107
  8  8   63   75
  3  9  276  281
  4  9  236 -232
  6  9  104  -97
  7  9  321  321
  8  9  182 -170
  0 10  506 -499
```

```
  2 10  379  350    -3 -2  327  322     5  6  678  639    -6 -5  464  432     6  2  132 -161     1 12  186  158     4  1  318 -323
  3 10  193 -178    -2 -2 1707 1678     9  6  262  243    -5 -5 1054-1046     8  2  245  238                        5  1  290 -311
  4 10  294 -308    -1 -2  786  817    10  6  117  145    -3 -5  757  756     0  3  521  541      L =   3            7  1  500  455
  5 10  213  195   -10 -1  299  266     0  7  147  194    -2 -5  511  500     1  3  151 -175     H  K   FO   FC     9  1   71  -88
  1 11  132  110    -6 -1  158 -152     1  7  297  311    -1 -5  876 -918     2  3  673 -720    -1-13  277  281     0  2  923  876
  2 11   82  -94    -5 -1  512 -492     2  7  185  175    -8 -4  382  288     3  3  203 -233    -2-12  364  337     1  2  285 -270
  3 11  187 -176    -4 -1  197  202     4  7  213  195    -7 -4  107 -133     4  3  165  206    -5-11  249 -222     2  2  781  783
  4 11  143  128    -3 -1  817  790     5  7  213  219    -6 -4  533 -532     5  3  392  429    -1-11  361 -344     3  2  910 -936
  5 11  178  163    -2 -1  382 -367     7  7  202 -192    -4 -4  871  775     6  3  446 -480    -3-10   92   82     4  2  291 -258
  0 12   71   22    -1 -1  532  584     0  8  542  558    -2 -4  331 -242     0  4  705 -498    -1-10  180 -160     5  2  280  257
  1 12  129 -163     0  1  285  308     1  8  217 -229    -1 -4  764 -835     1  4   60  -48     0-10   79   78     6  2  696  692
  2 12  139  125     1  1  848  871     2  8  428 -440    -9 -3  142 -121     2  4  413 -408    -2 -9  364 -385     8  2  452 -443
  1 13   75   77     2  1 1100-1086     3  8  108   98    -6 -3  137 -149     3  4  690  747     0 -9   86  -94     9  2  201  190
  3 13  193 -187     4  1  226 -195     4  8  342  350    -5 -3  485  473     4  4  416  446    -4 -8  495  491     0  3  267 -308
                     6  1  388 -426     9  8   57  -66    -4 -3  240 -255     5  4  626 -635    -2 -8  281 -315     1  3  320  301
   L =   1           7  1  176 -145     1  9  211 -233    -3 -3  622 -601     6  4  590 -602    -9 -7  177  174     2  3  147  108
  H  K   FO   FC     8  1  349  365     3  9  205  203    -1 -3  168  141     7  4  351  340    -8 -7  208  195     3  3  688 -655
 -1-13  199 -177     9  1  249  228     4  9  131 -135    -5 -2  141 -155     8  4  225  230    -6 -7  248 -221     4  3  594  631
 -2-12  255 -258    10  1  146 -155     5  9  344 -362    -3 -2  274  243    10  4  162 -167    -5 -7  461  481     5  3  166 -180
 -4-11   62   49    11  1  178 -159     1 10  203  199    -2 -2  596  560     0  5   89  -98    -3 -7  511 -531     7  3  413 -415
 -3-11  132 -117     0  2 2125 2302     3 10  200 -186    -1 -2 1134 1113     1  5  268 -297    -2 -7   59  -82     8  3  366  336
 -2-10  335  346     1  2  325  394     5 10  102  -88   -10 -1  121 -119     2  5  397 -413    -1 -7  698  749     0  4  331  333
 -1 -9  264 -273     2  2  756 -739     0 11  272 -241    -9 -1  182  193     3  5  243  252     0 -7  102 -106     1  4  516  524
 -8 -8  125 -139     3  2   80  -78     3 11  207  234    -7 -1  349 -367     4  5   87  -80    -8 -6  150 -155     2  4 1348-1456
 -2 -8  277  272     4  2  165 -149     4 11  156 -156    -6 -1  379  333     5  5   71   76    -6 -6  153  175     3  4  179  195
 -9 -7  184 -178     5  2  101 -122     6 11  122  118    -5 -1   72  109     8  5  346 -327    -3 -6  354 -358     4  4  396  475
 -7 -7  166  179     6  2  237 -255     0 12  195 -197    -4 -1  962  944     0  6  632 -458    -1 -6  610  613     6  4  109 -146
 -5 -7  417 -427     7  2  482  495     1 12  170  148    -3 -1  754 -788     2  6  991  997    -5 -5  641 -605     8  4  335  359
 -3 -7  374  357     9  2  191 -208     2 12  235  240    -1 -1  207  218     3  6   73  -80    -2 -5  325  315    10  4   57   40
 -2 -7  227  203    10  2  158 -162     4 12  268 -281    -8  0  430 -410     4  6  289 -302    -1 -5  348  318     0  5   93   94
 -1 -7  904 -894    11  2  145  143     5 12  190  203    -7  0  215 -216     5  6  165 -177    -7 -4  295  278     1  5  451 -450
 -7 -6  246  242     0  3 1774 1789     1 13  139  128    -6  0  255  297     6  6  385  404    -4 -4  381 -377     2  5  408 -423
