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Synthesis and reactions of organometallic complexes of 2,3-dihydrothiophene and dithiocarbenes

George N. Glavee
Iowa State University

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Glavee, George N., Ph.D.

Iowa State University, 1988

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Synthesis and reactions of organometallic complexes of 2,3-dihydrothiophene and dithiocarbenes

by

George N. Glavee

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

Department: Chemistry
Major: Inorganic Chemistry

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For the Major Department

Signature was redacted for privacy.

For the Graduate College

Iowa State University
Ames, Iowa

1988

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DEDICATION

To my mom

PREFACE

Chemistry of 2,3-Dihydrothiophene

Studies aimed at the elucidation of the mechanism of catalytic hydrodesulfurization (HDS) of thiophene have led to the proposal of 2,3-dihydrothiophene as an intermediate in the desulfurization thiophene. In an effort to examine the coordination modes of 2,3-DHT on the catalyst surface, a variety of phosphine-substituted complexes have been prepared. The hydrogenation of 2,3-DHT to tetrahydrothiphene (THT) is also explored in the reactions of 2,3-DHT and metal hydride complexes.

Reactions of $[\mathrm{CpFe(CO)_2(carbene)}]^+$ Complexes

The $\mathrm{CpFe(CO)_2(carbene)^+}$ complexes have received considerable attention in the quest to generate stable, isolable and yet reactive carbene complexes. A wide range of reactions of these complexes appears in the literature. However, there are no reports of studies involving reducing agents such as Na-amalgam or sodium naphthalenide. The second part of this dissertation involves the reduction $\mathrm{CpFe(CO)_2(=\overline{COCH_2CH_2O})}$, $\mathrm{CpFe(CO)_2[=C(SMe)]^+}$ and related carbene complexes. Also a novel equilibrium between $\mathrm{Cp(CO)\overline{Fe[C(S}Me)(SMe)_2]}$ and $\mathrm{Cp(CO)Fe(SMe)[=C(SMe)_2]}$ is described.

This thesis consists of five sections. The first section is a literature review of vinyl sulfide and mercaptovinyl complexes and the following sections represent research as it was submitted for journal publication. Literature citations, tables and figures pertain only to the sections in which they are included.

SECTION I. TRANSITION METAL VINYL SULFIDE AND MERCAPTOVINYL COMPLEXES

INTRODUCTION

Hydrodesulfurization (HDS), the process of catalytic removal of sulfur from sulfur-containing organic compounds such as thiophene and benzo[b]thiophene in crude oil, is carried out on a Co-Mo/Al_2O_3 catalyst. The common structural forms of sulfur-containing compounds found in crude oil are shown in Fig. 1a. The 2,3-dihydrothiophene

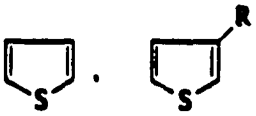
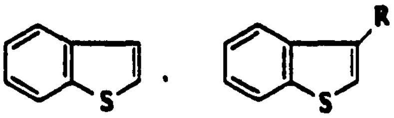
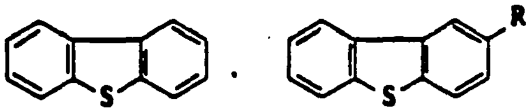
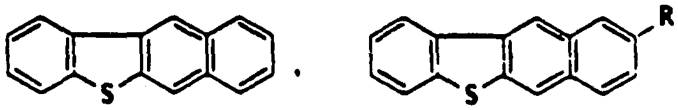
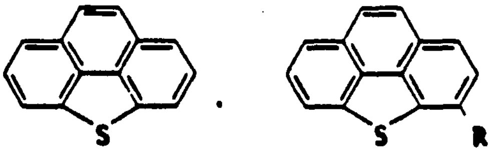
Compound class	Structure
Thiols (mercaptans)	RSH
Disulfides	RSSR'
Sulfides	RSR'
Thiophenes	
Benzothiophenes	
Dibenzothiophenes	
Benzonaphthothiophenes	
Benzo[*def*]dibenzothiophenes	

Figure 1a. Common sulfur containing compounds in petroleum

(2,3-DHT, Fig. 1b), which is a vinyl sulfide, has been suggested[1] as a possible intermediate in the HDS of thiophene. Transition metal complexes of 2,3-DHT, as well as other vinyl sulfides such as thiophene and benzothiophene, are important in efforts to understand the types of reactions a vinyl sulfide might undergo when bound to a transition metal on the catalytic surface. This dissertation deals with the reactions of 2,3-DHT and transition metal complexes. Below is a review of previously known vinyl sulfide and related mercaptovinyl complexes.

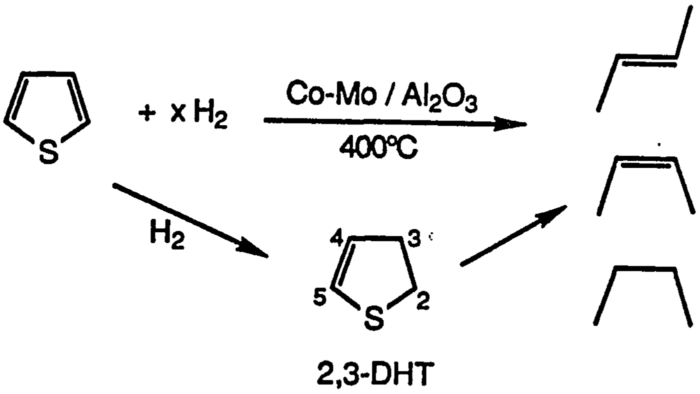


Figure 1b. HDS of thiophene

Vinyl sulfide in transition metal complexes could, in principle, act as a monodetate, bidentate or bridging (Fig. 2) ligand toward one or two

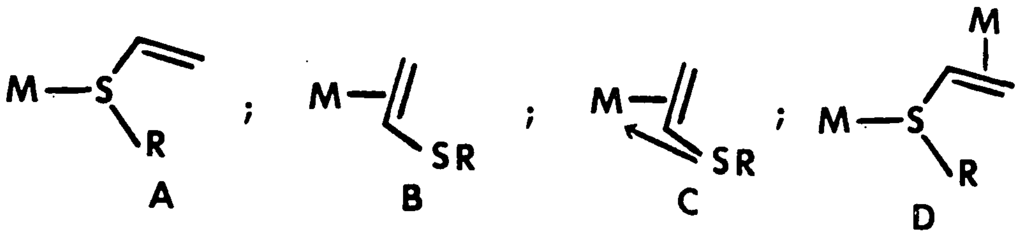


Figure 2. Possible coordination modes for the vinyl sulfide ligand

metal centers. As a monodentate ligand the vinyl sulfide may coordinate through the sulfur or olefin as shown in Fig. 2A and B. The vinyl sulfide ligand may act as a bidentate ligand when both the olefin and sulfur ends are involved in coordination in one complex as shown in Fig. 2C and D. The possible reaction of the vinyl sulfide to form a bridging ligand is also demonstrated in Fig. 2D.

The hydrogen on the C2 of a vinyl sulfide may be replaced by an organometallic fragment to give a compound which is referred to as a mercaptovinyl complex (Fig. 3A). The mercaptovinyl may also act as a bidentate, Fig. 3B, or bridging ligand, Fig. 3C. Aside from the relevance

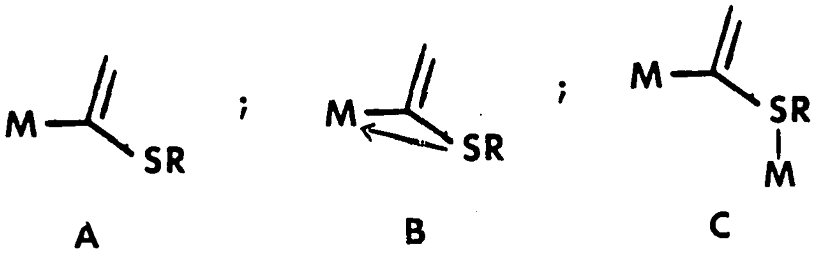


Figure 3. Possible coordination modes of the mercaptovinyl ligand

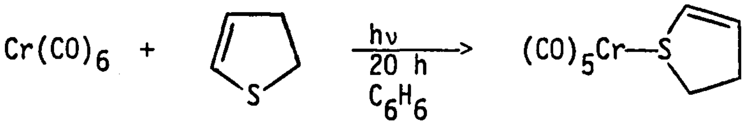
to HDS process, and the unique structural and coordination chemistry generated by the interaction of this group of ligands with organometallic fragments, the transition metal vinyl sulfides and mercaptovinyl complexes are important because they are used in the preparation of organic compounds of pharmaceutical, agricultural and biological importance[2] which contain the vinyl sulfide unit and thiophenic fragments.

This discussion covers the sulfur and olefin coordinated transition metal vinyl sulfides, as well as the mercaptovinyl complexes reported in Chemical Abstracts from 1892 to March 1988. However, only thienyl compounds will be discussed even though there are a number of sulfur and π-coordinated thiophene complexes.[3]

Sulfur Coordinated Vinyl Sulfides

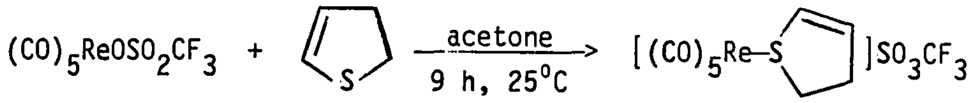
2,3-Dihydrothiophene (2,3-DHT) complexes

The first 2,3-DHT complex was reported by Eekchof[4] and coworkers in 1978. This sulfur-coordinated chromium pentacarbonyl complex was obtained by irradiation of a benzene solution of $Cr(CO)_6$ and 2,3-DHT (eq. 1).



1

Recently, the tungsten analog was synthesized by the reaction of $W(CO)_5(THF)$ and 2,3-DHT.[5] Routes to $(CO)_5Re(2,3\text{-DHT})^+$ (eq. 2), $Ru(CO)_3Cl_2(2,3\text{-DHT})$ (eq. 3), and $PdCl_2(2,3\text{-DHT})_2$ (eq. 4) have also been



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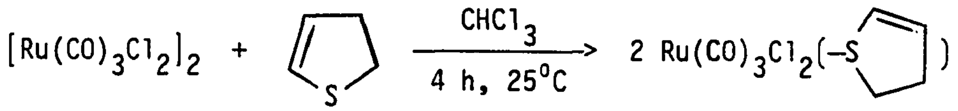

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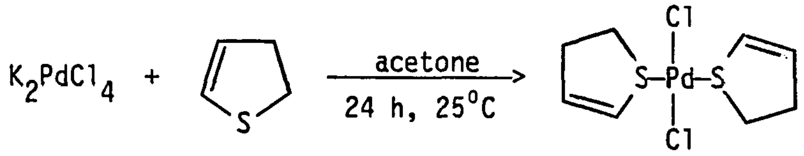


4

described.[5] The reaction shown in equation 4 was carried out in the hope of generating an η^3 complex (Fig. 4). The formation of such an η^3 compound was proposed in the reaction of the allyl sulfide I with HCl (eq. 5),[6] however, it was not clear based on the spectroscopic data that the

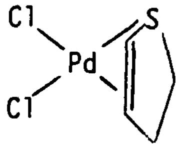
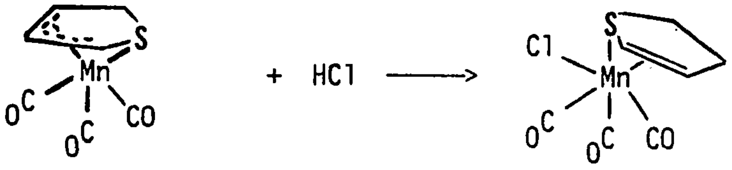


Figure 4. η^3-2,3-DHT complex



I II (5)

product of the reaction was II or the dimer shown in Fig. 5. Structural

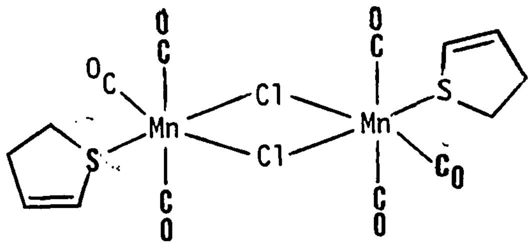
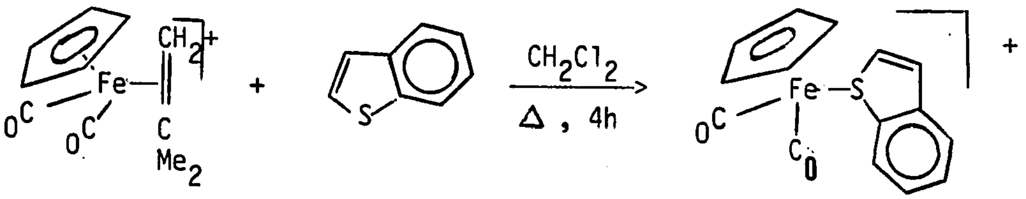


Figure 5. A possible formulation for complex II

studies were not done on this compound because of its instability.

Benzothiophene complexes

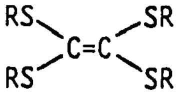
To date, only one sulfur-coordinated benzo[b]thiophene complex has been reported in the literature.[7] This compound was obtained by the reaction of $[CpFe(CO)_2(CH_2{=}CMe_2)]BF_4$ and BT in refluxing CH_2Cl_2 (eq. 6).


6

There are, however, a number of η^6-benzo[b]thiophene transition metal complexes in which the metal is coordinated to the arene portion of the ligand: (η^6-BT)Cr(CO)$_3$,[8a,b] (η^6-BT)RuCp$^+$,[8c] and Cp*(η^6-BT)M^{2+}(M = Rh, Ir).[8c]

<u>Other vinyl sulfide complexes</u>

A range of zerovalent Group VI metal complexes with ligands shown in Fig. 6 have been reported.[9,10] Photolysis of M(CO)$_6$ (M = Cr, Mo, W) in the presence of III leads to the formation cis-M(CO)$_4$[(RS)$_2$C=C(SR)$_2$] (Scheme 1). These compounds can also be made by reacting M(CO)$_6$ and III in the presence of NaBH$_4$. The reaction of [NEt$_4$][M(CO)$_5$Cl] with III results in the formation of the monodentate sulfide complex VI which goes


III

R = Me, Et

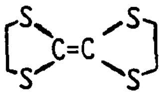
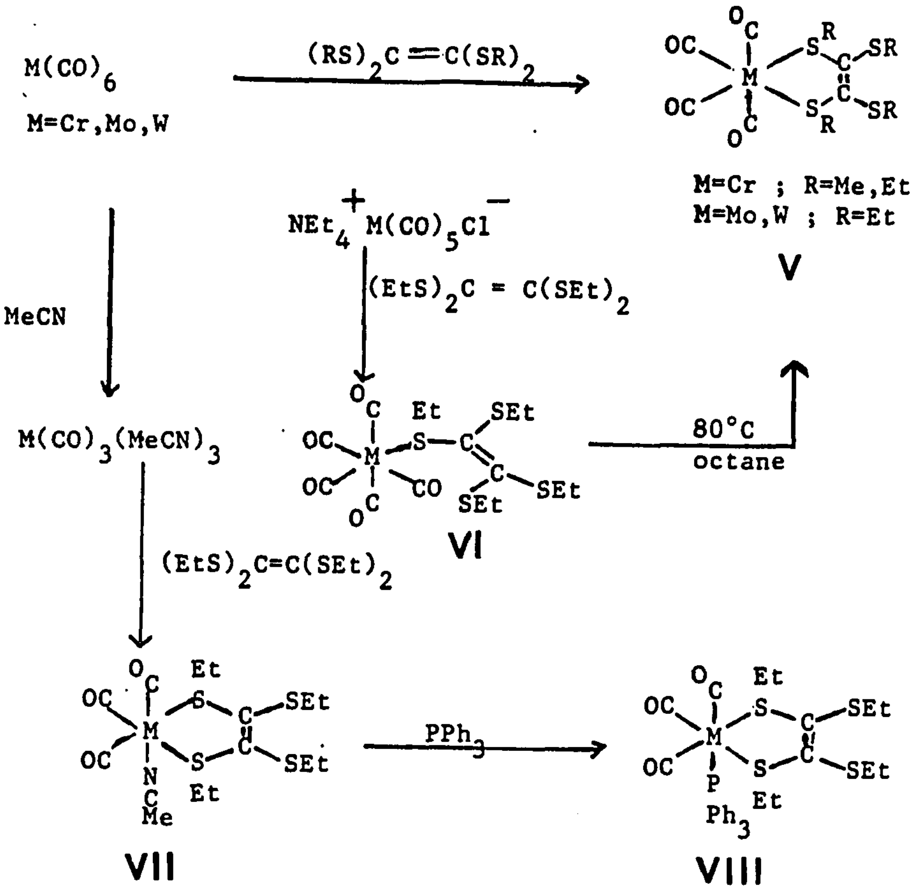
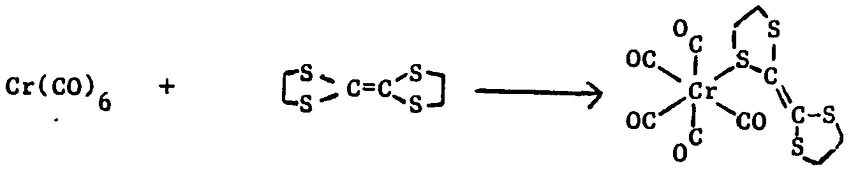

IV

Figure 6. Tetrakis(alkylthio)ethene ligands



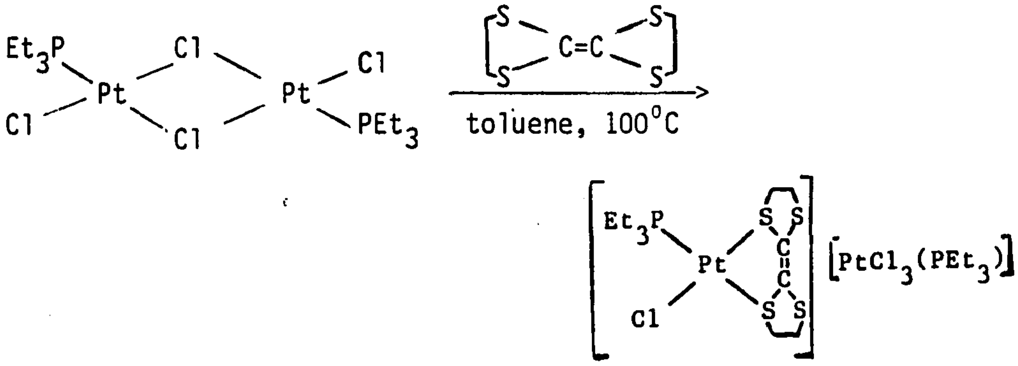
Scheme 1

to the cis bidentate complex V upon heating. The facial complex VIII is



7

prepared by the reaction of $M(CO)_3(MeCN)_3$ with $(EtS)_2C=C(SEt)_2$ and PPh_3. Irradiation of the cyclic vinyl sulfide **IV** with $Cr(CO)_6$, however, results in only the monodentate sulfur coordinated complex (eq. 7). In contrast, the reaction of **IV** with the platinum compound (eq. 8), leads to a bidentate complex.[11] The reaction of this platinum dimer and $(RS)_2C=C(SR)_2$ (R = Me) results in a C-S bond cleaved product which was structurally characterized (eq. 9). The ^{31}P-NMR monitored reaction of tetrakis(ethylthio)ethene analog shows that both the cis and trans



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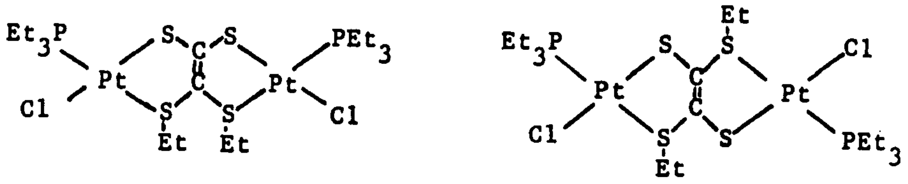
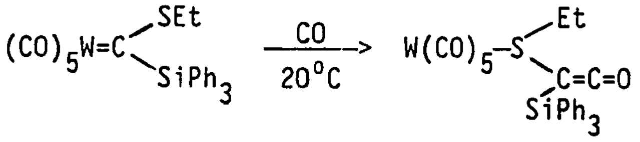
$$[PtCl_2(PEt_3)]_2 + (RS)_2C=C(SR)_2 \xrightarrow[120\ oC]{xylene}$$ 9



complexes are formed (eq. 9), and the reaction proceeds through a bridging sulfide intermediate: $Cl(PEt_3)Pt(SEt)_2C{=}C(SEt)_2Pt(PEt_3)Cl$. One sulfur coordinated $\{CpFe(CO)_2[(MeS)_2C{=}C(SMe)_2]\}BF_4$ has been prepared by the reaction of $CpFe(CO)_2(THF)BF_4$ and $(MeS)_2C{=}C(SMe)_2$.[11b] The following sulfur-coordinated compounds of $(MeS)_2C{=}C(SMe)_2$ have also been prepared: $(CL)MePt[\eta^2\text{-}(MeS)_2C{=}C(SMe)_2]$ and $(Br)Me_3Pt[\mu\text{-}\eta^4\text{-}(MeS)_2C{=}C(SMe)_2]\text{-}PtMe_3(Br)$.[11c]