 -6 -6  281 -304     1  3  879-1048     3 13  198 -167    -5  0  901  842     7  6  205 -223    -3 -4  210  221     4  5  107  142
 -3 -6  325  349     2  3  286 -294                       -4  0 1103-1051     1  7  502  506    -2 -4  211  210     5  5  336  343
 -2 -6  503 -525     3  3  284  284      L =   2          -3  0 1418-1224     2  7  424 -450    -1 -4  586  556     6  5  238 -258
 -6 -5  473  462     4  3   75  -53     H  K   FO   FC    -2  0 1879 1987     7  7   79  -65    -9 -3  342 -333     8  5  216 -205
 -5 -5  278  274     5  3  358 -377    -4-11   55  -78    -1  0  944  877     9  7  108 -105    -7 -3  481  453     9  5  177  170
 -3 -5  341 -343     6  3  374  377    -3-11  261  265     0  0 1104-1423     0  8  451 -415    -6 -3  447  449     0  6  544  542
 -2 -5  284 -286     8  3  385 -363    -7-10  227  218     1  0  932-1089     1  8  218  214    -5 -3  341 -359     1  6  360 -402
 -1 -5  221  246     9  3   67 -102    -2-10  445 -459     2  0  252 -281     4  8  272 -208    -4 -3  621 -634     2  6  411 -430
 -7 -4  409  409     1  4   74  -57    -1-10   57   98     3  0  723 -765     6  8  174  -99    -3 -3  937  961     3  6  355  395
 -5 -4  720 -772     2  4  939  983    -8 -9  121  131     4  0  513 -481     7  8   62  -64    -2 -3  309 -243     5  6  246 -253
 -4 -4  326  300     4  4  315 -337    -3 -9  191 -171     5  0   99   88     8  8  129 -161   -10 -2  181 -188     6  6  396 -394
 -3 -4  192 -174     5  4  335  327    -1 -9  421  432     6  0  783  789     0  9  342  334    -8 -2  595  577     7  6   62   74
 -2 -4   97  -64     6  4  756  807    -6 -8  293  286     7  0  439 -416     1  9  248  270    -6 -2  629 -662     8  6   68   86
  0 -4   87  104     7  4  530 -542    -3 -8  285 -300     8  0  294 -315     2  9  162 -170    -5 -2  583 -587     1  7  571 -618
-10 -3  175 -164     9  4   73  -81    -2 -8  263  257     9  0  302  293     3  9  265 -304    -4 -2  527  449     2  7  284  300
 -9 -3  243  245    10  4   97  110    -1 -8  124  127     0  1  871 -920     4  9  143  159    -3 -2  301  267     3  7  311  339
 -8 -3  295 -293     0  5  446 -435    -7 -7  268  244     1  1 1621 1636     5  9  218  206    -1 -2  199  219     4  7  277 -272
 -6 -3  331 -353     1  5  571  581    -5 -7  310 -301     2  1  691 -685     6  9  161 -131    -7 -1  307 -317     5  7  288 -262
 -5 -3  899  966     2  5  436 -470    -3 -7  157  127     4  1  265  308     7  9  164 -147    -6 -1  203 -196     6  7  155  138
 -3 -3 1389-1346     3  5  116  125    -2 -7  198  204     5  1  468  488     0 10  446  433    -4 -1  839  747     7  7   67   45
 -2 -3  295 -214     4  5   76   77    -8 -6  221 -236     6  1  124 -108     1 10  213 -218    -3 -1  310 -332     0  8  206 -208
 -1 -3  352  367     5  5  134  128    -5 -6  294  339     7  1  656 -673     2 10  190 -152    -2 -1  868  810     2  8   81   57
-11 -2  212 -215     7  5  250 -248    -4 -6  384 -342     8  1  579  574     4 10  267  263    -1 -1  966  869     3  8  168 -164
 -9 -2   88  111     0  6  348 -339    -3 -6  186  167     0  2  239 -208     1 11  400 -396     0  1 1294-1341     6  8  131  153
 -8 -2  128 -105     1  6  469 -467    -2 -6  145  123     1  2  506 -425     3 11  214  172     1  1 1637-1756     7  8  189 -180
 -5 -2  561  522     2  6  263  257    -1 -6   93   98     2  2  344 -260     5 11  115 -114     2  1  917  905     1  9  466  460
 -4 -2 1229-1278     4  6  466 -463    -7 -5  219  196     3  2  664  652     6 11   81   94     3  1  543  572     2  9  154 -157
```

```
  3  9   171 -162    -10 -2    81  -81      2  4  1254 1260     -1 -7   625 -586      1  5   350 -346     -3 -5   629  641      0  4   817  750
  4  9    67   96     -8 -2   232 -166      3  4   314 -276     -4 -6   501  472      3  5   261  288     -1 -5   649 -669      1  4   278 -280
  6  9    63   94     -5 -2   429 -456      4  4   737 -740     -2 -6   355 -359      4  5    44  -51     -6 -4   507 -502      2  4   164 -141
  8  9    61   79     -3 -2   180 -196      5  4    94   76     -1 -6   208  208      6  5   134 -134     -4 -4   763  764      4  4   157  -70
  1 10   356  370     -2 -2   646  668      6  4   356  336     -9 -5    71   67      0  6   843 -870     -2 -4   785 -792      5  4   305 -302
  3 10   111  112     -1 -2   409 -452      0  5   343  368     -7 -5   281  316      1  6   188 -198     -1 -4   329 -322      6  4   266  248
  4 10   145 -140     -9 -1   332 -352      1  5   306  280     -2 -5   176  197      2  6   804  848     -5 -3   358  375      7  4   147  127
  5 10   118  175     -8 -1   215 -217      2  5   139 -176     -1 -5   212  190      4  6   225 -236     -3 -3   290 -302      9  4   185 -175
  0 11   269  261     -7 -1   177  177      4  5   847  882     -6 -4   297 -296      5  6   313 -321     -2 -3   278 -282      0  5    86  -84
  1 11   195  184     -6 -1   265  250      6  5   267 -257     -4 -4   299  317      9  6   221  213     -1 -3   360  323      1  5   476 -481
  2 11   118 -106     -4 -1   801 -729      7  5   134 -103     -3 -4   257  251      0  7   218  222    -10 -2    76  -86      2  5   384  393
  5 11   209  216     -3 -1   388  403     10  5   177 -184     -2 -4   496 -529      1  7   582  555     -8 -2   233  200      4  5   463 -467
  6 11   195 -180     -2 -1   613 -545      0  6   368  354     -1 -4   142 -172      2  7   231 -268     -6 -2   457 -433      5  5   363 -381
  0 12   391  346     -1 -1  1149-1096      1  6   129  115     -8 -3   380  390      4  7   149  141     -4 -2   492  479      6  5   324  331
  2 12   176 -193    -10  0   344 -282      2  6   386 -410     -7 -3   481 -491      5  7   265  270     -2 -2   537 -498      8  5    58  -80
  4 12   126  170     -9  0   482 -431      4  6   268  265     -6 -3   108 -121      1  8   234 -230     -1 -2  1192  989      0  6   552 -547
  1 13   151 -190     -8  0   536  483      5  6   378 -389     -5 -3   440  450      2  8   125 -118     -7 -1   290 -315      1  6   693  694
                      -7  0   694  654      7  6   162  140     -3 -3   537 -481      4  8   283  284     -5 -1   685  698      2  6   298  342
    L =   4           -6  0   535 -470      0  7   233 -222     -1 -3   429  461      5  8   324 -319     -3 -1   520 -476      5  6   325  338
  H  K    FO   FC     -5  0   440  387      1  7   392  351     -9 -2   368  335      6  8   130 -132     -2 -1    78  -93      0  7   256  262
 -1-13    79   93     -4  0   815 -724      2  7   512 -521     -8 -2   208 -203      7  8   184  190     -1 -1  1196 1232      1  7   542 -530
 -2-12   302 -286     -3  0   801  823      6  7   132 -150     -7 -2   357 -354      8  8   145  142    -10  0   122  106      2  7   260  260
 -1-12    71   94     -2  0   733 -591      7  7   117   98     -6 -2   236  252      0  9   176 -191     -9  0   231  255      4  7    62   70
 -3-11   287 -285     -1  0  1520 1578      0  8   746  741     -5 -2   413 -389      1  9   369  321     -8  0   155 -192      6  7    74  -80
 -2-11    78  -73      0  0   382 -292      1  8   502 -528     -3 -2   506  533      3  9    76   97     -7  0   105 -129      0  8   229 -234
 -1-11   200  218      1  0   226  171      2  8   157 -194     -2 -2   818  809      4  9   241 -254     -6  0   172  150      1  8   293 -307
 -6-10   352  309      2  0   395 -376      4  8   257  270     -1 -2   419 -430      5  9    82  -85     -3  0   137   25      2  8   264  257
 -2-10   336  298      3  0   355 -295      5  8   121  123     -7 -1   177  185      1 10   176 -157     -2  0   908  860      5  8   192 -196
 -3 -9   316  303      4  0  1067 1113      6  8   196 -149     -4 -1   258  236      5 10    64   80     -1  0  1263-1270      6  8   175  165
 -1 -9   466 -461      5  0   210 -206      1  9   614 -622     -3 -1   336  355      0 11   157  164      0  0   957 -957      0  9   135 -133
 -4 -8   201  174      6  0   390 -364      4  9    66   82     -1 -1  1227-1292      1 11   308 -294      1  0   511 -524      1  9   238  236
 -3 -8   145 -176      7  0   228  236      5  9   298 -302      0  1   537  535      2 11   121  113      2  0   505  546      5  9   113  143
 -6 -7   459 -456      8  0   528  500      3 10   144 -133      1  1   309  302      3 11    61   76      3  0   255  291      6  9   155 -148
 -3 -7   461  424      9  0   470 -431      4 10   116 -128      3  1   566 -538      4 11    88  -86      4  0   474 -541      0 10   123  110
 -7 -6   283 -282      0  1  1075-1094      5 10   199  167      5  1   220  194      0 12   217 -208      5  0   490  483      3 10   234  239