Reaction of $[Et_4N][Cr(CO)_5Br]$ with the divinyl sulfide, $(C_2H_3)_2S$ in the presence of Et_3OBF_4 in CH_2Cl_2 at ambient temperature leads to the formation of sulfur-coordinated compound, $Cr(CO)_5[S(C_2H_3)_2]$.[12] A sulfur-coordinated (ethylthio)(triphenylsilyl)ketene has been prepared from the reaction of $W(CO)_5[{=}C(SEt)(SiPh_3)]$ with CO (eq. 10).[13] Raubenheimer and coworkers have also shown that the $(CO)_5W[{=}C(Ph)(OEt)]$ reacts with the lithium reagent shown in eq. 11 to give a dimetallic vinyl sulfide complex.[14] It has also been reported that the sulfur-coordinated thioether X (Scheme 2) results from the reaction of IX and Me_3OBF_4.[15] Platinum and palladium complexes of the form MX_2L where X = Cl, I and L = MeSCH=CHSMe have been prepared by refluxing an ethanol/water solution of



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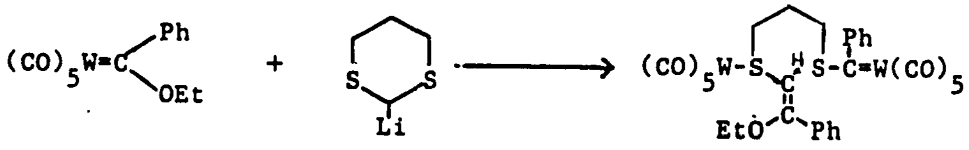

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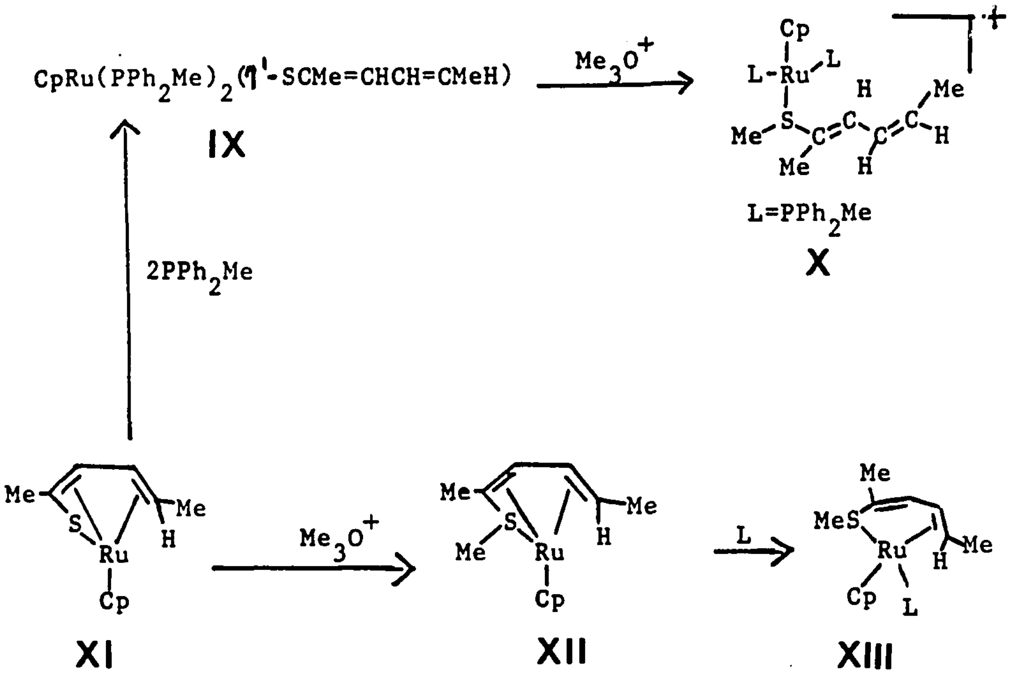
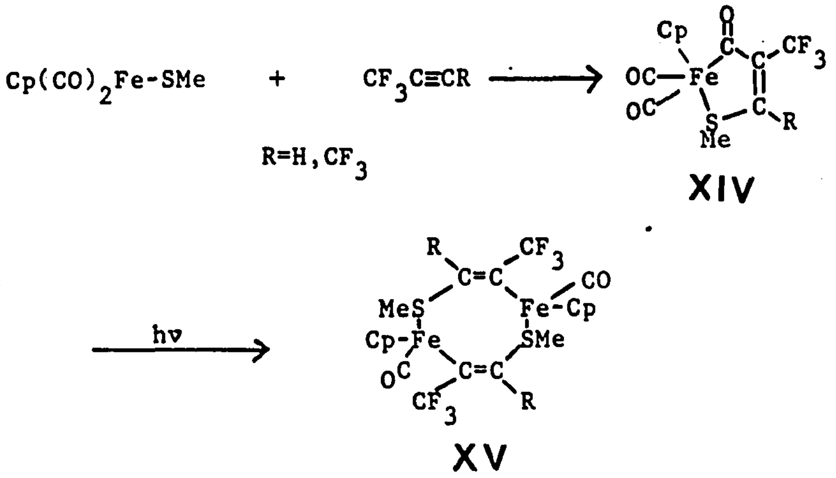


Scheme 2

K_2MX_4 and MeSCH=CHSMe.[16] The reaction of $CpFe(CO)_2SMe$ and trifluoropropyne give the structurally characterized compound XIV which upon pholysis results in the formation of the dimer XV (eq. 12).[17] The W

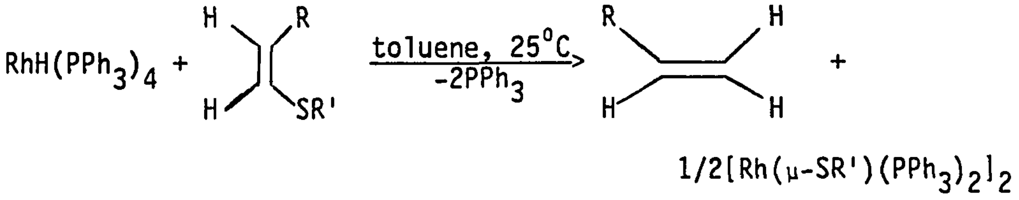


12

and Mo analogs have been prepared using $CpM(CO)_3SMe$ and a variety of acetylenes.[17]

Olefin-Coordinated Vinyl Sulfides

Only one compound is known in which the olefin end of the vinyl sulfide is coordinated, XII (Scheme 2). The vinyl sulfide in this compound acts as a multidentate ligand in which the sulfur is also coordinated. Also, equation 13 describes a reaction in which olefin coordination is suggested to occur prior to insertion and elimination of alkene.[18]



13

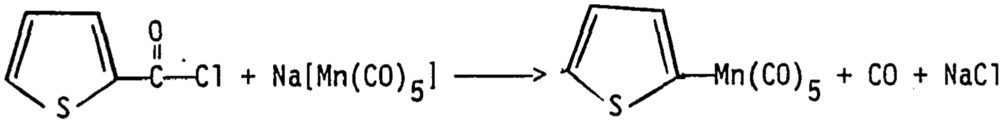
R = H, Me. R' = Ph, tolyl.

MERCAPTOVINYL METAL COMPLEXES

There are no mercaptovinyl compounds of this kind involving metals from the Ti, V, or Cr triads.

Mn and Fe

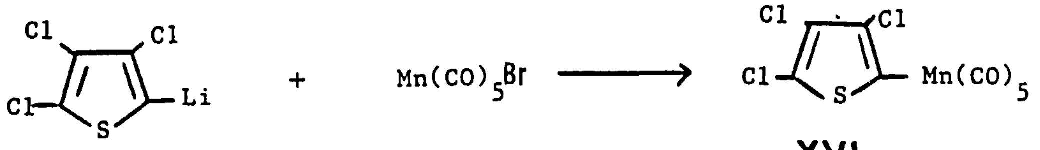
An unstable σ-bonded manganese thiophene compound was prepared by the reaction of the thiophene acyl chloride derivative with the pentacarbonyl manganese anion (eq. 14). This compound slowly decomposes under nitrogen



14

XIX

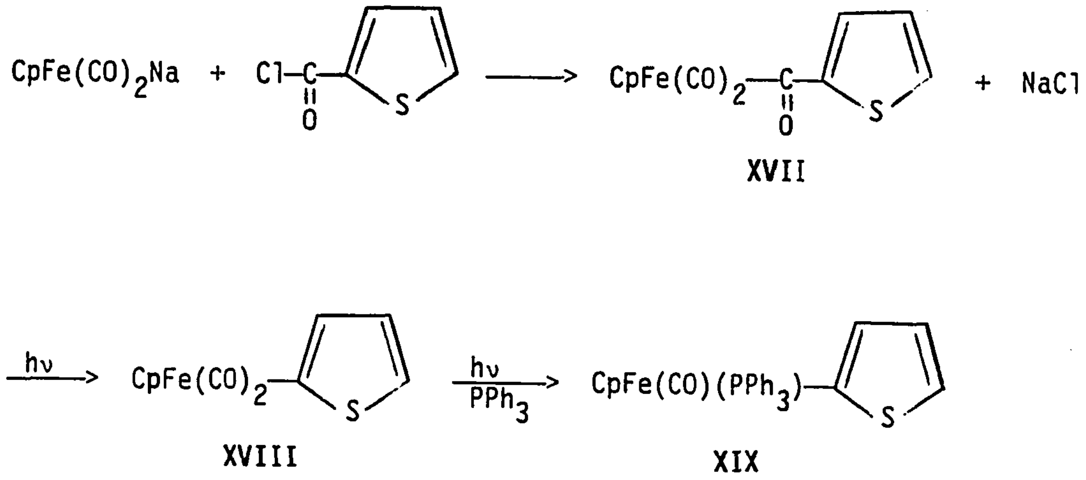
but extensively in air at room temperature. In contrast, the σ-(trichloro-2-thienyl)pentacarbonylmanganese (eq. 15) remains unchanged



15

XVI

even after heating to 110°C for 24 h.[19,20] The cyclopentadienyldicarbonyliron analog **XVI**, $CpFe(CO)_2(C_4Cl_3S)$ is prepared by reacting $CpFe(CO)_2I$ with the lithium thienyl salt. Kolobova and his coworkers[21] report that the thiophene analog of the iron compound can be generated as shown in eq. 16.[21] They also report that the iron complex XVIII undergoes



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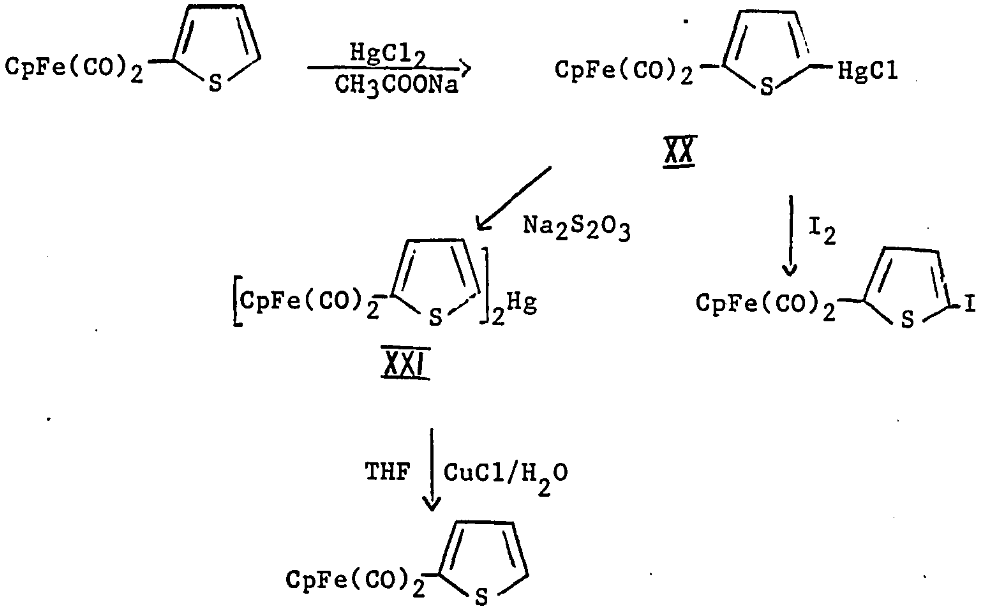
phosphine substitution upon photolysis to yield the monophosphine substituted compound **XIX**. When compound **XVIII** is treated with $HgCl_2$/CH_3COONa a mercury chloride adduct is obtained (Scheme 3). This

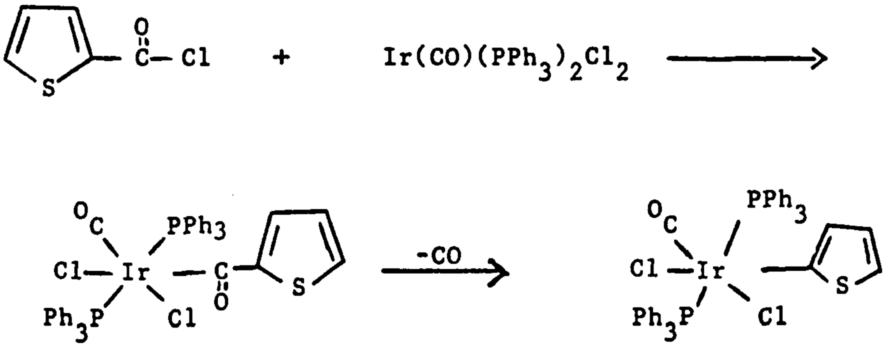


Scheme 3

chloromercury derivative undergoes symmetrization when treated with $Na_2S_2O_3$ to yield **XXI** in which the Fe-C σ-bond is retained. Complex **XVIII** is regenerated when **XX** is treated with $CuCl_2$ in H_2O/THF. An iodothienyl complex is obtained when **XX** is reacted with iodine.

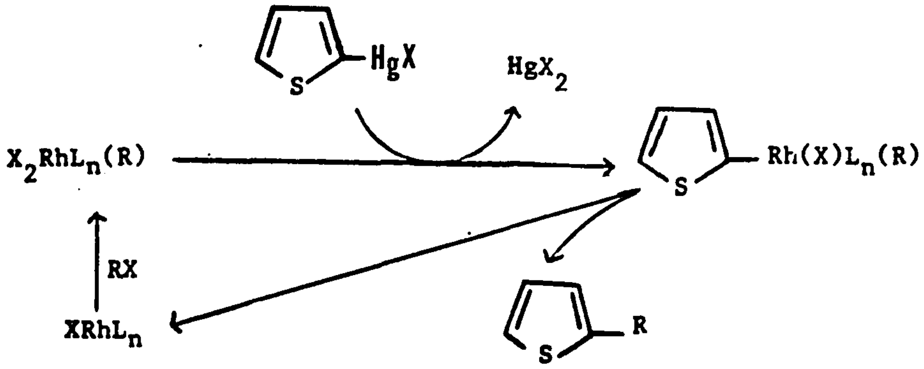
Rh and Ir

An unusually stable iridium complex **XXII** (eq. 17) has been reported by Blum and coworkers.[22] This compound does not decompose on heating to temperatures above its melting point of 271°C. A range of Rh(I) and Rh(III) complexes are known to catalyze carbonylation and alkylation of organomercury compounds.[23] These C-C bond forming reactions are thought to involve intermediates in which the organic substrate (e.g., thienyl) is bonded in a sigma fashion to the rhodium metal (Scheme 4). The carbonylation reaction which results in the formation of $(C_4H_3S)_2C{=}O$ is catalyzed by number of rhodium complexes including $Rh(CO)Cl(PPh_3)_2$, $RhCl_3{\cdot}H_3O$, $RhCl(PPh_3)_3$, $[RhCl(NBD)]_2$ and $[Rh(CO)_2Cl]_2$, the most efficient being the dimer $[Rh(CO)_2Cl]_2$.



XXII

17

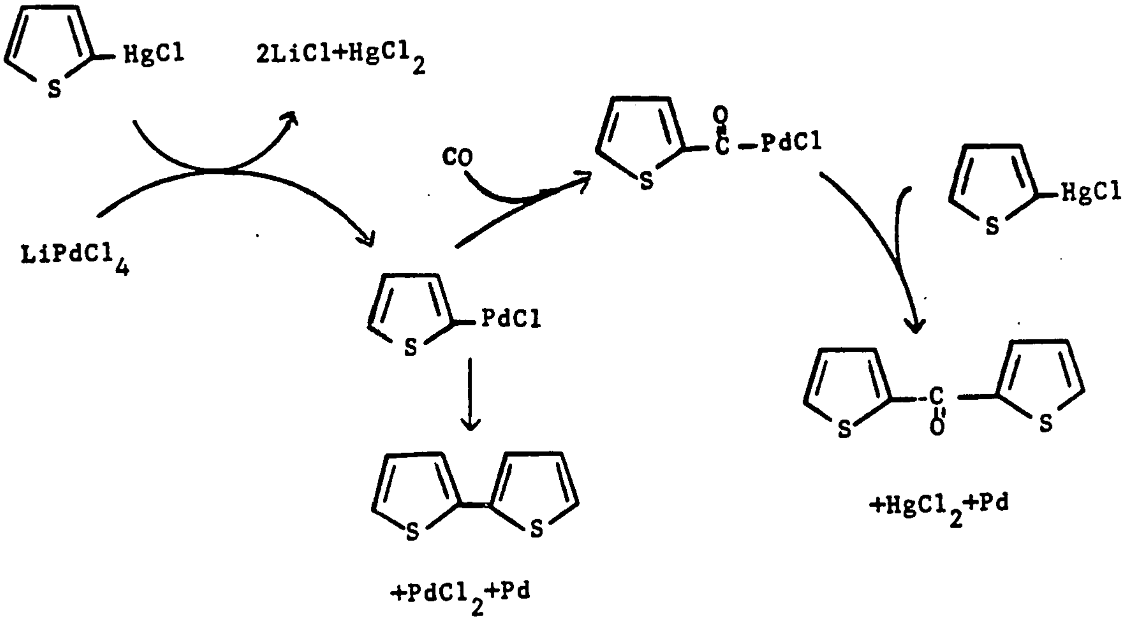


Scheme 4

Ni, Pd and Pt

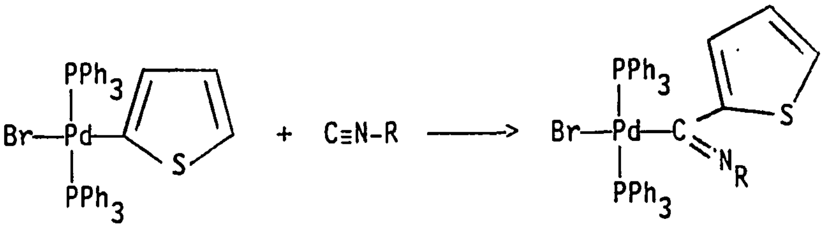
Two sigma bonded nickel thiophene complexes, $CpNi(PR_3)(C_4Cl_3S)$[20] (PR_3=PPh_3,$PMePh_2$) and $Ni(C_6Cl_5)(PMe_2Ph)_2(C_4H_3S)$[24] have been reported. Both the $CpNi(PR_3)(C_4Cl_3S)$ and $Ni(C_6Cl_5)(PMe_2Ph)_2(C_4H_3S)$ compounds were obtained by displacing a chloride with the appropriate thienyl group using the appropriate 2-lithiothienyl compound. The reaction of $(C_4H_3S)ZnCl$ with $BrCH_2COOEt$, and the reaction of the same thienyl zinc chloride with bromoacetonitrile are catalyzed by $Ni(acac)_2$ in the presence of $PPh_2(C_6H_{11})$[25] and results in the formation of thienylacetic ester and thienylacetonitrile respectively, presumably via a thienyl nickel complex.

Carbonylation, coupling and cross coupling reactions of thiophene and thiophenic reagents such as thienylmercury halide and thienylzinc halide are catalyzed by a variety of palladium complexes.[26-28] These carbon-carbon bond forming reactions generally involve organic moieties such as alkyl- or arylhalide, acid chlorides or carbon monoxide and are thought to proceed via a 2-thienylpalladium complex as shown for the CO in Scheme 5.