 -6 -6   112  -19      1  1   589 -548      6 10   205  185      8  1   119  104      2 12   264  258      6  0   109  109      6 10   237 -205
 -4 -6   205  201      2  1    67  -82      1 11   162  176     10  1   181 -174      3 12   119 -165      7  0   371 -357      2 11    75   78
 -3 -6   243  195      3  1   674  690      2 11   113  -96      0  2   744  779                          10  0   128  133      3 11   222  204
 -2 -6   675 -702      4  1   376 -380                          1  2   117 -107        L =   6            0  1   564  542      5 11   108 -165
 -1 -6   197 -178      5  1   341 -350        L =   5           2  2   665 -687      H  K    FO   FC      1  1   365  354                 
 -8 -5   509  508      9  1   146 -153      H  K    FO   FC      3  2    54  -69     -1-11   150 -165      3  1    42  -60        L =   7  
 -7 -5   599 -609      0  2   906 -873     -1-12   102 -130      4  2   509  517      0-11   167  143      5  1   191  191      H  K    FO   FC
 -6 -5   321 -277      1  2   427 -376     -3-11   293 -275      5  2   310 -332     -6-10   153 -142      6  1   374 -340     -2-12   127  147
 -5 -5   190  233      2  2   706 -545     -1-11   130  149      0  3   213 -253     -6 -9   144 -129      7  1    77  124     -2-10   238 -245
 -4 -5   285  298      3  2   365  373     -5-10   171  162      1  3   571 -578     -1 -9   246  235      8  1   204  173     -1-10   198  201
 -3 -5   746 -766      4  2   212 -154     -4-10    75  -53      2  3   587  588     -4 -8   322 -280     10  1   185 -177     -4 -9   141  166
 -2 -5   322  312      5  2   219  170     -3-10   275  271      3  3   350  403     -2 -8   433  420      0  2   513 -406     -3 -9    65  -69
 -1 -5   785  741      6  2   300 -273     -2-10   134 -130      4  3   451 -500     -1 -8   148 -144      2  2   422   79     -2 -9   139  142
-10 -4   140  144      8  2   376 -373     -5 -9   424  415      7  3   148  128     -7 -7   448 -431      3  2   254  248     -1 -9    87 -102
 -8 -4   303 -295      9  2   109  136     -3 -9   169 -149      9  3   256 -228     -5 -7   313  282      4  2    81   24     -4 -8   319  303
 -4 -4   420 -405      0  3   815 -836     -2 -9   239 -241     10  3   184  190     -2 -7   313 -282      6  2   199  187     -3 -8   135 -103
 -2 -4   362  232      1  3   173 -207     -1 -9   165  187      0  4   570 -607     -7 -6   296 -312      8  2   132 -102     -2 -8   197 -198
 -1 -4   151  150      2  3   620  581     -6 -8   287  286      1  4   344  330     -6 -6   374  334      0  3   222 -212     -1 -8   215  213
  0 -4    58  -28      3  3   816  836     -1 -8   161 -159      2  4   228  214     -2 -6   447  434      1  3   100   94     -5 -7   228  243
 -8 -3   185 -202      4  3   144  177     -8 -7   281 -253      4  4   233 -227     -1 -6   176 -155      2  3   760  723     -3 -7   419 -417
 -7 -3   283  263      5  3   322 -313     -7 -7   200  226      5  4   124  116     -8 -5   301 -276      3  3   415 -427     -1 -7   380  390
 -5 -3   221 -213      7  3   230  225     -5 -7   204 -225      6  4   114 -107     -7 -5   330  323      5  3   298 -295     -6 -6   263  267
 -3 -3   123  126      9  3    68  109     -4 -7   212 -234      9  4    60   67     -6 -5   192 -212      8  3   292  278     -5 -6   159  139
 -1 -3   172  149      1  4   145  148     -3 -7   464  457      0  5   150 -153     -4 -5   260  277      9  3    54  -65     -4 -6   547 -560
```

-3	-6	262	-237
-2	-6	390	401
-6	-5	314	-297
-4	-5	135	-145
-2	-5	41	4
-1	-5	339	322
-10	-4	201	219
-7	-4	625	-636
-6	-4	731	702
-1	-4	278	-271
-5	-3	529	-515
-4	-3	570	568
-2	-3	253	200
-1	-3	950	-987
-6	-2	721	-720
-5	-2	118	185
-4	-2	829	890
-3	-2	226	-219
-2	-2	710	-696
-7	-1	313	-306
-6	-1	200	-185
-5	-1	686	708
-3	-1	471	-460
-2	-1	764	-807
-1	-1	773	675
0	-1	118	136
3	1	175	195
6	1	645	655
7	1	123	-115
8	1	435	-403
0	2	917	-868
1	2	811	810
2	2	236	-214
3	2	299	-291
4	2	146	-160
5	2	486	494
6	2	199	166
7	2	337	-319
8	2	133	-120
1	3	631	684
2	3	330	-284
5	3	415	428
6	3	494	-484
7	3	63	-100
8	3	109	99
9	3	123	124
0	4	564	543
1	4	414	-432
3	4	55	-89
5	4	60	-63
6	4	62	-77
7	4	191	178
0	5	449	-471
2	5	121	162
3	5	88	-98
4	5	306	294
5	5	77	-153
7	5	161	-161
9	5	100	129
1	6	321	331
4	6	102	-89
5	6	139	-124
6	6	140	-155
7	6	187	184
8	6	101	107
1	7	410	-372
2	7	243	236
3	7	224	225
5	7	280	-299
7	7	133	123
8	7	189	-164
0	8	515	-495
1	8	485	489
3	8	174	-210
4	8	312	-296
6	8	126	160
2	9	137	-113
5	9	251	226
6	9	85	-113
0	10	221	233
1	10	267	-250
2	10	149	136
5	10	70	65
3	11	229	-194
4	11	229	221
0	12	134	135

L = 8

H	K	FO	FC
-1	-11	247	225
-2	-10	372	318
-1	-10	144	-131
-6	-8	197	-166
-1	-8	301	298
-2	-7	102	-102
-7	-6	135	128
-6	-6	291	-274
-2	-6	255	-247
-5	-5	324	337
-3	-5	579	-544
-1	-5	333	333
-8	-4	278	-290
-6	-4	643	653
-4	-4	662	-716
0	-4	221	157
-7	-3	541	490
-4	-3	427	-400
-3	-3	83	48
-1	-3	485	478
-10	-2	121	118
-8	-2	77	-60
-7	-2	285	-282
-6	-2	271	258
-4	-2	374	-326
-2	-2	316	-235
-1	-2	156	-147
-9	-1	354	-332
-8	-1	63	46
-6	-1	584	555
-5	-1	802	-785
-3	-1	263	257
-1	-1	545	-531
-8	0	417	415
-6	0	368	-358
-5	0	295	-255
-4	0	1156	1168
-3	0	367	-375
-2	0	622	-531
-1	0	111	-125
0	0	915	958
1	0	294	-259
2	0	165	167
3	0	559	612
4	0	281	268
5	0	256	-214
6	0	548	-544
7	0	269	253
8	0	207	104
1	1	403	-407
2	1	161	189
3	1	62	60
4	1	361	-377
5	1	325	-324
6	1	505	486
7	1	116	93
1	2	35	54
3	2	429	-443
4	2	237	210
6	2	182	130
8	2	59	9
0	3	481	483
2	3	324	329
4	3	373	-375
6	3	226	222
1	4	694	680
5	4	393	398
6	4	249	225
8	4	199	-174
1	5	959	948
2	5	529	-538
4	5	147	168
5	5	291	288
6	5	110	-124
0	6	444	385
1	6	217	-218
2	6	321	-321
7	6	186	167
0	7	325	341
1	7	386	-343
2	7	224	240
3	7	116	-117
6	7	72	100
0	8	240	-249
3	8	86	94
4	8	279	192
5	8	112	-133
7	8	54	49
0	9	254	-272
1	9	108	126
3	9	203	201
0	10	257	-248
2	10	235	217
4	10	114	-132
1	11	264	261
0	12	55	-13

L = 9

H	K	FO	FC
-3	-11	53	-35
-1	-11	159	166
-3	-9	243	-259
-4	-8	510	-510
-2	-8	474	448
-1	-7	409	-373
-7	-6	311	278
-6	-6	246	-254
-1	-6	350	338
0	-6	93	-84
-8	-5	161	146
-7	-5	260	-260
-6	-5	166	167
-3	-5	177	198
-4	-4	189	196
-9	-3	321	327
-7	-3	262	-252
-6	-3	324	-324
-5	-3	574	567
-3	-3	509	-520
-1	-3	221	269
0	-3	88	-103
-10	-2	175	211
-8	-2	373	-402
-6	-2	289	284
-5	-2	343	360
-4	-2	726	-692
-2	-2	439	459
-9	-1	209	-210
-6	-1	334	315
-5	-1	100	137
-4	-1	518	-492
-3	-1	83	-107
0	-1	202	222
1	1	742	736
2	1	534	-533
3	1	352	-353
4	1	249	259
5	1	380	335
6	1	289	-288
0	2	530	511
1	2	559	-557
2	2	552	-511
3	2	392	413
4	2	350	342
5	2	76	-83
6	2	370	-344
1	3	579	-550
2	3	593	575
3	3	193	208
4	3	161	-150
5	3	237	-223
8	3	124	-108
1	4	131	107
3	4	339	-319
5	4	68	105
6	4	283	276
7	4	287	-262
0	5	233	-244
1	5	250	205
3	5	116	103
7	5	40	13
1	6	384	359
2	6	128	135
4	6	280	-306
5	6	111	120
0	7	302	322
3	7	349	-379
5	7	198	191
6	7	82	-72
0	8	347	339
1	8	70	67
2	8	162	-155
5	8	64	-67
0	9	112	110
1	9	253	-231

L = 10

H	K	FO	FC
-4	-10	317	314
-2	-10	288	-278
0	-10	179	185
-5	-9	269	263
-4	-9	200	-203
-1	-9	242	238
-2	-8	42	12
-4	-7	216	224
-1	-7	162	-149
-8	-6	192	-218
-9	-5	235	-243
-7	-5	214	221
-5	-5	347	-341
-3	-5	478	447
-1	-5	289	-295
-9	-4	193	-184
-6	-4	259	-223
-5	-4	228	224
-2	-4	310	-277
-1	-4	279	273
0	-4	359	327
-5	-3	194	-176
-4	-3	188	-193
0	-3	397	-403
-9	-2	90	-77
-8	-2	238	203
-6	-2	243	245
-5	-2	333	-329
-3	-2	266	-240
-2	-2	422	351
-1	-2	208	182
0	-2	149	130
-8	-1	212	220
-7	-1	281	-288
-5	-1	86	101
-3	-1	393	-396
-2	-1	791	775
0	-1	173	-175
-8	0	287	-275
-6	0	217	-205
-5	0	544	550
-4	0	872	-827
-3	0	220	224
-2	0	631	679
-1	0	484	-506
0	0	590	-609
1	0	304	-229
2	0	1121	1042
8	0	225	196
1	1	646	594
4	1	178	173
7	1	194	-199
2	2	352	-335
3	2	391	413
6	2	249	-204
7	2	153	159
8	2	86	79
1	3	289	277
2	3	427	-403
3	3	167	-137
5	3	110	99
7	3	76	100
2	4	506	-518
3	4	262	258
4	4	247	213
5	4	104	-99
1	5	428	-432
2	5	120	113
3	5	236	278
4	5	224	-197
7	5	112	120
1	6	111	-129
0	7	93	-80
2	7	327	-318
4	7	226	208
5	7	140	-145
0	8	356	-327
1	8	329	311
4	8	198	-214
0	9	294	286
1	10	77	-65

L = 11

H	K	FO	FC
-3	-10	136	-151
-3	-9	171	171
-1	-8	90	85
-3	-7	293	-266
-3	-6	271	240
-2	-6	110	110
-5	-5	302	-293
-4	-5	296	296
0	-5	105	-133
-8	-4	247	-228
-2	-4	346	342
-7	-3	512	459
-6	-3	229	-233
-5	-3	110	-132
-3	-3	554	595
-2	-3	112	-120
-1	-3	311	-342
-9	-2	185	-165
-6	-2	117	-116
-3	-2	54	19
-2	-2	864	-851
-1	-2	366	382
-6	-1	186	201
-5	-1	130	-133
-4	-1	175	-191
-3	-1	423	-401
-2	-1	586	583
-1	-1	580	542
0	1	346	-310
3	1	364	325
0	2	353	-345
2	2	584	564
3	2	107	-84
6	2	144	-138
0	3	128	142
1	3	101	-79
3	3	189	-200
4	3	318	307
4	4	196	188
5	4	217	-230
2	5	190	-168
3	5	230	227
0	6	545	539
1	7	175	-165
4	7	134	-142