Scheme 5

Studies of kinetic isotope effects and the influence of acidity on the substitution and coupling reactions of thiophene involving palladium in the +2 oxidation state indicate that these reaction types proceed through the same 2-thienylpalladium intermediate complex.[29] All the isolated thienylpalladium complexes are of the general form $Pd(PPh_3)_2(R)(X)$ (X = Cl, Br; R = thienyl, methyl thiophene).[2a] The reaction of 2-bromothiophene and $Pd(PPh_3)_4$ in refluxing benzene leads to the formation of trans-$[BrPd(2\text{-}C_4H_3S)(PPh_3)_2]$ (XXIII). The 3-methylthiophene and 4-methylthiophene analogs are obtained in a similar fashion. The chloride analog of XXIII is prepared from the reaction of $(2\text{-}C_4H_3S)HgCl$ and trans $Pd(PPh_3)_2Cl_2$. The 2-thienyl complex trans-$[PdBr(2\text{-}C_4H_3S)(PPh_3)_2]$ reacts with isocyanides to give the isocyanide inserted product XXIV.[30]

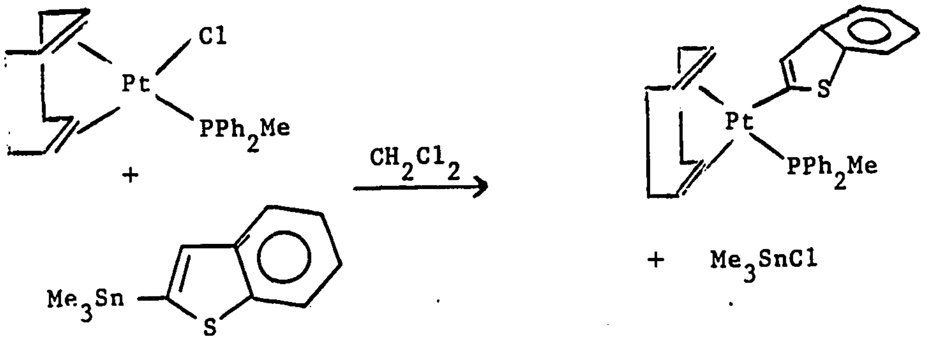


XXIII XXIV

18

$R = C\text{-}C_6H_{11}$, Bu^+, p-$OMeC_4H_4$

The following platinum compounds have been synthesized using routes described for the palladium analogs above: $PtCl(PPh_3)_2(2\text{-}C_4H_3S)$, $PtBr(PPh_3)_2(2\text{-}C_4H_3S)$, $PtBr(PPh_3)_2(2\text{-}4\text{-}MeC_4H_2S)$ and $PtBr(PPh_3)_2(2\text{-}3\text{-}MeC_4H_2S)$.[2a] Reaction of $[Pt(COD)Cl(PMePh_2)]BF_4$ and $SnRMe_3$ (R = 2-thienyl, 2-benzo[b]thienyl) at room temperature (eq. 19) results in the formation



19

of the thienyl and benzo[b]thienyl complexes.[31] These thienyl and benzo[b]thienyl complexes readily lose COD in the presence 4-dimethylaminopyridine ($4\text{-}Me_2NC_5H_4N$) or bisdiphenyl phosphinoethane (dppe) to give amine and phosphine substituted products. Both the thienyl and the benzo[b]thienyl complexes are formed when $Pt(COD)Cl_2$ is treated with one equivalent of $SnRMe_3$.[32] The bisthienyl compound is produced when two equivalents of $SnRMe_3$ is used. Also, the monothienyl platinum compound $Pt(COD)Cl(2\text{-}C_4H_3S)$ can be prepared in a less efficient manner by the reaction of $GeMe_3(2\text{-}C_4H_4S)$ and $Pt(COD)Cl_2$. The thienyl group is also readily transferred between platinum centers (as shown in eq. 20).

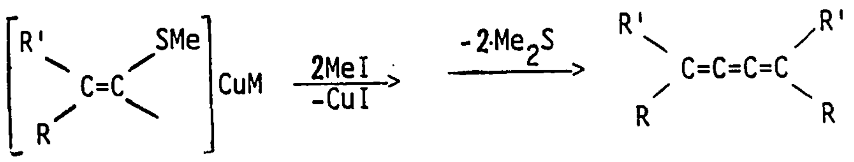
$$Pt(COD)(2\text{-}C_4H_3S)_2 + Pt(COD)Cl_2 \xrightarrow[12\ h,\ 20^{\circ}C]{dppe} Pt(dppe)Cl(2\text{-}C_4H_3S) \qquad 20$$

Anionic thienyl complexes have been isolated in $[K(18\text{-crown-}6)[Pt(CN)_3R]$ (R = 2 thienyl, 2 benzothienyl) by reacting Pt(COD)Cl(R) with KCN in the presence of 18-crown-6.[33]

Cu

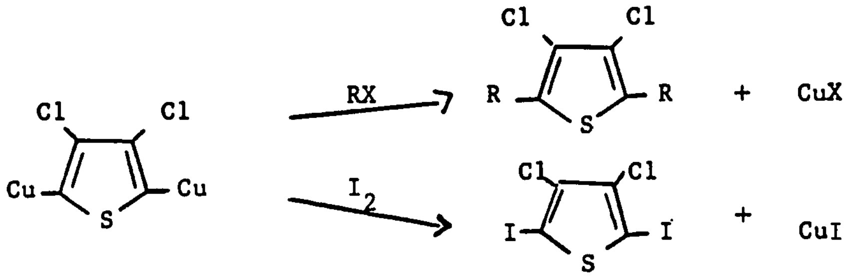
Thienyl copper compounds are in general less reactive than the corresponding lithium and Grignard reagents.

Reaction of R'C≡CSMe (R' = Ph, H) with R_2CuM (M = MgX, Li; R = Me, Et, i-Pr, Ph, t-Bu, n-pentane) at 30°C results in the formation of $[RR'C{=}C(SMe)]_2CuM$. This vinyl sulfide reagent reacts with MeI at 0°C to yield cumulenes (eq. 21).[34] Smith and coworkers have reported the



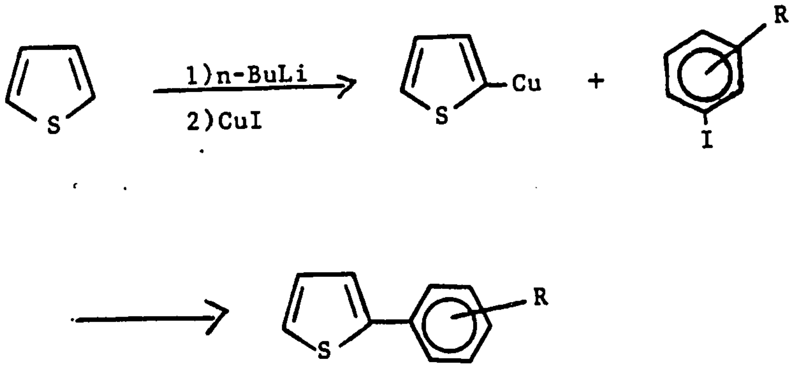
. 21

synthesis of $(2\text{-}C_4Cl_3S)Cu$.[2d] They also report the preparation of the bimetallic compound $(C_4Cl_2S)Cu_2$ from $(C_4Cl_2S)Li_2$ and CuCl.[35] The 2,5 dicopperdichlorothiophene compound reacts with acetyl chloride, iodine and allyl bromide to give the corresponding thiophene compounds (eq. 22). The



22

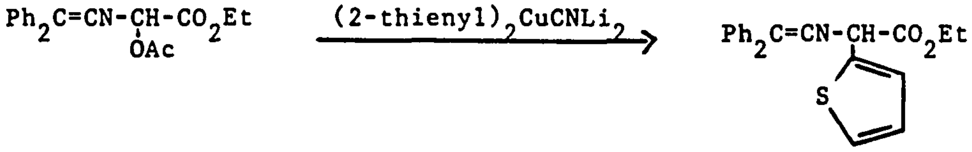
2-trichlorothienylcopper complex reacts with C_6F_5I at 100°C in dioxane to give the biaryl compound $C_6F_5\text{-}(2\text{-}\overline{C_4Cl_3S})$.[36] The preparation of 2-thienylcopper has been reported and its reactions with haloarenes to yield arene substituted biaryl compounds described (eq. 23).[37] The



23

2,2-bithienyl and other biaryl compounds such as 2-(thienyl)pyrazoles have been similarly prepared.[38]

The combination of organolithium (RLi) compounds and 2-thienyllithium with CuCN leads to the formation of a reagent, R(2-thienyl)$CuCNLi_2$, which selectively transfers the R ligand in substitution reactions with epoxides and organic halides.[2e,39] The bis-thienyl complex, $(2\text{-thienyl})_2CuCNLi_2$, is formed when 2-thienyllithium reacts with CuCN at 0°C. This reagent undergoes thienyl transfer (eq. 24) to give **XXV** which on hydrolysis yields



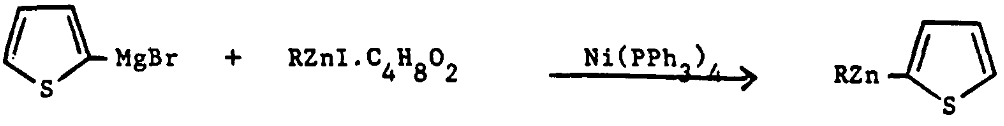
XXV

24

D,L-(2-thienyl)glycine.[3f] Mixed lithium organothienylcuprate reagents LiR(thienyl)Cu (R = Me, Bu, Ph, 2-pyridyl) are generated when 2-thienylcopper reacts with organolithium compounds.[40] The R groups in these compounds are selectively transferred in reactions with enones or enoates, and the 2-thienyl copper is regenerated. The bis(2-thienyl)copper lithio compound is also prepared from thienylcopper and thienyllithium.

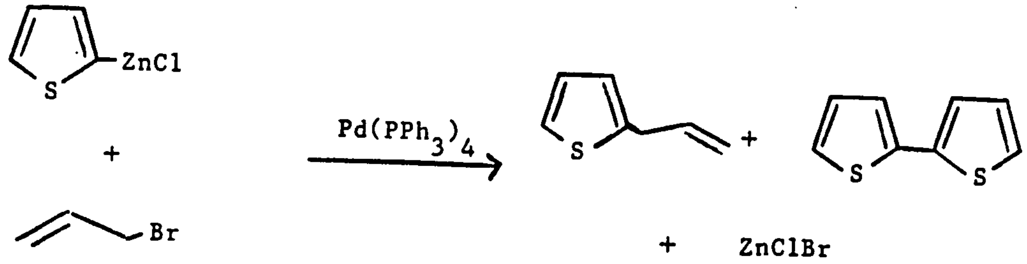
Zn, Cd and Hg

Thienylzinc compounds of the form $(2\text{-}C_4H_3S)ZnX$ (X = Cl, Br, I) may be prepared in three different ways.[41,42] The reaction of zinc halide with an equimolar proportion of the thienyl Grignard reagent in ether followed by addition of three equivalents of dioxane leads to the formation of $(2\text{-}C_4H_3S)ZnX{\cdot}C_4H_8O_2$ as a crystalline solid. The action of 2-thienylhalide on a zinc-copper couple at 78° with or without a solvent followed by addition of dixane also gives crystalline (2-C_4H_3S)ZnX•$C_4H_8O_2$. Thirdly, if the bis(2-thienyl)zinc is treated with zinc halide in a minimum amount of dry ether a disproportion reaction occurs to give (2-C_4H_3S)ZnX which upon addition of dioxane results in the formation of the crystalline dioxane adduct. In the case where X = Cl, the dioxane may be removed at 60°C in 2-4 mm Hg pressure to give (2-C_4H_3S)ZnCl. The latter compound decomposes when heated above 60°C in a sealed capillary tube under argon. The bis(2-thienyl)zinc compound is prepared by the reaction of zinc halide and thienyllithium or the Grignard reagent. This compound is isolated as the dioxane adduct which liberates the dioxane when heated to 100°C to give pure (2-$C_4H_3S)_2$Zn. The bisthienyl zinc compound decomposes without melting when heated above 150°C.[42] The unsymmetrical organozinc compounds (eq. 25) are prepared by the reaction of the organozinc iodide and the thienyl Grignard reagent.[43] The chloro-2-thienylzinc compound reacts with bromouracil in the presence of $Ni(PPh_3)_4$ in THF-ether to yield the thienyl adduct which upon reaction with HCl gives 5-(2-thienyl)uracil.[44] Allyl bromide reacts with (2-C_4H_3S)ZnCl in the presence of $Pd(PPh_3)_4$ to give allylthiophene and bithiophene compounds (eq. 26).[45]



25

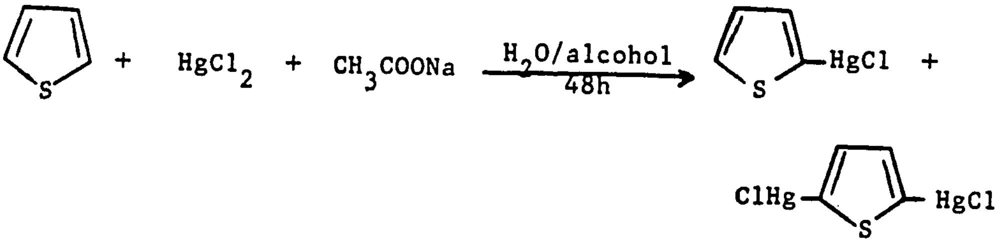
R = C_6H_5; $C_6H_5CH_2$



26

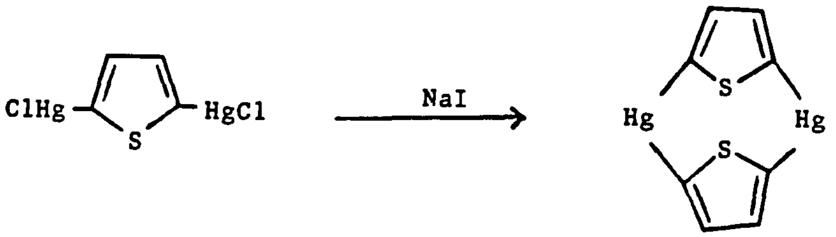
Bis(chlorocadmium)dichlorothiophene is prepared by the reaction of 2,5-dilithiodichlorothiophene with $CdCl_2$ in THF.[33] The reaction of bromo-2-thienylmagnesium and $CdBr_2$ in ether yields bis-2-thienylcadmium.[46] The compound phenyl-(2-thienyl)cadmium is obtained by the reaction of $CdI(C_6H_5)$ and bromo-(2-thienyl)magnesium. This compound is isolated as the dioxane adduct which is a white crystalline solid.

As noted by Smith and Gilman[35] in 1972, there are numerous mercury derivatives of thiophene. The synthesis of chloro-2-thienylmercury was reported as early as 1892. This reaction, as indicated by Hartough,[47]

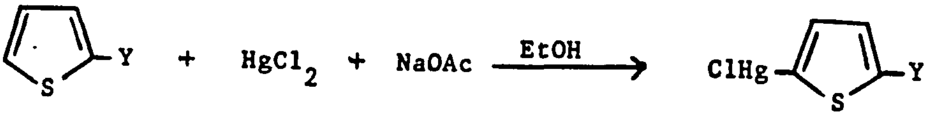


27

occurs at ambient temperature with the formation of small amounts of 2,5-bis(chloromercury)thiophene. The 2-chloromercurythiophene is converted to 2,2'-dithienylmercury in the presence of NaBr in boiling acetone.[48] The 2,5-bis(chloromercury)thiophene is converted to a cyclic mercury compound (eq. 28) on reaction with sodium iodide. An x-ray

 28

structural study has been carried out on the 2,2'-dithienylmercury compound.[49] The molecule is found to be centrosymmetric and the C-Hg-C bond angle is 180°. The thienyl rings are planar and the S atoms are in the anti conformation. The reaction of 2-chloromercurythiophene with anions such as thiocyanate, azide, acetate and trifluoromethanesulfonate results in the displacement of the chloride.[50] These compounds were studied by mass spectroscopy and shown to fragment in the same way as they do under thermal conditions. Aryl iodides react with halo-2-thienylmercury compounds to give the coupled arylthiophene products.[51] The reaction of (2-C_4H_3S)HgCl with Li_2CuMe_3 in excess MeI yields 2-methylthiophene.[52] When (2-C_4H_3S)HgCl is treated with Cu in pyridine in the presence of $PdCl_2$, the bithienyl compound is obtained.[53] Preparations of XXVI which are precursors to thiophene-containing prostaglandin

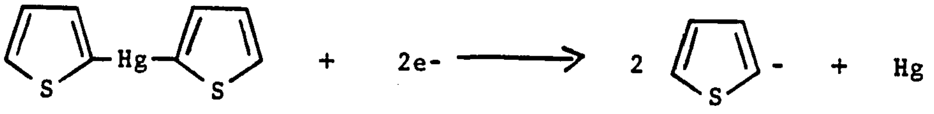


XXVI 29

Y = (E)-CH=$CHCO_2CH_3$; $CH_2CH_2CO_2CH_3$

endoperoxide are achieved in the same way as the unsubstituted compounds.[54]

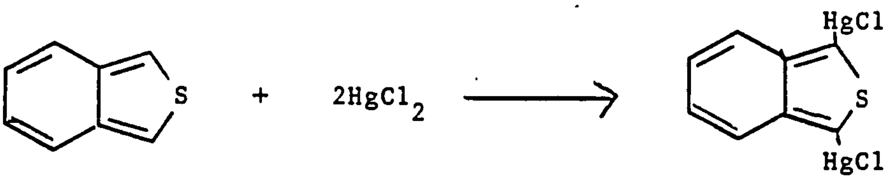
The 2,2'-dithienylmercury compound is generated when a chloroform solution of thienylmercury chloride is passed through a column of alumina treated with sodium cyanide.[55] This symmetrization process is also achieved in H_2O in the presence of sodium EDTA at pH < 4.3.[56] The 2,2'-dithienylmercury reacts with calcium activated with mercury to give 2,2'-dithienylcalcium.[57] Polarographic reduction studies show that the dithienylmercury compound undergoes a 2e irreversible reduction.[58] A similar reduction is observed for the bis(3-methyl-2-benzothienyl)mercury compound. A range of ^1H and ^{13}C NMR studies discussing aspects such as the effect of d-pπ interaction on the shifts and coupling constants in thienyl mercury compounds have been reported.[59] Correlation between proton coupling constants and substituent electronegativity in the 2-substituted thiophenes as well as factors affecting the magnitude of the ^{199}Hg-H spin-spin coupling have been described.



30

Hartough and Meisel[60a] report that the reaction of benzo[b]thiophene in aqueous methanol and acetic acid yield a mixture of 3-benzo[b]thienyl mercuriacetate and 2,3 benzothienyldimercuriacetate.

Reaction of isobenzothiophene and $HgCl_2$ results in the formation of XXVII in nearly quantitative yield.[60b]



XXVII

31

CONCLUDING COMMENTS

It is apparent from the preceding discussion that there are a wide range of transition metal thienyl complexes. A few mercaptovinyl complexes (Fig. 3) have been reported for benzo[b]thiophene. However, there are no examples of 2,3-DHT complexes of this kind. In fact, all the known 2,3-DHT compounds are of the type shown in Fig. 2A. Likewise, there are very few benzo[b]thiophene complexes of the kind shown in Fig. 2. In view of the fact that transition metal compounds of benzo[b]thiophene and 2,3-DHT may prove useful in biologically significant organic synthesis and catalysis, it is important that their chemistry is developed.

The next two sections of this dissertation deal with the synthesis and reaction of 2,3-DHT complexes. The reaction of 2,3-DHT with metal hydrides (Section II) and the synthesis of its tungsten complexes (Section III) are parts of studies aimed at modeling the coordination modes and the reactions of this vinyl sulfide in the hydrodesulfurization process of thiophene.

A novel equilibrium between a metallacyclopropane and its carbene mercaptide form and the reduction of dithiocarbene as well as other related carbene complexes are described in Sections IV and V respectively.

REFERENCES

1. (a) Angelici, R. J. submitted for publication. Acc. Chem. Res. 1988 and references therein. (b) Mitchell, P. C. H. In "Catalysis"; Kemball, C., Ed.; The Chemical Society: London, 1977; Vol. 1, p 223; Vol. 4, p 203 (Special Periodical Report). (c) Spies, G. H.; Angelici, R. J. J. Am. Chem. Soc. 1985, 107, 5569. (d) Sauer, N. N.; Angelici, R. J. Organometallics 1987, 6, 1146. (e) Huckett, S. C.; Sauer, N. N.; Angelici, R. J. Organometallics, 1987, 6, 591. (f) Hachgenei, J. W.; Angelici, R. J. Angew. Chem., Int. Ed. Engl. 1987, 26, 909. (g) Spies, G. H.; Angelici, R. J. Organometallics 1987, 6, 1897.

2. (a) Chia, L.-Y.; McWhinnie, W. R. J. Organomet. Chem. 1980, 188, 121. (b) Oshima, K.; Yamamoto, H.; Nozaki, H. J. Am. Chem. Soc. 1973, 95, 7926. (c) Oshima, K.; Yamomoto, H.; Nozaki, H. Bul. Chem. Soc. Jpn. 1975, 48, 1567. (d) Smith Jr., M. R.; Rahman, M. T.; Gilman, H. Organomet. Chem. Synth. 1971, 1, 295. (e) Lipshutz, B. H.; Kozlowski, J. A.; Parker, D. A.; Nguyen, S. L.; McCarthy, K. E. J. Organomet. Chem. 1985, 285, 437. (f) O'Donnel, M. J.; Falmagne, J.-B. Tetrahedron Lett. 1985, 26, 699.

3. (a) Kuehn, C. G.; Taube, H. J. Am. Chem. Soc. 1976, 98, 689. (b) Guerchais, V.; Astruc, D. J. Organomet. Chem. 1986, 316, 335. (c) Kuhn, N.; Schuman, H. J. Organomet. Chem. 1984, 276, 55. (d) Wasserman, H. J.; Kubas, G. J.; Ryan, R. R. J. Am. Chem. Soc. 1986, 108, 2294. (e) Draganjac, M.; Ruffing, C. J.; Rauchfuss, T. B. Organometallics 1985, 4, 1909. (f) Fischer, E. O.; Oefele, K. Chem. Ber. 1958, 91, 2395. (g) Bailey, M. F.; Dahl, L. F. Inorg. Chem. 1965, 4, 1306. Singer, H. J. Organomet. Chem. 1967, 9, 135. (h) Lee, C. C.; Iqbal, M.; Gill, U. S.; Southerland, R. G. J. Organomet. Chem. 1985, 288, 89. (i) Huckett, S. C.; Angelici, R. J. Organometallics, accepted for publication. (j) Sanchez-Delgado, R. A.; Marquez-Silva, R. L.; Puga, J.; Tiripicchio, A.; Tiripicchio, C. M. J. Organomet. Chem. 1986, 316, C35.

4. Eekchof, J. H.; Hogeveen, H.; Kellogg, R. M. J. Organomet. Chem. 1978, 161, 361.

5. Sauer, N. N.; Angelici, R. J. Inorg. Chem. 1987, 26, 2160.

6. Lesch, D. A.; Richardson, J. S.; Jacobson, R. A.; Angelici, R. J. J. Am. Chem. Soc. 1984, 106, 2901.

7. Goodrich, J. D.; Nickias, P. N.; Selegue, J. P. Inorg. Chem. 1987, 26, 3424.

8. (a) Fischer, E. O.; Goodwin, H. A.; Kreiter, C. G.; Simmons, H. D., Jr.; Sonogashira, K.; Wild, S. B. J. Organomet. Chem. 1968, 14, 359. (b) Lumbroso, H.; Segard, C.; Roques, B. J. Organomet. Chem. 1973, 61, 249. (c) Hucket, S. C.; Miller, L. L., Jacobson, R. A.; Angelici, R. J. Organometallics 1988, 7, 686.

9. Lappert, M. F.; Shaw, D. B.; MaLaughin, G. M. J. Chem. Soc., Dalton Trans. 1979, 427.

10. Cetinkaya, B.; Hitchcock, B. P.; Lappert, M. F.; Pye, P. L. J. Chem. Soc., Chem. Comm. 1975, 683.

11. (a) Cetinkaya, B.; Hitchcock, P. B.; Lappert, M. F.; Pye, P. L.; Shaw, D. B. J. Chem. Soc., Dalton Trans. 1979, 434. (b) Glavee, G. N., Angelici, R. J., unpublished work. (c) Abel, E. W.; Kite, K.; Williams, B. L. J. Chem. Soc., Dalton Trans. 1983, 1017.

12. Weiner, M. A.; Lattman, M. Inorg. Chem. 1978, 17, 1084.

13. Hornig, H.; Walther, E.; Schubert, U. Organometallics 1985, 4, 1905.

14. (a) Raubenheimer, H. G.; Fischer, E. O.; Schubert, U.; Krüger, C.; Tsay, Y. Angew. Chem., Int. Ed. Engl. 1981, 20, 1055. (b) Raubenheimer, H. G.; Kruger, G. J.; Lombard, A. van A.; Linford, L.; Viljoen, J. C. Organometallics 1985, 4, 275.

15. Hachgenei, J. W.; Angelici, R. J. J. Organomet. Chem., accepted for publication.

16. Abel, E. W.; Bhargava, S. K.; Kite, K.; Orrell, K. G.; Sik, V.; Williams, B. L. Polyhedron, 1982, 1, 289.

17. (a) Davidson, J. L.; Shiralian, M.; Manglovic-Muir, L.; Muir, K. N. J. Chem. Soc., Chem. Comm. 1979, 30. (b) Guerchais, J. E.; Floch-Perennou, F. L.; Petillon, F. Y.; Keith, A. N.; Monojlovic-Muir, L.; Muir, K. W.; Sharp, D. W. A. J. Chem. Soc., Chem. Comm. 1979, 410. (c) Rumin, R.; Manojlovi-Muir, L.; Muir, K. W.; Petillon, F. Y. Organometallics 1988, 7, 375.

18. Osakada, K.; Matsumato, K.; Yamamoto, T.; Yamamoto, A. Organometallics 1985, 4, 857.

19. Rausch, M. D.; Criswell, T. R.; Ignalowicz, A. K. J. Organomet. Chem. 1968, 13, 419.

20. (a) Nesmeyanov, A. N.; Anisimov, K. N.; Kolobova, N. E. Izv. Akad. Nauk SSSR, Ser. Khim. 1964, 2247. (b) Hurd, C. D. Thiophene Chemistry, Intra-Science Research Foundation: Santa Monica, 1969, 4, pp 193.

21. (a) Kolobova, N. E.; Goncharenko, L. O. *Izv. Akad. Nauk SSSR, Ser. Khim.* 1981, *3*, 667. (b) Nesmeyanov, A. N.; Kolobova, N. E.; Goncharenko, L. V.; Anisimor, K. N. *Izv. Akad. Nauk SSSR, Ser. Khim.* 1976, *1*, 153. (c) Nesmeyanov, A. N.; Kolobova, N. E.; Goncharenko, L. V.; Anisimor, K. N. *Izv. Akad. Nauk SSSR, Ser. Khim.* 1976, *5* 1179.

22. Blum, J.; Kraus, S.; Pickholtz, Y. *J. Organomet. Chem.* 1971, *33*, 227.

23. (a) Larock, R. C.; Hershberger, S. S. *J. Org. Chem.* 1980, *45*, 3840. (b) Larock, R. C.; Hershberger, S. S. *Tet. Lett.* 1981, *22*, 2446. (c) Larock, R. C.; Narayanan, K.; Hershberger, S. S. *J. Org. Chem.* 1983, *48*, 4377. (d) Larock, R. C.; Hershberger, S. S. *J. Organomet. Chem.* 1982, *225*, 31. (e) Larock, R. C.; Bernhardt, J. C. *J. Org. Chem.* 1977, *42*, 1680.

24. Wada, M.; Kusabe, K.; Oguro, K. *Inorg. Chem.* 1977, *16*, 446.

25. (a) Klingstedt, T.; Frejd, T. *Organometallics* 1983, *2*, 598. (b) Frejd, T.; Klingstedt, T. *Synthesis* 1987, *1*, 40.

26. Izumi, T.; Iino, T.; Kasahara, A. *Bull. Chem. Soc. Jpn.* 1973, *46*, 2251.

27. Neghishi, E.; Luo, F.; Frisbee, R.; Matsushita, H. *Heterocycles* 1982, *18*, 117.

28. (a) Bumagin, N. A.; Kalinovski, I. O.; Beletskaya, I. P. *Izv. Akad. Nauk SSSR, Ser. Khim.* 1983, *7*, 1619. (b) Bumagin, N. A.; Kalinovski, I. O.; Beletskaya, I. P. *Izv. Akad. Nauk SSSR, Ser. Khim.* 1984, *10*, 2347. (c) Bumagin, N. A.; Kalinovski, I. O.; Beletskaya, I. P. *Izv. Akad. Nauk SSSR, Ser. Khim.* 1984, *11*, 2586.

29. Rudakov, E. S.; Ignatenko, V. M. *React. Kinet. Catal. Lett.* 1983, *22*, 75.

30. Mantovani, A.; Calligaro, L.; Pasquetto, A. *Inorg. Chim. Acta* 1983, *76*, L145.

31. Eaborn, C.; Odell, K. J.; Pidcock, A. *J. Organomet. Chem.* 1978, *146*, 17.

32. (a) Eaborn, C.; Odell, K. J.; Pidcock, A. *J. Chem. Soc., Dalton Trans.* 1978, 357. (b) Eaborn, C. Odell, K. J.; Pidcock, A. *J. Chem. Soc., Dalton Trans.* 1979, 758.

33. Almeida, J. F.; Pidcock, A. J. *J. Organomet. Chem.* 1981, *208*, 273.

34. (a) Westmijze, H.; Meijer, J.; Vermeer, P. Tetrahedron Lett. 1975, 33, 2923. (b) van den Hoek, W. G. M.; Kroon, J.; Kleijn, H.; Westmijze, H.; Vermeer, P.; Bos, H. J. T. J. Chem. Soc., Perkin II 1979, 423.

35. Smith Jr., M. R.; Gilman, H. J. Organomet. Chem. 1972, 42, 1.

36. (a) Rahman, M. T.; Gilman, H. J. Indian Chem. Soc. 1979, LVI, 299. (b) Rahman, M. T.; Gilman, H. J. Indian Chem. Soc. 1979, LVI, 346.

37. (a) Nilsson, M.; Ullenius, C. Acta Chem. Scand. 1970, 24, 2379. (b) Baldwin, L. J.; Sudabeh, S.; Castle, R. N.; Lee, M. L. J. Heterocyclic Chem. 1985, 22, 1667. (c) Nilsson, M.; Ullenius, C. Acta Chem. Scand. 1971, 25, 2428.

38. (a) Spagnolo, P.; Zanirato, P. J. Org. Chem. 1982, 47, 3177. (b) Gjos, N.; Gronowitz, S. Acta Chem. Scand. 1971, 2S, 2596. (c) Liljefors, S.; Gronowitz, S. Chem. Scripta 1980, 15, 102.

39. (a) Lipshutz, B. H.; Parker, D. A.; Kozlowski, J. A.; Nguyen, S. L. Tetrahedron Lett. 1984, 25, 5962. (b) Lipshutz, B. H.; Kotsuki, H.; Lew, W. Tetrahedron Lett. 1986, 27, 4825.

40. Lindsledt, E.; Nilsson, M. Acta Chem. Scand. 1986, B40, 466.

41. Sheverdina, N. I.; Paleeva, I. E.; Abramova, L. V.; Yakovleva, V. S.; Kocheshlov, L. A. Izv. Akad. Nauk SSSR, Ser. Khim. 1967, 5, 1077.

42. Shererdina, N. I.; Paleeva, I. E.; Zaitseva, N. A.; Abramova, L. V.; Yakovleva, V. S.; Kocheshkov, K. A. Izv. Akad. Nauk SSSR, Ser. Khim. 1967, 3, 582.

43. Sheverdina, N. I.; Paleeva, I. E.; Kocheshkov, K. A. Izv. Akad. Nauk SSSR, Ser. Khim. 1967, 3, 587.

44. Gronowitz, S.; Hornfeldt, A.-B.; Kristjansson, V.; Musil, T. Chemica Scripta 1986, 26, 305.

45. Bumagin, N. A.; Kasatlain, A. N.; Beletskaya, I. P. Izv. Akad. Nauk SSSR, Ser. Khim. 1984, 8, 1858.

46. Paleeva, I. E.; Sheverdina, N. I.; Delinskaya, E. D.; Kocheshkov, K. A. Izv. Akad. Nauk SSSR, Ser. Khim. 1967, 5, 1083.

47. Hartough, H. D. The Chemistry of Heterocyclic Compounds, Thiophene and its Derivatives, Interscience Publishers Inc.: New York, 1952, pp 444-453.

48. (a) Steinkopf, W. Ann. 1920, 23, 424. (b) Steinkopf, W. Die Chemie des Thiophens, Steinkopf: Dresden, 1941, pp 108-122.

49. Grdenic, D.; Kamenar, B.; Zezelj, V. Acta Crystallogr. 1979, B35, 1889.

50. (a) Obafemi, C. A. J. Organomet. Chem. 1981, 219, 1. (b) Obafemi, C. A. Phosphorus and Sulfur, 1983, 17, 91.

51. Bumagin, N. A.; Kalinovskii, J. O.; Beletskaya, I. P. Khim. Geterotsik. 1983, 11, 1467.

52. Larock, R. C.; Leach, D. R. Organometallics 1982, 1, 74.

53. Kretchmer, R. A.; Glowinski, R. J. Org. Chem. 1976, 41, 2661.

54. Larock, R. C.; Leach, D. R.; Bjorge, S. M. J. Org. Chem. 1986, 51, 5221.

55. Roling, P. V.; Roling, S. B.; Rausch, M. D. Synth. Inorg. Met. Org. Chem. 1971, 1, 97.

56. Halpern, Y.; Garti, N. J. Organomet. Chem. 1975, 88, 315.

57. Paleeva, I. E.; Sheverdina, N. I.; Kocheshkov, K. A. Zh. Obsh. Khim. 1974, 44, 1135.

58. Butin, K. P.; Yudin, L. G.; Pavlyuchenko, I. P.; Beletskaya, I. P.; Kost, A. N. Zh. Org. Khim. 1971, 7, 2586.

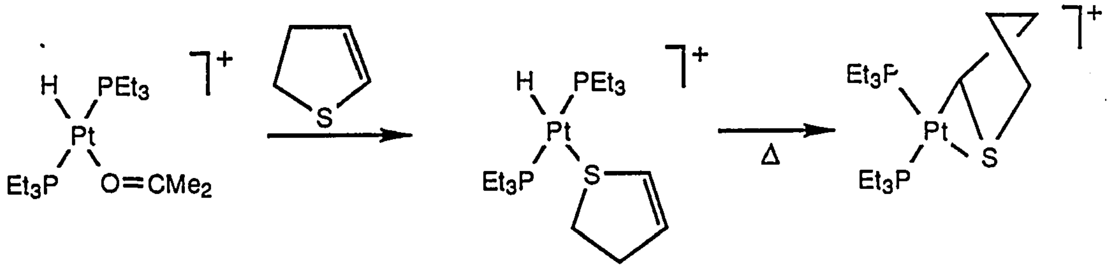
59. (a) Barbieri, G.; Taddei, F. J. Chem. Soc., Perkin II 1972, 1323. (b) Doddrell, D.; Lewis, K. G.; Mulquiney, C. E.; Adock, W.; Kitching, W.; Bullpit, M. Aust. J. Chem. 1974, 27, 417. (c) Evans, D. F.; Ridout, P. M.; Wharf, I. J. Chem. Soc. (A) 1968, 2127. (d) Bulman, M. Tetrahedron 1969, 25, 1433.

60. (a) Hartough, H. D.; Meisel, S. L. "The Chemistry of Heterocyclic Compounds. Compounds with Condensed Thiophene Rings," Interscience Publishers, Inc.: New York, pp 154. (b) Miller, J. S.; Epstein, A. J. Ann. N. Y. Acad. Sci. 1978, 313, 79.

SECTION II. INSERTION OF 2,3-DIHYDROTHIOPHENE INTO PLATINUM AND OSMIUM HYDRIDES: A MODEL FOR REACTIONS OCCURRING DURING THIOPHENE HYDRODESULFURIZATION

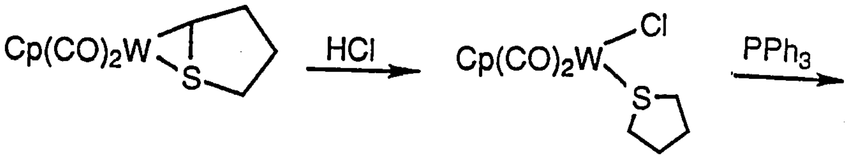
ABSTRACT

Reaction of HPt(acetone)$(PEt_3)_2^+$ with 2,3-DHT results in the formation of the sulfur-coordinated 2,3-DHT compound I. Subsequent rearrangement by slow insertion of the 2,3-DHT olefin into the Pt-H bond gives II, which was characterized by an X-ray diffraction study. Compound II reacts with H_2 at 150 °C to yield butane. A tungsten analog (VIIIa) of II is prepared from the reaction of $CpW(CO)_3^-$ with 2-chlorotetrahydrothiophene followed by photolytic decarbonylation. The reaction of VIIIa with HCl yields an unstable tetrahydrothiophene (THT) complex IX. These reactions serve as models for the conversion of thiophene to THT and C_4 products. Insertion of 2,3-DHT into a metal cluster hydride is achieved



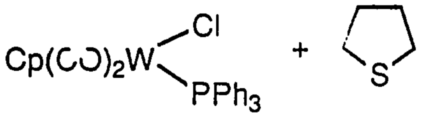
I

II

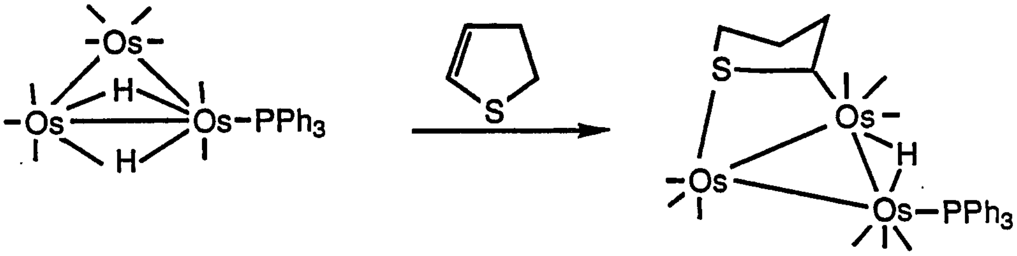


VIIIa

IX



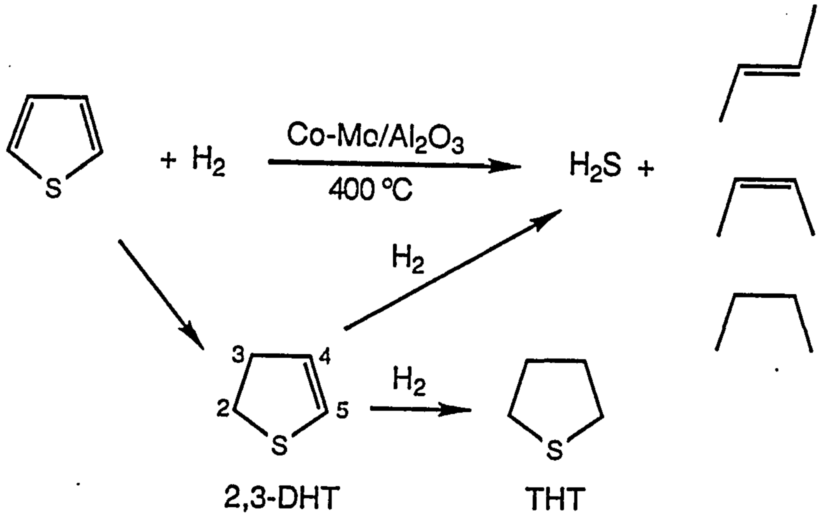
in the reaction of 2,3-DHT with $H_2Os_3(CO)_9PPh_3$ to form X whose structure was established by X-ray diffraction.



X

INTRODUCTION

Catalytic hydrodesulfurization (HDS), a process which is used to remove sulfur from thiophene and other sulfur-containing organics in crude oil and coal liquids is carried out over a sulfided Co-Mo/Al_2O_3 catalyst. Of the many organosulfur compounds present in petroleum feedstocks, thiophene has been studied most intensively as a representative component which is difficult to desulfurize. Numerous investigations have been directed at understanding how thiophene undergoes HDS on heterogeneous catalysts.[1] Dihydrothiophene (2,3-DHT) has been proposed as an intermediate in the HDS of thiophene (eq. 1) by investigators;[2] this proposal is supported by our model HDS studies.[1b,c] Catalytic reactor studies[3] of 2,3-DHT show that it undergoes rapid desulfurization and is, therefore, a plausible intermediate in thiophene HDS. However, considerable hydrogenation to tetrahydrothiophene (THT) also occurs (eq. 1). This latter reaction may occur by olefin insertion, a reaction that may be particularly favorable because of the coordinating ability of the



(1)

sulfur in 2,3-DHT,[4] which brings the olefinic group near the catalyst surface.

It was, therefore, of interest to explore the reactivity of 2,3-DHT with metal hydride complexes to see if hydrogen migration to the partly hydrogenated thiophene occurs. The results in this paper demonstrate that insertion of 2,3-DHT into metal hydride bonds occurs readily to give metallathiacyclopropane complexes which upon protonation yield tetrahydrothiophene.

EXPERIMENTAL SECTION

General Procedures

All reactions were carried out under an atmosphere of prepurified N_2 at room temperature using standard inert atmosphere and Schlenk techniques unless otherwise stated.[5] Tetrahydrofuran (THF) and Et_2O were distilled under N_2 from Na/benzophenone. Hexanes, MeCN and CH_2Cl_2 were distilled from CaH_2 under N_2. Acetone was purged with N_2 and dried over molecular sieves for several weeks. Benzene was distilled from $LiAlH_4$ under N_2 and stored over Na metal.