6	7	156	144
0	8	70	-64
2	8	65	35
0	9	111	114
2	9	114	-112
4	9	202	200
0	10	165	-169

L = 12

H	K	FO	FC
-1	-10	118	-126
-4	-8	326	304
0	-8	240	212
0	-7	314	321
-3	-6	138	122
-2	-6	252	-234
-1	-6	186	159

```
-7 -5  292 -283
-5 -5  243  245
-8 -4  179 -155
-6 -4  284  267
-4 -4  380 -363
-2 -4  595  503
 0 -4  304 -255
-5 -3  273 -293
-4 -3  168  170
 0 -3   82   96
-6 -2  230  203
-7 -1  279  267
-4 -1  186  191
-3 -1  313  299
-1 -1  466 -471
-7  0  185  214
-6  0  443 -460
-4  0  231  156
-3  0  207  239
-2  0  501 -461
-1  0  155  163
 0  0  306  282
 3  0  111   96
 5  0  466 -427
 6  0  115  123
 7  0  129  183
 1  1  115  107
 3  1  223  230
 4  1  269 -263
 6  1  221  180
 0  2  344 -318
 1  2  104  119
 4  2  183 -156
 5  2   76  112
 7  2   78   81
 1  3  222 -208
 2  3  173  166
 3  3  113 -111
 2  4  208  193
 3  4  190 -197
 5  4  215  176
 2  5  223 -223
 4  5  224  200
 6  5  215 -194
 1  6  204 -201
 2  6  182 -168
 3  6   89   99
 4  6  246  232
 5  6  165 -145
 3  7  135  150
 2  8   90  -72
 2  9  115  147

   L = 13
 H  K   FO   FC
 0 -9  104 -148
-2 -8  136  128
-1 -8  250 -241
-6 -6  182 -177

-4 -6  294  312
-2 -6  214 -197
 0 -6  102  139
 0 -5  101  126
-6 -4  216 -206
-4 -4   52   41
-2 -4  255 -280
-7 -3  346 -298
-5 -3  278  264
-4 -3  130 -154
-6 -2  468  462
-4 -2  244 -271
-2 -2  247  228
-7 -1   88  146
-5 -1  280 -327
 0 -1  103  116
 4  1   59   61
 1  2  343 -344
 3  2  235  217
 4  2  215  176
 0  3  276 -263
 1  3   48   54
 0  4  265 -255
 5  4   95   92
 4  5  121 -154
 2  6  131  139
 3  6  171 -173
 5  6  115  105
 4  7   96  143
 0  8   59   82
 1  8  173 -157

   L = 14
 H  K   FO   FC
-4 -7  225 -235
-3 -6  104  144
-4 -5   79   88
-6 -4  278 -259
-7 -3  119 -128
 0 -3  146 -134
-5 -1  277  290
-3 -1   88  103
 0 -1  207 -193
-7  0  173 -148
-6  0  395  365
-2  0  243 -264
-1  0  228 -225
 0  0  213 -217
 1  0  573  522
 4  0  339 -357
 5  0  253  225
 1  1  265  250
 2  1  327 -322
 5  1  193  175
 0  2  232  196
 2  2  132  162
 3  3   89 -114
 4  3   79  135
 0  5  327 -350

 2  5  326  317
 0  6  206 -219
 1  6  191  177
 3  7  116  105

   L = 15
 H  K   FO   FC
 0 -7  108 -152
-1 -6  127 -127
 0 -5  140  148
-6 -4  155  155
-4 -4  220 -223
-5 -3  221 -238
-4 -3  135  141
-3 -3  235  240
-1 -3  246 -244
 0 -3  233  221
-6 -2  113 -106
-4 -2  194  189
-3 -2  335 -359
-2 -1  115  115
 1  1  164 -158
 2  1  125  149
 0  2  240 -254
 1  2  290  287
 2  2  214  209
 3  2  128 -155
 4  2  107 -114

   L = 16
 H  K   FO   FC
 0 -5  158 -163
-2 -4  163  167
-4 -3   76   74
-2 -3   58  -25
-5 -1  192 -183
-3 -1  213  243
-2 -1  238 -252
-1 -1  138 -118
-5  0   78  122
-3  0  280 -306
-1  0  148  167
 0  0  380  317
 2  0  315 -298
 0  1   52  -45
 1  1  240 -230
 4  1  128 -112
 3  2  142 -130
 0  4  171 -184

   L = 17
 H  K   FO   FC
-2 -3  205  206
-4 -2  268 -256
 0 -2  144 -158
```

SUMMARY

Nitrosyl Complexes

The 18-electron complexes $Cp(NO)_2W(PR_3)^+$, where R is Ph, OPh, OMe, undergo facile one-electron reduction to give the 19-electron radical compounds, $Cp(NO)_2W(PR_3)$. This reduction is accomplished with chemical reducing agents (hydrazine, alkoxides or zinc) or electrochemically. Cyclic voltammetric studies reveal that the reduction is quasi-reversible, and the reduction potential increases as the σ donor/π acceptor ratio of the ligand decreases: $PPh_3 > P(OMe)_3 > P(OPh)_3$. ESR spectra of the PPh_3 and $P(OPh)_3$ complexes are obtained and show a ten-line pattern resulting from hyperfine coupling of the electron with the ^{31}P ($I = \frac{1}{2}$) and two equivalent ^{14}N nuclei ($I = 1$). X-ray structural data for the $P(OPh)_3$ derivative show that the N-W-N angle (102.7°) is noticeably larger than that (92.0°) in the 18-electron chloro analog, $Cp(NO)_2WCl$. In addition, the 19-electron complex has shorter W-N but longer N-O bonds than in $Cp(NO)_2WCl$. The structural differences between these complexes may be understood if the 19th electron occupies an orbital which has substantial NO 2π character, is antibonding between the two NO ligands, and is antibonding between the N and O atoms of each NO ligand.

The $P(OPh)_3$ radical derivative is readily oxidized back to $Cp(NO)_2W(P(OPh)_3)^+$ by oxidants such as Ag^+, Ph_3C^+, $MeOSO_2F$, CF_3SO_3H and I_2.