Infrared spectra were obtained using a Perkin Elmer 681 spectrophotometer; the spectra were referenced to the 1944.0 cm^{-1} band of polystyrene. The ^1H and $^{13}C\{H\}$ NMR data were obtained on a Nicolet NT-300 MHz spectrometer using Me_4Si as the internal reference. The ^{31}P and temperature dependent NMR spectra were recorded on a Bruker WM 300 MHz instrument. The ^{31}P signals which are upfield of the H_3PO_4 external reference are given as negative values. The ^{195}Pt NMR spectra were obtained on a Bruker WM 200 MHz instrument. Chemical shifts were measured relative to 0.2 M K_2PtCl_4 (in 0.4 M KCl/D_2O), which was used as an external reference (-1627.0 ppm vs. 0.2 M K_2PtCl_6 in H_2O).[6] Electron impact mass spectra (EIMS) and GC-MS spectra were obtained on a Finnigan 4000. Fast atom bombardment (FAB, glycerol matrix) mass spectra were obtained using a Kratos MS-50 spectrometer.

Diphenylmethylphosphine and PEt_3 were obtained from Strem Chemicals and used without further purification. Triphenylphosphine was used as received from SCM Chemicals. Adsorption (80-200 mesh) alumina was used as received from Fischer Scientific.

Photochemical reactions were carried out with a 254 nm light in a quartz Schlenk tube equipped with a cooling probe using a reactor obtained from Bradford Scientific, Inc., Marblehead, MA.

The compounds trans-$HPt(PEt_3)_2Cl$,[7] trans-$HPt(PMePh_2)_2Cl$,[8], trans-$HPt(PPh_3)_2Cl$,[9] $H_2Os_3(CO)_{10}$,[10] and $H_2Os_3(CO)_9(PPh_3)$,[11] were prepared using reported routes. The compounds $[HPt(acetone)(PR_3)_2]^+$ (PR_3 = PEt_3, $PMePh_2$, PPh_3) were generated as described by Clark and Jablonski.[12] The X-ray crystal structure analysis data are summarized in Table 4. In addition to the data given below, the compounds were characterized by their IR, NMR and mass spectra (Tables 1, 2, 3).

Reaction of $[HPt(acetone)(PR_3)_2]^+$ with 2,3-DHT

An acetone (15 mL) solution of $HPt(PEt_3)_2Cl$ (0.21 g, 0.48 mmol) was added to an acetone (15 mL) solution of $AgPF_6$ (0.12 g, 0.48 mmol). This mixture was stirred for 15 min and the AgCl formed was removed by filtration through a medium glass frit. The filtrate was then treated with 2,3-DHT[4] (0.20 M solution in pentane 2.5 mL, 0.50 mmol) and the mixture was stirred for 2 h. The volume of the solution was reduced to ~5 mL, layered with Et_2O (25 mL) and stored at -20 °C for 3 days. The white needle-like solid, $[HPt(PEt_3)_2(2,3\text{-DHT})]PF_6$, I, (0.19 g, 83%) was filtered off and dried. Anal. Calcd for $C_{16}H_{37}F_6P_3PtS$: C, 28.96; H, 5.62; S, 4.83. Found: C, 29.01; H, 6.02; S, 5.08. ^{13}C NMR ($CDCl_3$): δ 133.82 (m, C5), 121.35 (m, C4), 38.04 and 34.95 (C2, C3), 18.70 [m, $P(\underline{C}H_2CH_3)_3$], 8.60 [m, $P(CH_2\underline{C}H_3)$]. ^{31}P NMR ($CDCl_3$): δ 20.11 (J_{PtP} = 2565 Hz). ^{195}Pt NMR

Table 1. Infrared spectra of the complexes in hexanes

Complex	ν(CO), cm^{-1}
$[HPt(PEt_3)_2(2,3\text{-DHT})]PF_6$, I	
$[Pt(PEt_3)_2(DHT{\bullet}H)]PF_6$, II	
$[Pt(PPh_3)_2(DHT{\bullet}H)]PF_6$, III	
$[Pt(PPh_2Me)_2(DHT{\bullet}H)]PF_6$, IV	
$Cp(CO)_3W(DHT{\bullet}H)$, Va	2030 (ms), 1940 (s), 1927 (s)
$Cp(CO)_3Mo(DHT{\bullet}H)$, Vb	2033 (ms), 1951 (s), 1935 (s)
$Cp(CO)_2Fe(DHT{\bullet}H)$, VI	2020 (s), 1959 (s)
$[Cp(CO)_2Fe(DHT{\bullet}H{\bullet}Me]PF_6$, VII[a]	2040 (s), 1978 (s)
$Cp(CO)_2W(\eta^2\text{-}DHT{\bullet}H)$, VIIIa	1936 (s), 1849 (s)
$Cp(CO)_2Mo(\eta^2\text{-}DHT{\bullet}H)$, VIIIb	1944 (s), 1858 (s)
$Cp(CO)_2W(THT)Cl$, IX[a]	1954 (s), 1851 (s),
$HOs_3(CO)_9(PPh_3)(DHT{\bullet}H)$, X	2090 (mw), 2052 (s), 2030 (vs), 2009 (s), 1991 (ms), 1969 (s), 1965 (m, sh), 1955 (m), 1944 (w)
$HOs_3(CO)_{10}(DHT{\bullet}H)$, XI	2090 (w), 2082 (m), 2070 (s), 2060 (ms), 2047 (w), 2034(s), 2014 (m), 1991 (mw)

[a] In CH_2Cl_2 solvent.

Table 2. ^{1}H NMR data for the complexes in $CDCl_3$

	Hydrothiophene Ligand Resonances	Other Resonances
2,3-DHT[a]	3.22 (t, 2H, H2), 2.74(tt, 2H, H3), 5.63(dt, 1H, H4), 6.16(dt, 1H, H5)	
I	3.66(m, 2H, H2[a]), 3.08(m, 2H, H3), 6.14(m, 1H, H4), 6.27(m, 1H, H5)	1.93[m, 12H, $P(\underline{CH_2}CH_3)_3$], 1.14[m, 18H, $P(CH_2\underline{CH_3})_3$], -13.32 (9 lines, 1H, Pt-$\underline{H}$)[b]
II	3.70(m, 1H, H2[c]), 3.32(m, 1H, $H5_{exo}$), 3.18(m, 1H, $H5_{endo}$), 2.82(m, 1H, $H3_{endo}$), 2.79(m, 1H, $H3_{exo}$), 2.00(m, 1H, $H4_{exo}$), 1.74(m, 1H, $H4_{endo}$)	1.96(m, 12H, $P(\underline{CH_2}CH_3)_3$, 1.10(m, 18H, $P(CH_2\underline{CH_3})_3$
III[d]	3.74(m, 1H, H2[c]), 2.83(m, 1H, $H5_{exo}$), 2.56(m, 1H, $H3_{endo}$) 2.19(m, 1H, $H3_{exo}$), 1.83(m, 2H, $H5_{endo}$ and $H4_{exo}$) 1.53(m, 1H, $H4_{endo}$)	7.32(m, 15H, PPh_3)
Va[e]	3.35(dd,[f] 1H, H2[g]), 2.66(m, 2H, $H5_{\text{exo and endo}}$), 2.54(m, 1H, $H3_{exo}$), 1.86(m, 1H, $H4_{exo}$), 1.70(m, 1H, $H3_{endo}$), 1.38(m, 1H, $H4_{endo}$)	4.76(s, 5H, Cp)
Vb[e]	3.47(dd,[h] 1H, H2[g]), 2.68(m, 2H, $H5_{\text{exo and endo}}$),	4.76(s, 5H, Cp)

2.59(m, 1H, H3_{exo}), 1.90(m, 1H, H4_{exo}),
1.74(m, 1H, H3_{endo}), 1.35(m, 1H, H4_{endo})

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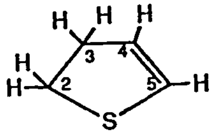
[a] 

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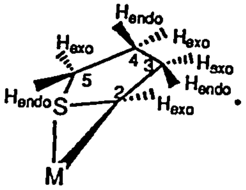
[b] J_{PH} = 14.4 Hz, J_{PtH} = 1242 Hz.

[c] 

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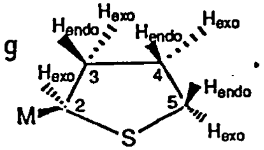
[d] Assignment made by comparison with II.

[e] In C_6D_6.

[f] J = 4.5 Hz, J = 11.8 Hz.

[g] 

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[h] J = 4.8 Hz, J = 11.6 Hz.

Table 2. Continued

	Hydrothiophene Ligand Resonances	Other Resonances
VI[e]	3.47(dd[i], 1H, H2[g]), 2.71(m, 2H, H5$_{\text{exo and endo}}$), 2.41(m, 1H, H3$_{\text{exo}}$), 1.97(m, 1H, H4$_{\text{exo}}$), 1.60(m, 1H, H3$_{\text{endo}}$) 1.41(m, 1H, H4$_{\text{endo}}$)	4.72(s, 5H, Cp)
VII	1.7-3.6[j]	5.17, 5.09(10:6, Cp) 2.54, 2.79 (10:6, Me)
VIIIa[e]	3.56(d[k], 1H, H2[c]), 2.49(dd[l], 1H, H5$_{\text{endo}}$), 1.95(m, 2H, H3$_{\text{endo}}$ and H5$_{\text{exo}}$) 1.56(m, 1H, H3$_{\text{exo}}$), 1.32(m, 1H, H4$_{\text{exo}}$), 0.97(m, 1H, H4$_{\text{endo}}$)	4.73(s, 5H, Cp)
VIIIb[e]	3.67(d[m], 1H, H2[c]), 2.46(dd[n], 1H, H5$_{\text{endo}}$), 1.87 (m, 2H,H3$_{\text{endo}}$ and H5$_{\text{exo}}$), 1.64(m, 1H, H3$_{\text{exo}}$), 1.24(m, broad, 1H, H4$_{\text{exo}}$), 0.87(m, 1H, H4$_{\text{endo}}$)	4.73(s, 5H, Cp)
IX[o]	3.16(m, 4H), 3.08 (m, 4H)	5.32(s, 5H, Cp)
X	3.18(m, 1H, H2[p]), 2.98(m, 1H, H5$_{\text{exo}}$), 2.82(m, 1H, H5$_{\text{endo}}$), 2.51(m, 2H, H3$_{\text{endo}}$ and H4$_{\text{endo}}$), 2.34 (m, 1H, H3$_{\text{exo}}$), 1.89(m, 1H, H4$_{\text{exo}}$)	7.49(m, 15H, PPh_3) -16.50[q](s, broad, 1H, Os-H)

XI[e,r]	3.00 (m, 1H, H2[p]), 2.68(m, 1H, $H5_{exo}$), 2.46(m, 1H, $H5_{endo}$) 2.33(m, 2H, $H3_{endo}$ and $H4_{endo}$), 1.92(m, 1H, $H3_{exo}$), 1.77(m, 1H, $H4_{exo}$)	-16.56(s, 1H, Os-$\underline{\mathrm{H}}$)

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[i] J = 4.6 Hz, J = 10.9 Hz.

[j] Two isomers of **VII** are apparent from the Cp and Me signals. The signals corresponding to the methylene protons, however, are indistinguishable.

[k] J = 5.6 Hz.

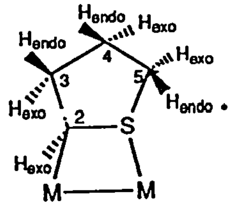
[l] J = 12.9 Hz, J = 6.3 Hz.

[m] J = 5.9 Hz.

[n] J = 13.5 Hz, J = 6.3 Hz.

[o] In CD_2Cl_2.

[p]



[q] Observed as two doublets at -54°C, w -16.48 J_{PH} = 2.6 Hz, -16.52 J_{PH} = 2.6 Hz.

[r] By comparison to **X**.

Table 3. Mass spectra of the complexes

I[a]	518(M^+), 489(M^+-Et), 431[M^+-(DHT+H), base peak], 399[M^+-(PEt_3+H)], 313($PtPEt_3^+$)
II[a]	518(M^+, base peak), 489(M^+-Et), 431[M^+-(DHT+H)], 399[M^+-(PEt_3+H)], 313($PtPEt_3^+$)
III[a]	806(M^+, base peak), 719[M^+-(DHT+H)], 457[M^+-(DHT+H+PPh_3)]
IV[a]	682(M^+, base peak), 595[M-(DHT+H)], 481[M^+-($PMePh_2$+H)], 395($PtPMePh_2^+$)
Vb	306(M^+-CO), 278(M^+-2CO), 248[M^+-(2CO+2H)], 220[M^+-(3CO+2H)], 87(DHT•H^+, base peak)
VI	236(M^+-CO), 208(M^+-2CO), 121($CpFe^+$), 87(DHT•H^+, base peak)
VII[a]	279(M^+, base peak), 223(M^+-2CO), 177($CpFe(CO)_2^+$), 102(DHT•H•Me)
VIIIa	392(M^+, base peak), 364(M^+-CO), 336(M^+-2CO), 87(DHT•H^+)
VIIIb	306(M^+), 278(M^+-CO), 248[M^+-(2CO+2H), base peak], 220($CpMo(CO)_2H^+$), 87(DHT•H^+)
X[a]	1174 (M^+, base peak), 1146 (M^+-CO), 1118(M^+-2CO), 1090(M^+-3CO)
XI	940(M^+), 912(M-CO), 882(M^+-2CO), 856(M^+-3CO), 828(M^+-4CO), 800(M^+-5CO), 86(DHT, base peak)

[a] By FAB.

Table 4. Summary of crystal data for $[Pt(PEt_3)_2(DHT{\bullet}H)]PF_6$, II, and $HOs_3(CO)_9(PPh_3)(DHT{\bullet}H)$, X

	II	X
Formula	$C_{16}H_{37}F_6P_3PtS$	$C_{31}H_{23}O_9Os_3PS$
Formula weight	663.59	1172.51
Space group	$P2_{1/n}$	$P2_{1/c}$
a, Å	8.0162(9)	9.474(2)
b, Å	35.246(8)	12.752(1)
c, Å	17.811(4)	27.020(3)
β, deg	90.82(1)	91.98
V, $Å^3$	5032(3)	3262(1)
Z	4	4
d_{calc}, g/cm^3	1.749	2.436
Crystal size, mm	0.25 x 0.27 x 0.15	0.3 x 0.3 x 0.2
$\mu(MoK_\alpha)$, cm^{-1}	59.46	118.4
Diffractometer	Enraf-Nonius CAD4 graphite monochromator MoK_α (λ = 0.71073A)	Enraf-Nonius CAD4 graphite monochromator MoK_α (λ = 0.71073A)
Orientation reflections, number, range (2θ)	17, 25-32°	25
Temperature, °C	22±1	22±1
Scan method	θ-2θ	θ-2θ
Data col. range, 2θ, deg	0-45	0-50

Table 4. Continued

	II	X
No. unique data, total:	5421	5728
with $F_o^2 > 3\sigma(F_o^2)$:	3933	4422
No. of parameters refined	482	406
Trans. factors, max., min. (psi-scans)	0.999, 0.752	0.999, 0.428
R[a]	0.0480	0.0277
R_w[b]	0.0685	0.0394
Quality-of-fit indicator[c]	2.44	1.12
Largest shift/esd, final cycle	0.02	<0.01
Largest peak, e/Å^3	1.03	0.97

[a] $R = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$.

[b] $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

[c] Quality-of-fit $= [(\Sigma w|F_o| - |F_c|)^2 / (N_{obs} - N_{parameters})]^{1/2}$.

$(CDCl_3)$ δ -3381.3 (pseudo dt, J_{PPt} = 59.3 Hz, J_{HPt} = 28.8 Hz). Compound I is stable in air and can be handled at ambient temperature for short periods of time. No changes were observed in I when stored at -20 °C for 9 months. However, when I was stored at room temperature it slowly became pale yellow. The yellow solid was found to be $[Pt(PEt_3)_2DHT{\bullet}H)]PF_6$, II. The complete conversion of I to II occurred over a period of three months in the solid state at room temperature. In solution at ambient temperature I is converted to II in a month and at 60 °C, I goes to II in one week. The conversion of I to II was monitored by ^1H and ^{195}Pt NMR at 60 °C and ^{31}P NMR at ambient temperature. Spectral data for II. ^{13}C NMR $(CDCl_3)$: δ 64.07 (d, J_{PtC} = 339 Hz, $J_{transPC}$ = 61.3 Hz,C2), [41.17 (pseudo triplet), 37.61 (s), 31.58 (J_{PtC} = 29.1 Hz) C3, C4, C5]. ^{31}P NMR $(CDCl_3)$: δ 15.75 (J_{PtP} = 2796 Hz), 17.01 (J_{PtP} = 4339 Hz). ^{195}Pt NMR $(CDCl_3)$: δ -3387.4 (pseudo dd, J_{PPt} = 4330 Hz, J_{PPt} = 2796 Hz).

As described for $HPt(PEt_3)_2Cl$, an acetone (20 mL) solution of $HPt(PPh_3)_2Cl$ (0.15 g, 0.20 mmol) was treated with an acetone (10 mL) solution of $AgPF_6$ (0.053 g, 0.21 mmol). After stirring for 15 min, the AgCl formed was filtered off through a medium frit. The filtrate was treated with 1.5 equivalents (0.30 mmol) of a 0.28 M pentane solution of 2,3-DHT. The mixture was stirred for 2 h. The resulting pale yellow solution was reduced in volume in vacuo to ~5 mL and layered with Et_2O (~25 mL) and stored at -20 °C for 3 days. Compound $[Pt(PPh_3)_2(DHT{\bullet}H)]PF_6$, III (0.12 g, 65%) was filtered off and dried. Anal. Calcd for $C_{40}H_{37}F_6P_3PtS$: C, 50.48; H, 3.92. Found: C, 50.73; H, 4.51.

Similarly an acetone (20 mL) solution of $HPt(PMePh_2)_2Cl$ (0.16, 0.25 mmol) was treated with $AgPF_6$ (0.058 g, 0.23 mmol) for 15 min. After filtration through a medium frit, a pentane solution of 2,3-DHT (3.8 mL, 0.15 M, 0.57 mmol) was added, and the solution was stirred for 2 h. Upon work up, as described for the PPh_3 analog, $[Pt(PMePh_2)_2(DHT{\bullet}H)]PF_6$, IV (0.097 g, 47%) was obtained.

X-ray Structure Determination of $[Pt(PEt_3)_2(DHT{\bullet}H)]PF_6$, II

A colorless, crystal of $[Pt(PEt_3)_2(DHT{\bullet}H)]PF_6$, formed by diffusion of Et_2O into a $CDCl_3$ solution at -20 °C, was mounted in a glass fiber in a random orientation. Cell constants and an orientation matrix for data collection were obtained from least squares refinement using the setting angles of 17 reflections in the range $25° < 2\theta < 34°$.

A total of 6089 reflections were collected in the +h, +k, ±l quadrant, of which 5421 were unique and not systematically absent. As a check on crystal and electronic stability three representative reflections were measured every 60 min. The total loss in intensity in the standards was 18.1%. A decay correction was therefore applied to the data.

Lorentz and polarization corrections were applied to the data. The linear absorption coefficient is 59.46 cm^{-1} for MoK_α radiation. An empirical absorption correction, based on a series of psi-scans, was applied to the data. Intensities of equivalent reflections were averaged. The agreement factors for the averaging of 847 observed and accepted reflections were 1.7% based on intensity and 1.4% based on F_o.

The positions of the two independent Pt cations in a unit cell were given by direct methods.[13a] Following isotropic refinement of the Pt atoms, the P and S atoms in the coordination sphere were placed based on a difference Fourier map. The remainder of the non-hydrogen atoms were then located via subsequent cycles of least-squares refinement followed by difference Fourier maps. While one of the PF_6^- ions behaved normally, the second could not be successfully refined as the expected seven-atom model. Peaks in the difference Fourier syntheses persisted which seemed to define a second significant orientation of the PF_6 unit. A model was, therefore, developed in which two F_6 octahedrons were refined about the single phosphorus labeled P(6). For the two sets of F atoms [labeled F(7) - F(12) and F(7') - F(12')] the expected P-F and F-F distances were added to the refinement as observations. Refinement was then carried out with the further requirement that the sum of the occupancies of the two F_6 groups equal 1. These groups so constrained refined to 58.0% occupancy in the major orientation, and 42.0% occupancy in the minor orientation. Hydrogen atom positions were calculated and added to the structure but were not refined. The atomic positional parameters are given in Table 5. The atoms Pt(1), S(1), P(1), P(2), P(5), F(1) - F(6) and C(1) - C(16) correspond to one independent molecule in the unit cell. The other atoms correspond to the other molecule of II in the unit cell.

Refinement of the structure was carried out using the SHELX76 package.[13] Scattering factors were taken from Cromer and Waber.[14] Anomalous dispersion effects were included in F_c;[15] the values for f' and f" were those of Cromer.[16] Only those reflections having intensities greater than 3.0 times their standard deviation were used in the refinements.

Table 5. Table of positional parameters and their estimated standard deviations for $[Pt(PEt_3)_2(DHT \cdot H)]PF_6$, II

Atom[a]	x	y	z	$B(A^2)$[b]
Pt(1)	0.67560(9)	0.20692(2)	0.23616(3)	3.36(2)
S(1)	0.5140(7)	0.2575(2)	0.2772(3)	6.1(2)
P(1)	0.7976(7)	0.1507(1)	0.2578(3)	4.5(1)
P(2)	0.7265(6)	0.2159(1)	0.1103(2)	3.7(1)
C(1)	0.793(3)	0.1363(5)	0.357(1)	6.0(6)
C(2)	0.572(2)	0.2212(5)	0.3416(7)	3.8(5)
C(3)	0.691(3)	0.2381(7)	0.401(1)	7.2(7)
C(4)	0.793(3)	0.2697(6)	0.357(1)	7.3(7)
C(5)	0.665(3)	0.2925(5)	0.312(1)	6.5(6)
C(6)	0.855(3)	0.0960(6)	0.375(2)	9.5(9)
C(7)	0.710(2)	0.1738(5)	0.0477(9)	5.2(5)
C(8)	0.734(3)	0.1845(7)	-0.038(1)	7.6(7)
C(9)	0.576(3)	0.2489(5)	0.070(1)	4.6(5)
C(10)	0.398(3)	0.2336(6)	0.079(1)	6.4(7)
C(11)	0.925(2)	0.2372(6)	0.088(1)	6.7(7)
C(12)	0.969(3)	0.2710(6)	0.144(1)	7.4(7)
C(13)	0.685(3)	0.1098(5)	0.208(1)	6.4(7)
C(14)	0.505(3)	0.1115(6)	0.223(1)	8.2(8)
C(15)	1.016(2)	0.1473(6)	0.229(1)	5.6(6)
C(16)	1.122(3)	0.1791(7)	0.265(1)	8.4(8)
Pt(2)	-0.29645(9)	0.04237(2)	0.71497(4)	3.66(2)
S(2)	-0.4570(8)	-0.0046(2)	0.6582(3)	7.0(2)

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[a] Starred atoms were refined isotropically.

[b] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3) * [a^2*B(1,1) + b^2*B(2,2) + c^2*B(3,3) + ab(\cos\ \text{gamma})*B(1,2) + ac(\cos\ \text{beta})*B(1,3) + bc(\cos\ \text{alpha})*B(2,3)]$.

Table 5. Continued

Atom^a	x	y	z	B(A^2)^b
P(3)	-0.2650(6)	0.0284(1)	0.8407(2)	3.7(1)P
(4)	-0.1688(7)	0.0988(1)	0.7056(2)	4.1(1)
C(17)	-0.272(3)	0.0662(6)	0.910(1)	6.5(6)C
(18)	-0.278(3)	0.0541(6)	0.992(1)	7.3(7)
C(19)	-0.073(3)	0.0036(6)	0.864(1)	6.7(7)
C(20)	-0.036(3)	-0.0287(6)	0.813(2)	9.2(9)
C(21)	-0.430(3)	-0.0048(6)	0.870(1)	6.5(7)
C(22)	-0.605(3)	0.0130(7)	0.860(1)	7.8(8)
C(23)	0.059(2)	0.0978(6)	0.730(1)	5.5(6)
C(24)	0.147(3)	0.0668(7)	0.685(1)	7.4(8)
C(25)	-0.254(3)	0.1362(5)	0.767(1)	6.2(7)
C(26)	-0.442(3)	0.1387(6)	0.760(1)	7.9(8)
C(27)	-0.183(2)	0.1192(5)	0.6132(9)	5.3(5)
C(28)	-0.116(3)	0.1588(6)	0.603(1)	7.6(7)
C(29)	-0.311(3)	-0.0398(6)	0.623(1)	8.0(8)
C(30)	-0.175(3)	-0.0157(6)	0.584(1)	7.7(8)
C(31)	-0.259(3)	0.0192(6)	0.546(1)	7.3(7)
C(32)	-0.390(3)	0.0341(5)	0.6016(9)	6.1(6)
P(5)	0.3314(8)	0.1387(2)	0.4920(3)	5.5(2)
P(6)	0.2073(8)	0.1161(2)	-0.0100(3)	6.2(2)
F(1)	0.323(2)	0.1437(4)	0.5789(6)	11.5(5)
F(2)	0.347(2)	0.1330(3)	0.4055(5)	8.5(4)
F(3)	0.487(2)	0.1662(4)	0.4927(8)	12.5(6)
F(4)	0.217(2)	0.1733(4)	0.4816(8)	12.5(6)
F(5)	0.457(2)	0.1042(4)	0.5013(8)	11.5(5)
F(6)	0.182(2)	0.1110(4)	0.4947(7)	10.2(5)
F(7)	0.052(2)	0.1132(7)	0.044(1)	8.4(8)*
F(8)	0.329(4)	0.115(1)	0.060(2)	18.0(1)*
F(9)	0.357(3)	0.1156(9)	-0.063(2)	14.0(1)*

Table 5. Continued

Atom[a]	x	y	z	B(A^2)[b]
F(10)	0.086(3)	0.1205(8)	-0.082(1)	10.7(9)*
F(11)	0.201(3)	0.0713(6)	-0.014(2)	11.5(9)*
F(12)	0.198(3)	0.1613(6)	-0.002(2)	11.0(1)*
F(7')	0.353(4)	0.0889(9)	0.017(2)	12.0(1)*
F(8')	0.178(4)	0.087(1)	-0.076(2)	12.0(1)*
F(9')	0.067(4)	0.142(1)	-0.050(2)	14.0(2)*
F(10')	0.235(4)	0.143(1)	0.059(2)	12.0(1)*
F(11')	0.078(5)	0.094(1)	0.040(2)	21.0(3)*
F(12')	0.347(4)	0.1405(9)	-0.050(2)	10.0(1)*

Reaction of $[Pt(PEt_3)_2(DHT\bullet H)]PF_6$, II, and H_2

A THF (3.0 mL) solution of II (0.050 mg, 0.075 mmol) was placed in an autoclave in a glass liner under H_2. The H_2 pressure was increased to 500 psi and the autoclave heated to 150 °C. The mixture was allowed to cool to ambient temperature after 3 h. An evacuated Schlenk flask was filled with a portion of the gas phase of the reaction mixture and the GC-MS obtained. Analysis of the GC showed butane (0.023 mmol, 30%) was produced. It is also evident from the GC-MS of the solution that some butane was present in the liquid phase. A black-brown residue was generated in this reaction. The ^1H NMR ($CDCl_3$) and MS spectra of this residue showed that it contained Pt, PEt_3 and S. However, we were unable to determine its exact nature.

Synthesis of $Cp(CO)_3M(DHT\bullet H)$, (**Va**, M = W; **Vb**, M = Mo)

To a stirred THF (25 mL) solution of $CpW(CO)_3^-$ prepared as described by Gladysz and coworkers[17] from $[CpW(CO)_3]_2$ (0.97 g, 1.5 mmol) and $Na(BEt_3H)$ (1.0 M in THF, 2.5 mL, 2.5 mmol), a benzene (20 mL) solution of chlorotetrahydrothiophene was added. The chlorotetrahydrothiophene was prepared by slowly adding N-chlorosuccinimide (NCS) (1.5 g, 11.2 mmol) (over a period of 15-30 min) to a benzene (20 mL) solution of tetrahydrothiophene (1.0 mL, 11.4 mmol) under N_2.[18] After stirring for 1 h, the succinimide generated was filtered off. The $CpW(CO)_3^-$ and chlorotetrahydrothiophene mixture was stirred for 1 h and the solvent removed in vacuo. The residue was dissolved in a minimum amount of Et_2O and transferred onto a column of alumina (1 x 10 cm). Elution with hexanes led to the isolation of **Va** from the first yellow band. Removal of solvent from the yellow solution yielded **Va** (0.69 g, 55%) as a yellow oil. The elemental analysis of **Va** was not obtained because it was air and thermally unstable.

The Mo analog of **Va**, **Vb**, was prepared in a similar fashion starting with $[CpMo(CO)_3]_2$ (0.50 g, 1.0 mmol) in THF (30 mL), $Na(BEt_3H)$ (1.0 M in THF, 2.5 mL, 2.5 mmol) and a benzene (10 mL) solution of chlorotetrahydrothiophene prepared from THT (0.12 mL, 1.4 mmol) and NCS (0.15 g, 1.12 mmol). Compound **Vb** (0.20 g, 30%) was isolated as a yellow oil upon workup as described in the synthesis of the W analog. Because of the instability of **Vb**, its elemental analysis was not obtained.

Synthesis of $CpFe(CO)_2(DHT{\bullet}H)$, **VI**

To a stirred THF (40 mL) solution of $CpFe(CO)_2^-$ prepared from $[CpFe(CO)_2]_2$[19] (1.4 g, 3.8 mmol) using sodium amalgam generated from sodium metal (0.32 g, 14 mmol) and 8 mL of Hg was added a benzene (10 mL) solution of chlorotetrahydrothiophene synthesized as described in the preceding procedure from THT (1.0 mL, 11 mmol) and NCS (1.6 g, 11 mmol). The mixture was stirred for 1 h and the volume of the solvent reduced to 2 mL in vacuo. Diethylether (5 mL) was added to the mixture and the slurry transferred on to a column of alumina (2.5 x 12 cm). Elution with hexanes led to the isolation of **VI** (0.60 g, 29%) as a yellow-brown oil. Because of the instability of **VI**, its elemental analysis was not obtained. Some $[CpFe(CO)_2]_2$ (0.50 g, 37%) was recovered on elution with Et_2O. ^{13}C NMR (C_6D_6) of **VI**: δ 217.26 and 216.68 (CO); 85.78 (Cp); 45.88, 33.78, 31.71 and 29.98 (DHT•H).

Reaction of $CpFe(CO)_2(DHT{\bullet}H)$, **VI**, with $[Me_3O]BF_4$

A CH_2Cl_2 (20 mL) solution of **VI** (0.093 mg, 0.35 mmol) was treated with $[Me_3O]BF_4$ (0.072 mg, 0.49 mmol). The mixture was stirred for 1 h, KPF_6 (~1.0 g) was added and stirring continued for 30 min. Addition of excess Et_2O (~80 mL) led to the precipitation of a yellow solid. After filtration, the residue was washed with several portions of Et_2O and then extracted with CH_2Cl_2 (20 mL). The CH_2Cl_2 extract was layered with hexanes (100 mL) and stored at -20 °C for 3 days. The air-stable yellow solid, $[CpFe(CO)_2(DHT{\bullet}H{\bullet}Me)]PF_6$, **VII**, (0.097, 65%) was filtered off and dried in vacuo. Anal. Calcd for $C_{12}H_{15}F_6FeO_2PS$: C, 33.99; H, 3.57; S, 7.55. Found: C, 33.99; H, 3.93; S, 7.97.

Synthesis of $Cp(CO)_2M(\eta^2\text{-}DHT{\bullet}H)$, (**VIIIa**, M = W; **VIIIb**, M = Mo)

A hexanes (30 mL) solution of **Va** (0.16 g, 0.38 mmol) was placed in a quartz tube equipped with a water-cooled probe and purged with N_2. The solution was irradiated with a 254 nm light for 90 min. The mixture was then transferred onto a column of alumina (1 x 10 cm). A yellow band containing unreacted **Va** was first eluted with hexanes. Elution with hexanes/Et_2O (8:2) gave pure **VIIIa**, as the second yellow band. Slow removal of the solvent in vacuo yielded an air-stable yellow crystalline solid, **VIIIa** (0.11 g, 75%). ^{13}C NMR (C_6D_6): δ 237.78 and 233.70 (CO); 90.44 (Cp); 35.94, 35.30, 34.59 and 32.52 (DHT•H). Anal. Calcd for $C_{11}H_{12}O_2SW$: C, 33.70; H, 3.08; S, 8.16. Found: C, 33.62; H, 2.95; S, 8.33.

The Mo analog, **VIIIb**, was prepared similarly starting with **Vb** (0.10 g, 0.30 mmol). Chromatographic purification on a column of alumina (1 x

15 cm) eluting with hexanes/Et_2O (5:1) led to the isolation of **VIIIb** as the first yellow band which yielded 0.020 g (22%) of **VIIIb** as a yellow solid when the solvent was removed in vacuo.

Attempts to prepare Cp(CO)Fe(η^2-DHT•H) by photolysis of VI were unsuccessful.

Reaction of $CpW(CO)_2(\eta^2\text{-DHT}\cdot H)$, VIIIa, with HCl

Hydrogen chloride gas (3.5 mL, 0.18 mmol) was syringed into a stirred CH_2Cl_2 (20 mL) solution of **VIIIa** (0.048 g, 0.12 mmol). An instant color change from yellow to red was observed which signified the formation of the unstable compound $CpW(CO)_2(THT)Cl$, IX (IR and ^1H NMR are given in Tables 1 and 2, respectively). The reaction mixture was immediately treated with PPh_3 (0.033 mg, 0.13 mmol), and stirring was continued for 15 min. After removal of solvent, the residue was extracted with $CHCl_3$. Removal of the solvent from $CHCl_3$ extract under vacuum led to the isolation of $CpW(CO)_2(PPh_3)Cl$[20] (0.060 g, 81%), which was identified by comparing its IR and ^1H NMR with those reported in the literature. Free tetrahydrothiophene [^1H NMR (CD_2Cl_2): δ 2.78 (m, 4H), 1.91 (m, 4H)] was also generated in this reaction.

Reaction of $H_2Os_3(CO)_9L$ (L = CO, PPh_3) with 2,3-DHT

To a stirred hexane (50 mL) slurry of $H_2Os_3(CO)_9(PPh_3)$ (0.25 g, 0.23 mmol) was added a 0.22 M solution of 2,3-DHT[4] in pentane (7.5 mL, 1.6 mmol). The mixture was stirred continuously for 7 days after which it was transferred onto a column of silica gel (1.0 x 12 cm). The long reaction time was presumably due in part to the fact that $H_2Os_3(CO)_9(PPh_3)$ is only sparingly soluble in hexanes. Elution with hexanes resulted in the removal of a small amount of unreacted $H_2Os_3(CO)_9(PPh_3)$. Addition of hexane/Et_2O (1:1) to the column resulted in the elution of a yellow band. The solvent was removed in vacuo and the residue redissolved in a minimum amount of hexanes and stored at -20 °C for 3 days. Extremely stable gold cube-like crystals of $HOs_3(CO)_9(PPh_3)$(DHT•H), X (0.21 g, 78%) were obtained. Anal. Calcd for $C_{31}H_{23}O_9Os_3PS$: C, 31.76; H, 1.98. Found: C, 31.85; H, 1.92.

The analogous reaction of $H_2Os_3(CO)_{10}$ (0.071 g, 0.083 mmol) with 0.36 M 2,3-DHT[4] (4.4 mL, 1.6 mmol in pentane) in hexane (20 mL) for 40 h resulted in the formation of $HOs_3(CO)_{10}$(DHT•H), XI (0.051 g, 72%) as an air-stable yellow powder which was only sparingly soluble in common organic solvents such as hexanes, THF, toluene, CH_2Cl_2, DMSO, $(CH_3)_2C{=}O$ and CH_3CN. Anal. Calcd for $C_{14}H_8O_{10}Os_3S$: C, 17.91; H, 0.86. Found: C, 17.85; H, 1.09.

X-ray Structure Determination of $HOs_3(CO)_9(PPh_3)$(DHT•H), X

A yellow crystal of $HOs_3(CO)_9(PPh_3)$(DHT•H) was mounted on a glass fiber in a random orientation. Cell constants and an orientation matrix for data collection were obtained from least squares refinement using setting angles of 25 reflections in the range 20° < 2θ < 35°. A total of 6298 reflections were collected in the +h +k ±l quadrant of which 5728 were unique and not systematically absent. No decay correction was applied.

Lorentz and polarization corrections were applied to the data. The linear absorption coefficient is 118.4 cm^{-1} for MoK_α radiation. An empirical absorption correction based on a series ψ-scans of five reflections and their Friedel mates was applied to the data. The 4422 reflections having intensities greater than 3.0 times their standard deviation were used in the refinement.

The positions of the 3 Os atoms were given by the direct method. Following isotropic refinement of the Os atoms, the P and S atoms in the coordination sphere were placed based on a difference Fourier map. The remainder of the non-hydrogen atoms were then located via subsequent cycles of least-squares refinement followed by difference Fourier maps. The position of the hydrogen atoms were calculated for the PPh_3 and hydrothiophene (DHT•H) but were not included in the refinement.

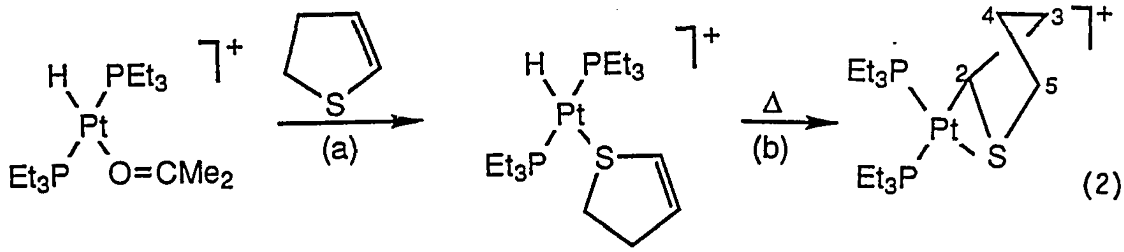
The largest peak in the final difference Fourier had a height of 0.97 e/Å^3. This peak was 2.053Å from Os(2) and 1.912Å from Os(3) (Fig. 2). The Os(2)-Os(3) distance of 3.0178(5) Å was the longest Os-Os distance in the molecule. While attempts to refine this peak as a hydride led to lower R and R_w values, the isotropic thermal parameters associated with this peak were negative. This peak was, therefore, excluded from the final solution of X.

Procedures for structure solution were the same as described for II.[13-16]

RESULTS AND DISCUSSION

Reaction of HPt(acetone)(PEt$_3$)$_2^+$ and 2,3-DHT

The reaction of trans-HPt(acetone)(PEt$_3$)$_2^+$, and 2,3-DHT leads to the formation of the sulfur coordinated trans-HPt(2,3-DHT)(PEt$_3$)$_2^+$, I, which is isolated as a colorless crystalline solid [eq. 2 step (a)]. Compound I

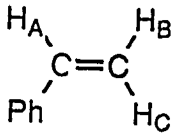


(2)

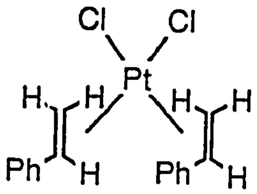
I

II

is characterized by its mass spectrum, ^{1}H NMR as well as elemental analysis. The FAB mass spectrum of I shows an m/e value of 518 (M$^+$) which represents HPt(2,3-DHT)(PEt$_3$)$_2^+$. The hydride of I is observed at -13.32 ppm as a triplet with coupling constants of J_{PtH} = 1242 Hz and J_{PH} = 14.4 Hz. The olefin signals of the 2,3-DHT in compound I (Table 2) are shifted downfield with respect to that of the free ligand [6.16(H5), 5.63(H4), 2.74(H3), 3.22(H2)]. In coordinated olefin complexes, there is an upfield shift of the olefin signals with respect to the free ligand as illustrated in compound B[21]; in free styrene (A), protons H_A, H_B, and H_C occur



A



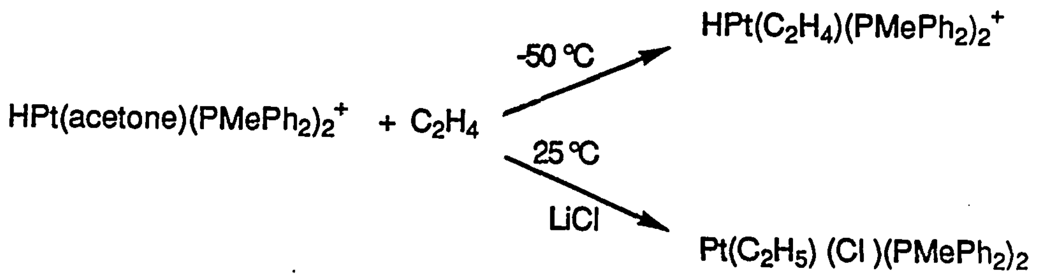
B

at 6.71, 5.27, and 5.82, respectively, as compared with (4.77, 4.50), (4.84, 5.70), and 4.48 for the same protons in B. Such upfield shifts upon coordination of olefins have been well documented in the literature.[22] The downfield shift observed for the olefin signals in I, therefore, suggests that the 2,3-DHT is coordinated through the sulfur. Similar downfield shifts have been observed in previously reported sulfur-coordinated 2,3-DHT complexes: trans-$PdCl_2(2,3\text{-DHT})_2$,[4a] $Ru(CO)_3Cl_2(2,3\text{-DHT})$,[4a] $[Re(CO)_5(2,3\text{-DHT})]^+$,[4a] $W(CO)_5(2,3\text{-DHT})$[4a] and $Cr(CO)_5(2,3\text{-DHT})$.[23]

Compound I slowly rearranges to II [eq. 2, step (b)] by migration of the terminal hydride ligand to the β-olefin carbon with the formation of a Pt-C σ-bond. Compound II was isolated as a pale yellow crystalline solid and characterized by its FAB mass spectrum, ^1H and ^{13}C NMR, and an X-ray structural study (see below). This rearrangement occurs both in solution and in the solid state at ambient temperature over a period of 30 and 90 days, respectively. A relatively fast (7 days) rearrangement is observed at 60 °C in $CDCl_3$ solution.