Carbene Complex

In the course of these investigations, we improved the synthesis of $Cp(CO)(L)Fe[CH(SMe)]^+$, which had been previously prepared in small quantities, by the reaction of $Cp(CO)(L)Fe[C(SMe)_2]^+$ with $(Et_3BH)Li$, followed by acidification (Eqn. 1).

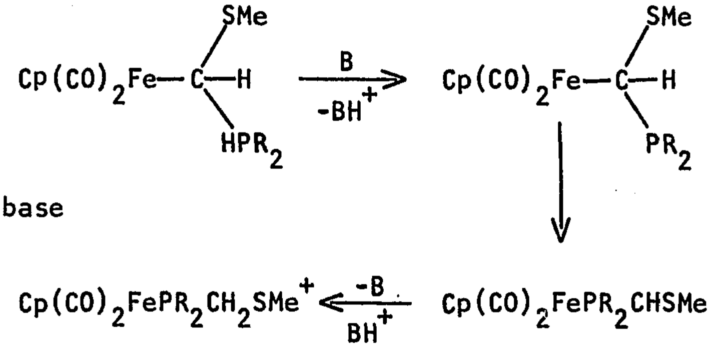
$$\begin{array}{lcc} Cp(CO)(L)Fe[C(SMe)_2]^+ + [Et_3BH]Li & \longrightarrow & Cp(CO)(L)Fe[CH(SMe)_2] \\ L = CO,\ PPh_3,\ P(OPh)_3 & & \Big\downarrow H^+ \\ & & Cp(CO)LFe[CH(SMe)]^+ \\ & & + \\ & & HSMe \end{array} \qquad (1)$$

These thiomethoxyl secondary carbene complexes are modestly stable in air. In the case where L is CO, this complex decomposes upon contact with H_2O to give $Cp(CO)_3Fe^+$ and $Cp(CO)_2FeCH_2SMe$ in equal amounts. This disproportionation reaction is presumed to go through a formyl intermediate, $Cp(CO)_2FeCHO$.

The $Cp(CO)_2Fe[CH(SMe)]^+$ complex reacts with a variety of tertiary phosphines, phosphites and amines to afford the corresponding adducts, $Cp(CO)_2Fe[CH(SMe)(L)]^+$, where L is $MePPh_2$, PPh_3, $ClPPh_2$, PCl_3, $P(OPh)_3$, $P(OCH_2)_3CMe$ or pyridine. These adducts are noticeably more stable than the parent carbene complex. An X-ray structural determination of the $P(OCH_2)_3CMe$ adduct shows that the iron methine, Fe-C1, bond distance is close to that typical of σ bonds in $Cp(CO)_2FeR$ complexes; the C1-P bond distance is similar to those in single-bond carbene phosphine adducts, $MCH(R)PR'_3$. The C1-S bond length is normal for a σ bond such as those in MeSR(R = H, Me).

The PPh_3 and $P(OCH_2)_3CMe$ adducts decompose at elevated temperatures to provide $Cp(CO)_2FeL^+$ (L = PPh_3, $P(OCH_2)_3CMe$, respectively); the other product identified in the pyrolysis reaction of the PPh_3 adduct are cis and trans MeSCH=CHSMe, $HC(SMe)_3$ and Cp_2Fe.

Dialkyl and alkyl phosphines also form stable adducts, $Cp(CO)_2Fe[CH(SMe)(L)]^+$, (L = PPh_2H, PCy_2H, $PPhH_2$ or $PCyH_2$), with $Cp(CO)_2Fe[CH(SMe)]^+$. The solid PPh_2H and PCy_2H adducts readily decompose to give the phosphine complexes, $Cp(CO)_2Fe[PR_2(CH_2SMe)]^+$, (R = Ph, Cy), in low yields at 168°C and 200°C, respectively. It is not entirely clear how the rearrangement reaction takes place, but it appears to be base catalyzed. The base involved in the rearrangement is believed to be PR_2H which may be formed by dissociation from the adduct (Scheme 1).

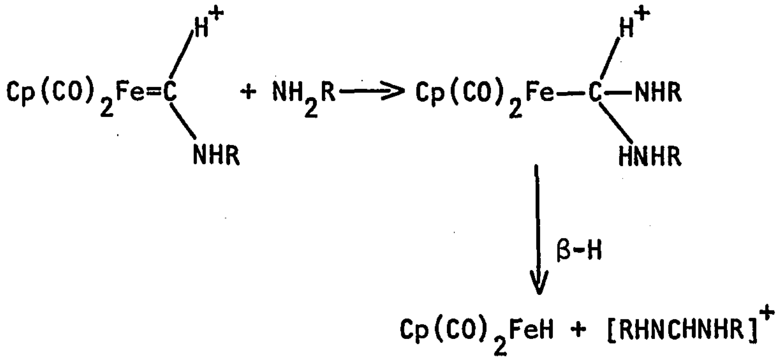


Scheme 1

The PPh_2H adduct reacts with strong bases (n-BuLi or Et_3N) to afford $Cp(CO)_2Fe[CH(SMe)(PPh_2)]$ and a small amount of $Cp(CO)_2Fe[PPh_2(CH_2SMe)]^+$.

The $Cp(CO)(L)Fe[CH(SMe)]^+$ (L = CO, $P(OPh)_3$) complexes react with Et_2NH to furnish the amino carbene complexes, $Cp(CO)(L)Fe[CH(NEt_2)]^+$. The ^1H and ^{13}C spectra of both compounds display two distinctive methylene and methyl groups which are indicative of a high C-N bond rotational barrier caused by strong N to C p-p π-bonding. Likewise, $Cp(CO)_2Fe[CH(NMe_2)]^+$ is prepared by reacting Me_2NH with the corresponding thiomethoxyl carbene complex. This compound is found to react with excess Me_2NH to give $Cp(CO)_2FeH$ and NNN'N'-tetramethyl foramidinium.