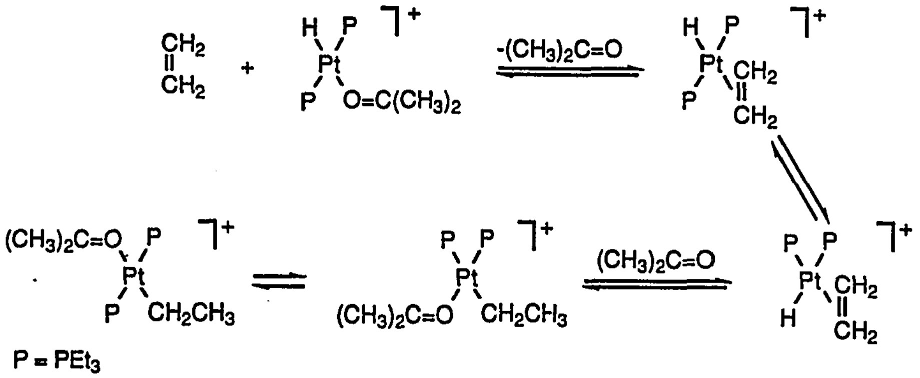
Similar reactions of $HPt(acetone)(PMePh_2)_2^+$ and $HPt(acetone)(PPh_3)_2^+$ result in the direct formation of the DHT•H inserted products analogous to II with no ^1H NMR evidence for S-coordinated 2,3-DHT intermediates. A similar effect of phosphine ligands is observed for ethylene insertion into the Pt-H bond in $HPt(C_2H_4)(PMePh_2)_2^+$, which is much faster than the analogous reaction of $HPt(C_2H_4)(PEt_3)_2^+$.[12,24]

The mechanism of reaction (2) is probably related to that of other olefin insertions into Pt-H bonds. Clark and Kurosawa[24a] reported that $HPt(acetone)(PMePh_2)_2^+$ rapidly coordinates ethylene at -50 °C to give a square planar hydrido olefin complex (eq. 3). The same reaction carried out at room temperature results in facile insertion of ethylene into the



(3)

Pt-H bond to give, after halide quenching the alkyl product trans-$Pt(C_2H_5)X(PMePh_2)_2$. A mechanistic scheme (Scheme I) involving reversible ethylene substitution and a slower rate-determining insertion step was suggested based on kinetic studies carried out with trans-$HPt(acetone)(PEt_3)_2^+$.[12] It was noted by these authors that the kinetic studies could not distinguish between insertion from a rearranged four-coordinate intermediate and an insertion which is essentially

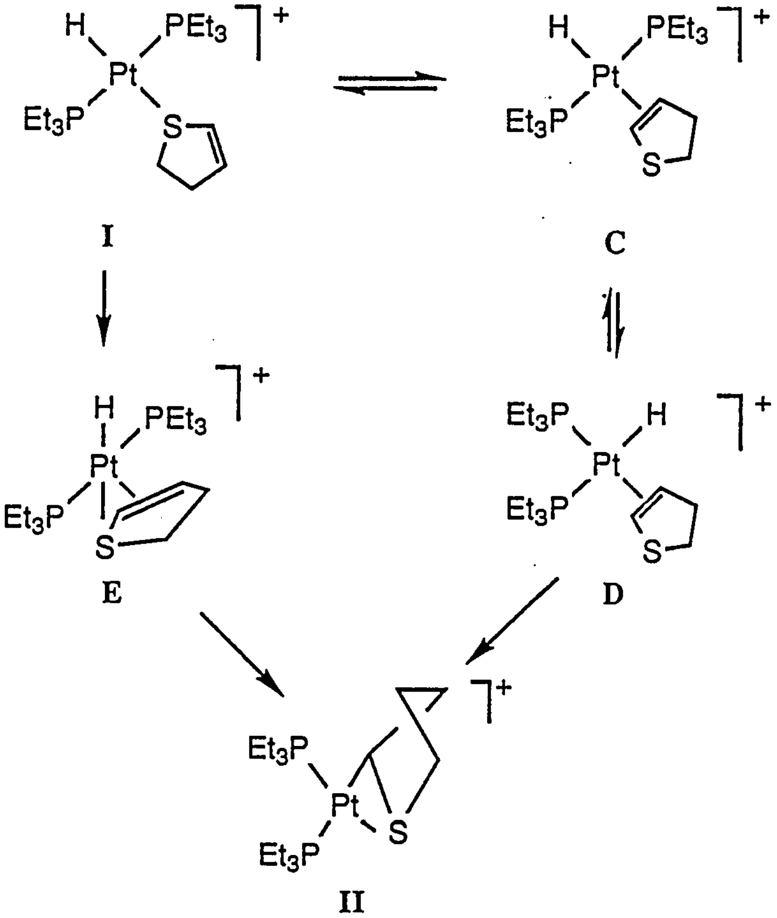


Scheme I

associative in nature proceeding from a five coordinate solvent-containing complex.

In light of the above results, it is reasonable to envisage the insertion of 2,3-DHT into trans-HPt(acetone)$(PR_3)_2^+$ as occurring via a similar mechanism (Scheme II). The initial coordination of 2,3-DHT via the S is supported by the isolation of trans-HPt(2,3-DHT)$(PEt_3)_2^+$, I, in good yield (83%). Subsequent rearrangement of I to give the olefin-inserted product $Pt(PEt_3)_2(DHT{\bullet}H)^+$, II, has been monitored by ^1H NMR at 60 °C. The spectrum obtained 30 min after a $CDCl_3$ solution of I was warmed to 60 °C shows the growth of a new hydride peak at -4.73 ppm. A steady-state concentration of this hydride is observed in the spectrum recorded 5 h later. This signal, which corresponds to the hydride in C is a 9-line pattern (J_{Pt-H} = 954 Hz, $J_{P_{cis}-H}$ = 13.4 Hz). If one assumes there is little or no coupling between the hydride and the olefin protons because their dihedral angle approaches 90°, one would not expect to see coupling between the hydride and the olefinic protons, as is observed. A new set of hydride signals becomes apparent in the spectrum obtained within 90 min after heating the $CDCl_3$ solution to 60 °C. This 18-line pattern (J_{Pt-H} = 792 Hz, $J_{P_{trans}-H}$ = 158 Hz, J_{HH} = 16.3 Hz due to coupling with the olefinid protons) at -6.29 ppm corresponds to D (Scheme II), and like the hydride signal observed at -4.73 ppm, reaches a steady-state concentration in the spectrum recorded 5 h later. A cis phosphorus hydride coupling is not observed, presumably because it is small. It is also worth noting that examples of Pt^{II} (e.g., $\{HPt(AsEt_3)_2[P(OMe)_3]\}ClO_4$,

$J_{P_{cis}-H}$ = <2 Hz) have been reported where the cis phosphorus-hydride coupling constants are extremely small.[25,26] The stationary-state of C and D persists for 2-3 days as the starting hydride signals slowly disappear and II forms by slow transfer of the H ligand to the β-olefin carbon with concomitant Pt-C and Pt-S bond formation. At the end of the reaction, C and D disappear. An associative mechanism in which the 2,3-DHT is coordinated in an η^3 manner through both the sulfur and the



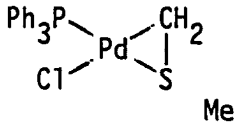
Scheme II

olefin E (Scheme II) followed by H transfer to the β-olefin carbon cannot be ruled out.

Structure of $Pt(PEt_3)_2(DHT{\cdot}H)^+$

A perspective view of II showing the numbering scheme and thermal ellipsoids is given in Fig. 1. Selected angles and distances are listed in Table 6.

There are two independent cationic Pt complexes in a unit cell, one of which has a distorted PF_6^- anion. The bond angles and distances for both of them are, however, the same within experimental error; the discussion is, therefore, limited to one of the cations. The core atoms of the cation in II, Pt, S, C(2), P(1), and P(2), lie in a plane. The angle between this plane and that defined by S, C(2), C(3) and C(5) is 107.3(6)°. The Pt-S distance of 2.328(6) Å is similar to Pt-S distances found in the following compounds: the α and β isomers of $[(Pr_3P)ClPt(\mu\text{-}SCN)_2PtCl(PPr_3)]$[27] (2.327 and 2.408 Å, respectively) as well as the Pd-S distance of 2.371(1) Å in F.[28] The Pt-C bond distance of 2.12(1) is comparable to the bond distances found in the following compounds: Pd-C in F [2.042(6)], and cis-$\{(Ph_3P)_2Pt[(NC)_2C{=}C(CN)_2]\}$ (2.11 Å),[29] which has a metallacyclopropane geometry. Of the Pt-P bond distances in II, the longer (2.306(4) Å) is trans to the carbon; it is similar to the Pt-P



F

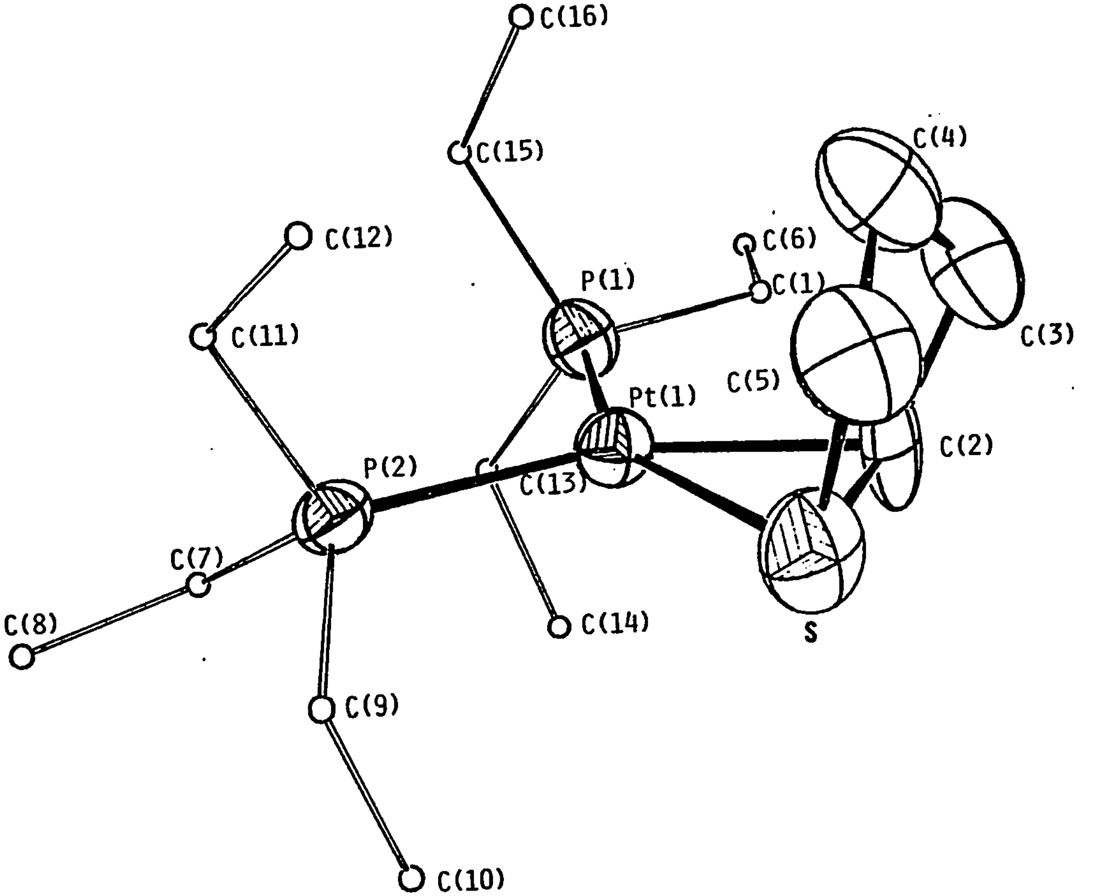


Figure 1. An ORTEP drawing of the $[Pt(PEt)_2(DHT{\bullet}H)]^+$ cation in II showing the numbering scheme

Table 6. Selected bond distances (Å) and angles (deg) for $[\mathrm{Pt(PEt_3)_2(DHT{\bullet}H)]PF_6}$, II

Bond Distances (Å)

Pt(1) - S(1)	2.328(6)[a]	S(1) - C(2)	1.78(2)
Pt(1) - P(1)	2.242(5)	C(5) - C(4)	1.52(3)
Pt(1) - P(2)	2.306(4)	C(4) - C(3)	1.59(3)
Pt(1) - C(2)	2.12(1)	C(3) C(2)	1.53(3)
S(1) - C(5)	1.83(2)		

Bond Angles (deg)

S(1) - Pt(1) - P(2)	107.9(1)	Pt(1) - S(1) - C(2)	60.6(6)
S(1) - Pt(2) - C(2)	46.7(4)	Pt(1) - C(2) - S(1)	72.7(5)
P(1) - Pt(1) - P(2)	101.8(2)	Pt(1) - C(2) - C(3)	117.0(1)
P(1) - Pt(1) - C(2)	103.5(5)	Pt(1) - S(1) - C(5)	104.8(7)
C(2) - S(1) - C(5)	95.7(8)	S(1) - C(2) - C(3)	109(1)
S(1) - C(5) - C(4)	105(1)	C(2) - C(3) - C(4)	105(1)
C(5) - C(4) - C(3)	106(2)		

[a] The numbers in parentheses are estimated standard deviations.

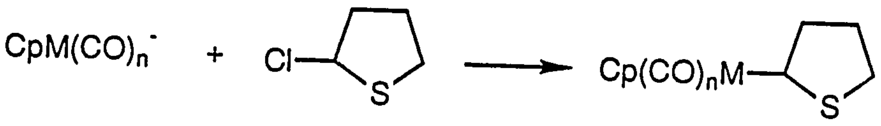
distance in cis-{$(Ph_3P)_2Pt[(NC)_2C{=}C(CN)_2]$} (2.29 Å).[29] The short Pt-P distance (2.242(5) Å) is comparable to the Pd-P bond distance (2.267(1) Å in F.[28] The longer Pt(1)-P(2) is a result of the stronger trans-influence of C(2) then S(1).[30,31] The S(1)-C(2) bond (1.78(2) Å) is a relatively short S-C(alkyl) distance (range: 1.80-1.84),[32] but is not nearly as short as the C=S double bond (1.618(8) Å) in the thioacetone ligand of $W(CO)_5(S{=}CMe_2)$.[33] The S-C bond length in F [1.756(6) Å][28] is also slightly shorter than a S-C(alkyl) distance. Miki and coworkers[28] argue that the S-C bond in F is a single bond which may have partial double bond character. In light of the similarity between the interaction of the η^2-CH_2SMe ligand with the Pd metal center in F and the η^2-DHT•H ligand with Pt in II, it is reasonable to suggest there may be some double bond character in the S-C bond in II, albeit small. The Pt-S-C(2) bond angle [60.6(6)°] in II is comparable to the 57.0(2)° observed for Pd-S-C in F. Other angles in the DHT•H ligand are given in Table 6. The C-C distances in the DHT•H ligand which range between 1.50-1.59 Å are comparable to reported[34] $C(sp^3)$-$C(sp^3)$ distances. Even though C4 is puckered in such a way as to place one of its hydrogens above the Pt, the calculated Pt-H distance (2.85 Å) is much longer than Mo-H distances (2.27(8) and 1.88(8) Å) observed in molybdenum complexes in which agostic interactions have been established.[35] The metallic radius of Pt is similar to that of Mo (1.39 and 1.36 Å, respectively).[36]

Reaction of $[Pt(PEt_3)_2(DHT{\bullet}H)]PF_6$, II with H_2

HDS studies of 2,3-DHT show[3] that both desulfurization and THT formation occur (eq. 1). These reactions may proceed via initial olefin insertion as in eq. 2, followed by subsequent desulfurization or hydrogenation. That desulfurization is possible is demonstrated by the reaction of II with H_2 at 150 °C in THF over a period of 3 h to yield butane in greater than 30% yield. Although this reaction did not yield H_2S in the gaseous phase, the mass spectrum of the black oily residue generated in this reaction showed fragments which were made up of S, Pt and PEt_3. Hardly any reaction occurred between II and H_2 at 90 °C in 5 h.

Synthesis and Reactions of $Cp(CO)_{n-1}M(DHT{\bullet}H)$

The compounds **Va**, **Vb** and **VI** are prepared by the reaction of $Na[CpM(CO)_n]$ and C_4H_7ClS (eq. 4). The yellow oils, **Va,b**, were



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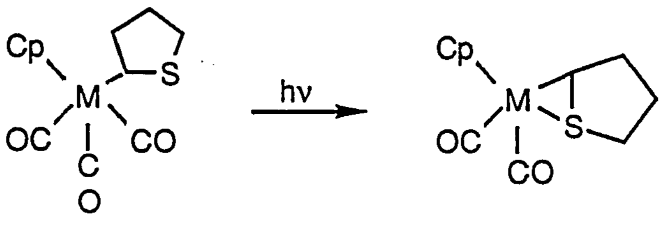
M = W; n = 3, Va
M = Mo; n = 3, Vb
M = Fe; n = 2, VI

characterized by their mass, IR, and ^1H NMR spectra. The yellow-brown iron analog VI was also characterized by its MS, IR, ^1H and ^{13}C NMR spectra. Because the hydrogens on the DHT•H are all inequivalent, a complicated ^1H NMR pattern was obtained. A combination of 2-dimensional NMR (COSY) and selective decoupling were employed in making proton assignments to VI (Table 2). The ^1H assignments to **Va** and **Vb** were done by analogy.

Compounds **VIIIa** and **VIIIb** were obtained by photolysis of **Va** and **Vb**, respectively. Compound **VIIIa** was isolated as a yellow crystalline solid in 75% yield whereas the less stable Mo analog, **VIIIb**, was obtained in 22%



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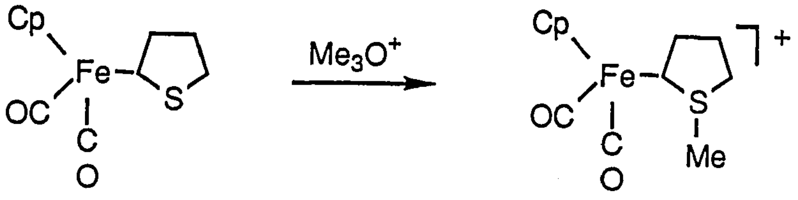
V

M = W, VIIIa
M = Mo, VIIIb

yield. The metallathiacyclopropane, **VIIIa**, was characterized by its MS, IR, ^{1}H and ^{13}C NMR spectra, as well as by elemental analysis. A combination of 2-dimensional NMR (COSY) and selective decoupling experiments were employed in making the ^{1}H assignments (Table 2) to the complicated spectrum of the DHT•H ligand. Proton assignments in **VIIIb** were done by analogy. Attempts to form CpFe(CO)(η^2-DHT•H) by photolysis of CpFe(CO)$_2$(DHT•H) were unsuccessful.

However, **VI** reacts with Me_3O^+ to give the corresponding alkylated product (eq. 6), which was characterized by IR, MS, and ^{1}H NMR spectra and



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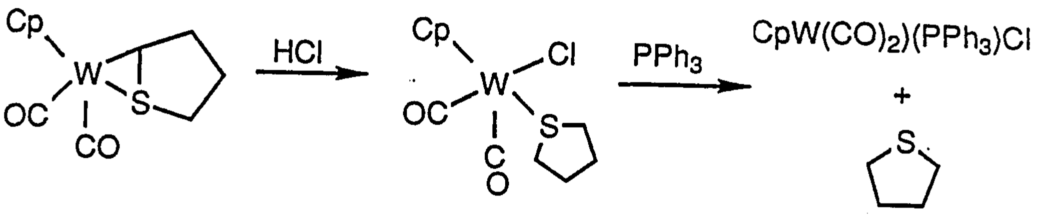
VI

VII

by elemental analysis. The ^{1}H NMR shows there are two isomers of **VII** (eq. 6) which presumably result from slow inversion at the pyramidal sulfur at room temperature.

Reaction of **VIIIa** with HCl leads to the formation of an unstable tetrahydrothiophene (THT) complex **IX** (eq. 7), which was only characterized by its IR and ^1H NMR spectra. The THT is readily displaced by PPh_3 to give $CpW(CO)_2(PPh_3)Cl$[20] and free THT which was observed by ^1H NMR.



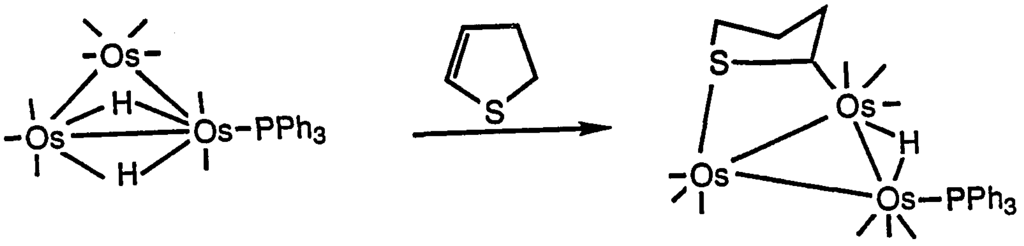
IX

7

Compound VIIIa does not react with PMe_3 at ambient temperature. The Pt analog, II, does not react with PPh_3 or [PPN]Cl at 25 °C.