Other primary amines ($MeNH_2$, $CyNH_2$, i-$PrNH_2$, t-$BuNH_2$) also react with $Cp(CO)_2Fe[CH(SMe)]^+$ to give the corresponding amino carbene complexes, $Cp(CO)_2Fe[CH(NHR)]^+$ (R = Me, Cy, i-Pr, t-Bu). The yields of these reactions are in the range of 28-38%. The poor yields are due to a secondary reaction, in which, the amino carbene reacts further with excess amine to give $Cp(CO)_2FeH$ and the NN'-dialkyl foramidinium ion. The most likely mechanism of this secondary reaction is believed to be a β-hydrogen elimination of the ammonium complex (Scheme 2).



Scheme 2

The primary amino hydrido carbene complexes, $Cp(CO)_2Fe[CH(NHR)]^+$, are exclusively in the trans (E) configuration. When the amino hydrogen is removed with NaOH-EtOH, syn and anti isomers of $Cp(CO)_2Fe[CHNR]^+$ are detected in the ^1H NMR spectra of the compounds with R = i-Pr or Cy. On the other hand, the anti isomer is the sole form of the t-Bu analog. The mechanism for the rapid interconversion of the iminoylformyl compounds upon deprotonation of the carbene precursors is believed to be an inversion about the nitrogen atom (lateral shifting) rather than a C-N bond rotation. When the $Cp(CO)_2Fe[CHNR]^+$ (R = i-Pr, Cy) is alkylated with excess $MeOSO_2F$, E and Z isomers of $Cp(CO)_2Fe[CH(NMeR)]^+$ are obtained, and the E isomer predominates when the concentration of $MeOSO_2F$ is reduced.

The carbonyl ligand of $Cp(CO)_2Fe[CH(NHCy)]^+$ is photolytically labile; ultraviolet irradiation of the complex in MeCN gives $Cp(CO)(MeCN)Fe[CH(NHCy)]^+$. The identical complex may also be prepared by reacting $Cp(CO)_2Fe[CH(NHCy)]^+$ with Me_3NO in MeCN.

The complex $Cp(CO)_2Fe[CH(NH_2)]^+$ has also been prepared by the reaction of $Cp(CO)_2Fe[CH(SMe)]^+$ or $Cp(CO)_2Fe[CH(SMe)(Pyr)]^+$ with NH_3. Finally, $Cp(CO)_2Fe[CH(SMe)]^+$ reacts with diazomethane at room temperature, yielding a stable deep red S-bound olefin complex, $Cp(CO)_2Fe[SMe(CH{=}CH_2)]^+$.

ADDITIONAL LITERATURE CITED

1. Connelly, N. G. Inorg. Chim. Acta Rev. 1972, 6, 47.
2. Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry," 3rd ed.; Wiley: New York, 1972; pp. 713-719.
3. McCleverty, J. A. Chem. Rev. 1979, 79, 53.
4. Fischer, E. O.; Maasböl, A. Angew. Chem. Int. Ed. 1964, 3, 580.
5. Brown, F. J. Prog. Inorg. Chem. 1981, 27, 1.
6. Cardin, D. J.; Cetinkaya, B.; Lappert, M. F. Chem. Rev. 1972, 72, 545.
7. Haines, R. J.; Leigh, G. J. Chem. Soc. Rev. 1975, 4, 155.
8. Calderon, N.; Ofstead, E. A.; Judy, W. A. Angew. Chemie Int. Ed. Eng. 1976, 15, 401.
9. Master, C. Adv. Organomet. Chem. 1976, 17, 61.
10. Muetterties, E. L.; Stein, J. Chem. Rev. 1979, 79, 479.
11. Pruett, R. L. Science 1981, 211, 11.
12. Kirmse, W. "Carbene Chemistry"; Academic Press: New York, 1971, Vol. 1.
13. Jones, J, Jr.,; Moss, R. A. "Carbene"; Wiley: New York, 1973, Vol. 1.
14. Schilling, B. E. R.; Hoffmann, R.; Lichtenberger, D. L. J. Am. Chem. Soc. 1979, 101, 585.
15. Kostic, N. M.; Fenske, R. F. Organomet. 1982, 1, 974.
16. Schilling, B. E. R.; Hoffmann, R.; Faller, J. W. J. Am. Chem. Soc. 1979, 101, 592.
17. Gladysz, J. A. Adv. Organomet. Chem. 1982, 20, 1.
18. Brookhart, M.; Trucker, J. R.; Flood, T. C.; Jensen, J. J. Am. Chem. Soc. 1980, 102, 1203.

19. Kegley, S. E.; Brookhart, M.; Husk, G. R. Organomet. 1982, 1, 760.

20. Bodnar, T.; Cutler, A. R. J. Organomet. Chem. 1981, 213, C31.

21. Schrock, R. R. Acc. Chem. Res. 1979, 12, 98.

22. McCormick, F. B.; Angelici, R. J. Inorg. Chem. 1981, 20, 1111.

ACKNOWLEDGMENTS

I am deeply indebted to my brothers and sisters: Judy, Helen, Simon, Raymond, Myron, Allen and Kwai-Fong, for their love, support and constant encouragement. I would like to express my gratitude to Professor Robert Angelici whose direction and enthusiasm have made this work possible. I wish to thank Professor Robert Jacobson and Jim Richardson for their helpful assistance on X-ray studies, and Professor Glen Russell for his consultation. I would like to offer special thanks to Professor John Gladysz for introducing me to chemical research. It has been a distinct pleasure working with Dan Plummer and Norm Schroeder, and friendships from Steve Socol, Pui-Kwan Tse, Peter Gottschalk and Mrs. Bev Mullen are dearly treasured.