Reaction of $H_2Os_3(CO)_9L$ (L = CO, PPh_3) with 2,3-DHT

Reaction of $H_2Os_3(CO)_9(PPh_3)$ with 2,3-DHT at ambient temperature over a period of 7 days results in the formation of $HOs_3(CO)_9(PPh_3)(DHT{\bullet}H)$, X (eq. 8). Compound X was obtained as a yellow crystalline solid and



X

8

characterized by its IR, MS, ^1H NMR, elemental analysis, and X-ray structure analysis. In the analogous reaction of $H_2Os_3(CO)_{10}$, the DHT•H complex is formed in only 40 h and precipitates out of hexanes as a yellow powder which is only sparingly soluble in most organic solvents. Compound $COs_3(CO)_{10}(DHT{\bullet}H)$ XI was characterized by its IR, MS and elemental analysis.

The hydride in complex X is observed as a broad signal at -16.50 ppm at ambient temperature in the ^1H NMR ($CDCl_3$) spectrum. On cooling to -53 °C it becomes two doublets which integrate to 1/2 proton each which indicates equal occupancy of the bridging hydride positions on the two Os-Os bonds containing the $Os(PPh_3)$ group. Owing to the inequivalency of all the hydrogens in the DHT•H ligand, a complicated pattern is observed in the ^1H NMR spectrum; the assignments in Table 2 were made by a 2-D COSY experiment.

It has been reported that the reaction of $H_2Os_3(CO)_{10}$ with neat methyl vinyl ether, $MeOCH=CH_2$, at ambient temperature over a period of one week gives the 1-methoxyethyl compound $HOs_3(MeOCHMe)(CO)_{10}$, coordinated through a carbon and oxygen.[37] The methyoxyethyl cluster compound reverts to $H_2Os_3(CO)_{10}$ and methyl vinyl ether over several weeks in the absence of the ether. A similar reaction of $H_2Os_3(CO)_{10}$ and $PhSCH=CH_2$ over a period of 2 h gives the thioether compound $HOs_3(PhSCHMe)(CO)_{10}$ in 90% yield.[38] The reaction of 2,3-DHT and $H_2Os_3(CO)_{10}$ is considerably slower than the analogous reaction described for $PhSCH=CH_2$.

Structure of $HOs_3(CO)_9PPh_3(DHT{\bullet}H)$, X

A perspective view of the molecule showing the thermal ellipsoids and numbering scheme is given in Fig. 2. The carbons in the phenyl ring of the PPh_3 are not shown. Selected bond distances and angles are given in Table 7.

The plane described by the three osmium atoms is at an angle of 89.82° with respect to the plane defined by Os(1), Os(2), S and C(2). The latter plane is 117.7(2)° from the plane in which S, C(2), C(3), C(5) are

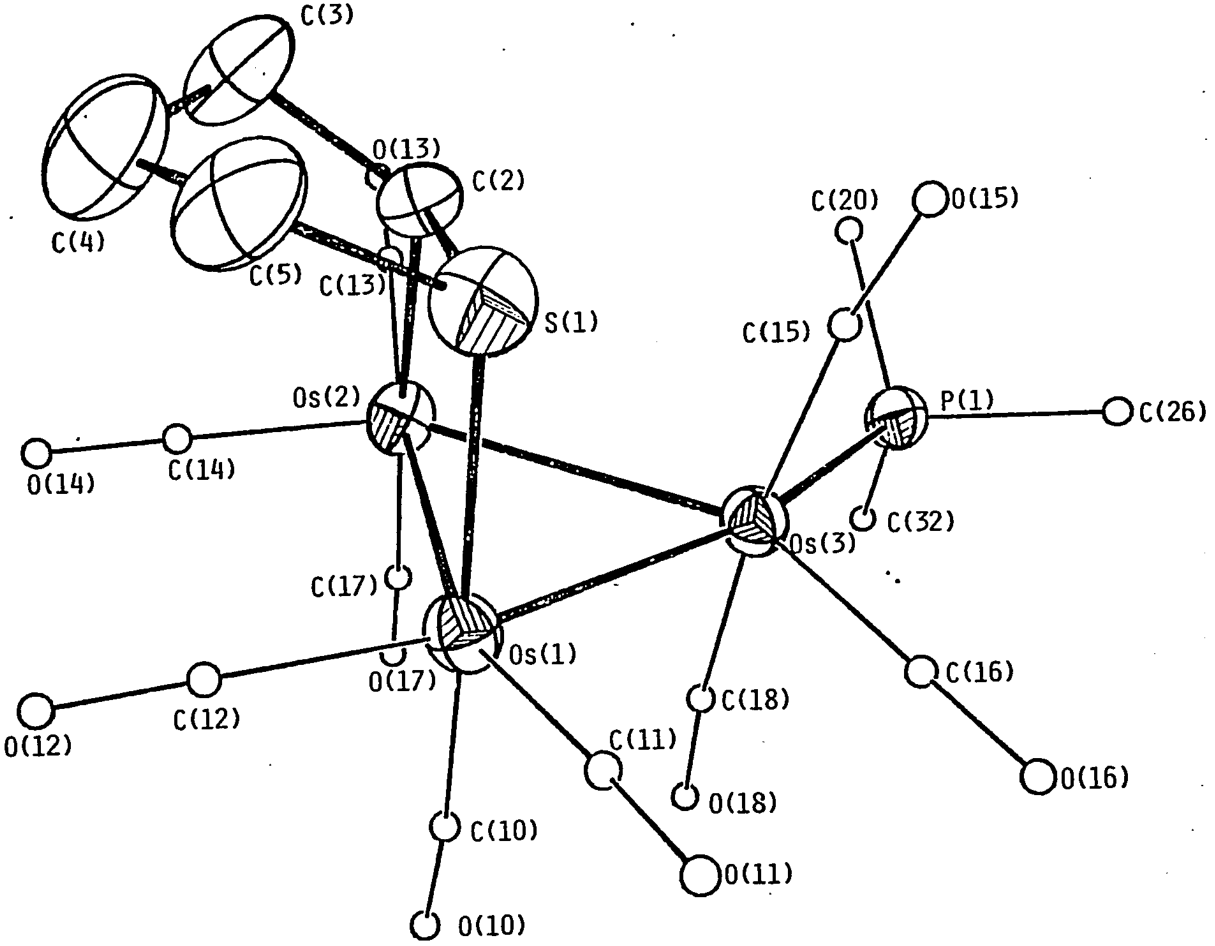


Figure 2. Molecular structure of $HOs_3(CO)_9(PPh_3)(DHT\cdot H)$, X

Table 7. Selected bond distances (Å) and angles (deg) for $HOs_3(CO)_9(PPh_3)(DHT\cdot H)$, X

Bond Distances (Å)

Os(1) - Os(2)	2.7907(4)[a]	Os(2) - C(2)	2.215(8)
Os(1) - Os(3)	2.8977(4)	Os(3) - P(1)	2.373(2)
Os(2) - Os(3)	3.0718(5)	S(1) - C(2)	1.815(8)
Os(1) - S(1)	2.407(2)	S(1) - C(5)	1.82(1)
C-C	1.52 (ave)	Os - C(0)	1.88-1.94

Bond Angles (deg)

Os(1) - Os(2) - Os(3)	59.01(1)[a]	Os(1) - S(1) - C(5)	112.7
Os(2) - Os(3) - Os(1)	55.65(1)	Os(2) - C(2) - C(3)	118.8
Os(3) - Os(1) - Os(2)	65.34(1)	S(1) - C(5) - C(4)	106.8
S(1) - Os(1) - Os(2)	76.64(6)	C(4) - C(3) - C(2)	109.3(8)
Os(1) - Os(2) - C(2)	78.8(2)	Os(2) - C(2) - S(1)	106.5(3)
Os(1) - S(1) - C(2)	97.9(4)	Os(3) - Os(2) - C(2)	86.4(2)

[a] See Table 5 for footnote.

Table 8. Table of positional parameters for $HOs_3(CO)_9(PPh_3)(DHT{\bullet}H)$, X

Atom[a]	x	y	z	B(A^2)
Os(1)	0.33432(3)	0.43523(2)	0.17478(1)	2.582(6)
Os(2)	0.12751(3)	0.58784(3)	0.15715(1)	2.615(6)
Os(3)	0.42534(3)	0.61317(2)	0.11730(1)	2.383(6)
S(1)	0.3661(3)	0.5522(2)	0.24417(9)	3.74(5)
P(1)	0.4423(2)	0.7725(2)	0.07251(8)	2.46(4)
O(10)	0.2464(8)	0.3158(5)	0.0822(3)	5.5(2)
O(11)	0.6222(7)	0.3324(6)	0.1969(3)	6.3(2)
O(12)	0.1633(8)	0.2782(6)	0.2317(3)	7.0(2)
O(13)	-0.053(1)	0.7851(6)	0.1587(3)	8.1(2)
O(14)	-0.0909(8)	0.4508(8)	0.2041(4)	8.4(2)
O(15)	0.5791(9)	0.7220(6)	0.2037(3)	6.7(2)
O(16)	0.7101(7)	0.5071(6)	0.1053(3)	6.0(2)
O(17)	0.0154(8)	0.5114(6)	0.0560(3)	5.7(2)
O(18)	0.3317(8)	0.4989(5)	0.0212(2)	4.9(2)
C(2)	0.2199(8)	0.6400(6)	0.2294(3)	2.4(1)
C(3)	0.127(1)	0.6333(8)	0.2767(4)	4.7(2)
C(4)	0.144(1)	0.5266(9)	0.3000(4)	5.7(3)
C(5)	0.295(1)	0.4994(8)	0.3008(4)	4.7(2)
C(10)	0.2833(9)	0.3626(6)	0.1156(4)	3.6(2)
C(11)	0.516(1)	0.3728(7)	0.1881(3)	3.6(2)
C(12)	0.229(1)	0.3369(7)	0.2109(4)	4.3(2)
C(13)	0.015(1)	0.7142(8)	0.1571(3)	4.4(2)
C(14)	-0.006(1)	0.5023(9)	0.1872(4)	5.2(3)
C(15)	0.514(1)	0.6811(7)	0.1743(4)	3.9(2)
C(16)	0.602(1)	0.5472(7)	0.1096(4)	3.9(2)
C(17)	0.0602(9)	0.5384(7)	0.0928(4)	3.8(2)
C(18)	0.3598(9)	0.5411(7)	0.0580(4)	3.6(2)

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[a] See Table 6 for footnotes.

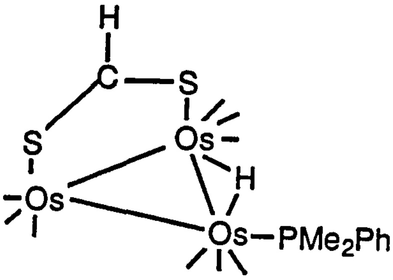
Table 8. Continued

Atom[a]	x	y	z	B(A^2)
C(20)	0.3517(9)	0.8871(6)	0.0986(3)	3.2(2)
C(21)	0.328(1)	0.8955(7)	0.1474(4)	5.4(3)
C(22)	0.261(1)	0.9815(9)	0.1677(4)	6.4(3)
C(23)	0.218(1)	1.0623(7)	0.1352(4)	5.1(3)
C(24)	0.238(1)	1.0560(7)	0.0853(4)	4.8(2)
C(25)	0.305(1)	0.9687(7)	0.0670(4)	3.9(2)
C(26)	0.6239(8)	0.8188(6)	0.0638(3)	2.6(2)
C(27)	0.6651(9)	0.9217(6)	0.0714(3)	3.2(2)
C(28)	0.802(1)	0.9516(7)	0.0618(4)	4.3(2)
C(29)	0.894(1)	0.8803(9)	0.0450(4)	4.8(2)
C(30)	0.8553(9)	0.7775(7)	0.0367(4)	3.9(2)
C(31)	0.7178(9)	0.7460(7)	0.0467(3)	3.5(2)
C(32)	0.3664(8)	0.7670(6)	0.0096(3)	2.7(2)
C(33)	0.4440(9)	0.7882(7)	-0.0327(4)	3.8(2)
C(34)	0.380(1)	0.7800(8)	-0.0788(4)	4.6(2)
C(35)	0.241(1)	0.7484(8)	-0.0852(4)	4.6(2)
C(36)	0.163(1)	0.7285(8)	-0.0440(4)	4.1(2)
C(37)	0.225(1)	0.7386(7)	0.0026(4)	3.9(2)
H(2)	0.2390	0.7122	0.2243	3*
H(3a)	0.0300	0.6440	0.2672	6*
H(3b)	0.1559	0.6856	0.2998	6*
H(4a)	0.0915	0.4761	0.2811	7*
H(4b)	0.1115	0.5280	0.3329	7*
H(5a)	0.3064	0.4253	0.3016	6*
H(5b)	0.3421	0.5296	0.3288	6*
H(21)	0.3586	0.8403	0.1687	7*
H(22)	0.2439	0.9853	0.2021	8*
H(23)	0.1746	1.1229	0.1481	6*
H(24)	0.2065	1.1106	0.0637	6*

Table 8. Continued

Atom[a]	x	y	z	B(A^2)
H(25)	0.3203	0.9637	0.0324	5*
H(27)	0.5999	0.9716	0.0831	4*
H(28)	0.8312	1.0221	0.0669	5*
H(29)	0.9879	0.9015	0.0387	6*
H(30)	0.9210	0.7285	0.0243	5*
H(31)	0.6895	0.6752	0.0417	4*
H(33)	0.5405	0.8081	-0.0292	4*
H(34)	0.4324	0.7963	-0.1071	5*
H(35)	0.1999	0.7404	-0.1175	6*
H(36)	0.0666	0.7079	-0.0477	5*
H(37)	0.1703	0.7258	0.0307	5*

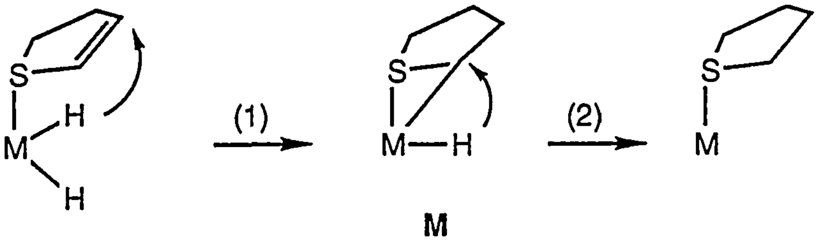
found. Carbon 4 lies 0.53(1) Å beneath the S, C(2), C(3), C(5) plane. The distances in the core of the complex are similar in many respects to those of the dithioformate-bridged complex, $(\mu\text{-H})(\mu\text{-}S_2CH)Os_3(CO)_9(PMe_2Ph)$, F.[39] The DHT•H-bridged Os(1)-Os(2) distance (2.7907(4) Å) is the shortest Os-Os bond length in **X**; likewise, the dithioformate-bridged Os-Os distance (2.854(1) Å) is the shortest in **F**. The longest Os-Os distance (3.043(1) Å) in **F** was assigned to the hydride-bridged Os-Os bond, as it is known[40-42] that metal-metal bonds are lengthened by a hydride bridge. In **X**, the longest distance (3.0718(5) Å) is Os(2)-Os(3), which is presumably also the site of the bridging hydride; this is supported by a peak of electron-density in this region found in the structure solution (see the Experimental Section). The Os(1)-C(2) bond in **X** is 2.215(8) Å. This distance is similar to the sum (2.21 Å) of the metallic and covalent radii[36] of Os and $C(sp^3)$. The distance [2.407(2) Å] between Os(1) and S(1) in **X** is comparable to the Os-S distances in **F** (2.424(2) and 2.442(2) Å) and $Os_3(\mu\text{-SPh})(\mu\text{-CH=CH}_2)(CO)_{10}$ [2.459(4) and 2.446(4) Å].[41] The average C-C distance (1.52 Å) in the DHT•H ligand and the C-S distances of 1.815 and 1.82 are in the range of normal C-C[34] and C-S[32] distances, respectively.



F

Relevance to Thiophene HDS

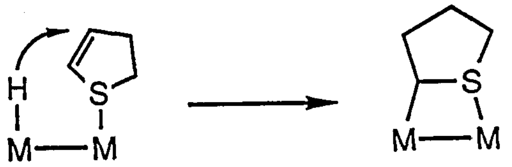
As noted in the Introduction, 2,3-DHT undergoes ready hydrogenation to tetrahydrothiophene (eq. 2) under HDS conditions. A possible mechanism (eq. 9) for this hydrogenation involves initial coordination of the S to a metal hydride site followed by hydrogen transfer to the β-carbon of the olefin to give an η^2-DHT•H intermediate (step 1). This transfer is



9

M

supported by the observation of a similar transfer in the reaction of $HPt(acetone)(PR_3)_2^+$ with 2,3-DHT. It is also possible that this H transfer could occur at 2 metal centers on a catalyst surface (eq. 10).



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N

An analogous transfer was observed in the reaction of $H_2Os_3(CO)_{10}$ with 2,3-DHT (eq. 8). The final conversion of the η^2-DHT•H intermediates, **M** in eq. 9 and **N** in eq. 10, to THT could occur by transfer of another hydrogen to the ligand. Perhaps related to this later step is the reaction (eq. 7) of $CpW(CO)_2(\eta^2\text{-DHT}\bullet H)$ with HCl to give $CpW(CO)_2(THT)Cl$. These studies demonstrate that there are model reactions of 2,3-DHT complexes which reasonably account for the hydrogenation of 2,3-DHT to THT on HDS catalysts.

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Supplementary material available: listings of bond distances (three pages), bond angles (five pages), planes (four pages), thermal parameters (12 pages), calculated and observed structure factors (43 pages) for $[Pt(PEt_3)_2(DHT{\bullet}H)]PF_6$ and $HOs_3(CO)_9(PPh_3)(DHT{\bullet}H)$. Ordering information is given on any current masthead page.

REFERENCES

1. (a) Mitchell, P. C. H. In "Catalysis"; Kemball, C., Ed.; The Chemical Society: London, 1977; Vol. 1, p 223; Vol. 4, p 203 ("Special Periodical Report"). (b) Lesch, D. A.; Richardson, Jr., J. W.; Jacobson, R. A.; Angelici, R. J. J. Am. Chem. Soc. 1984, 106, 2901. (c) Huckett, S. C.; Sauer, N. N.; Angelici, R. J. Organometallics 1987, 6, 591. (d) Spies, G. H.; Angelici, R. J. Organometallics 1987, 6, 1897. (e) Hachgenei, J. W.; Angelici, R. J. Angew. Chem., Int. Ed. Engl. 1987, 26, 909. (f) Hachgenei, J. W.; Angelici, R. J. J. Organomet. Chem. 1988, accepted for publication.

2. (a) Desikan, P.; Amberg, C. H. Can. J. Chem. 1964, 42, 843. (b) Zdrazil, M. Collect. Czech. Chem. Commun. 1975, 40, 3491. (c) Devanneux, J.; Marvin, J. J. Catal. 1981, 69, 202.

3. (a) Angelici, R. J. Acc. Chem. Res. 1988, accepted for publication. (b) Markel, E. J.; Sauer, N. N.; Angelici, R. J.; Schrader, G. L. J. Catal. 1988, submitted for publication.

4. (a) Sauer, N. N.; Angelici, R. J. Inorg. Chem. 1987, 26, 3424. (b) Sauer, N. N.; Angelici, R. J.; Huang, Y. C. J.; Trahanovsky, W. S. J. Org. Chem. 1986, 51, 113.

5. (a) Shriver, D. F.; Drezdon, M. A. "The Manipulation of Air Sensitive Compounds" 2nd Edition; John Wiley and Sons: New York, 1986. (b) Herzog, S.; Dehnert, J.; Luhder, K. "Technique of Inorganic Chemistry"; Jonassen, H. B., Ed.; Interscience: New York, Vol. VII, 1969.

6. Hollis, L. S.; Lippard, S. J. J. Am. Chem. Soc. 1983, 105, 3494.

7. Parshall, G. W. Inorg. Syn. 1970, 12, 26.

8. Clark, H. C.; Kurosawa, H. J. Organomet. Chem. 1972, 36, 399.

9. Cariati, F.; Ugo, R.; Bonati, F.; Inorg. Chem. 1966, 5, 1128.

10. Knox, S. A. R.; Koepke, J. W.; Andrews, M. A.; Kaesz, H. D. J. Am. Chem. Soc. 1975, 97, 3942.

11. Deeming, A. J.; Hasso, S, J. Organomet. Chem 1975, 88, C21.

12. Clark, H. C.; Jablonski, R. C. Inorg. Chem. 1974, 13, 2213.

13. (a) SHELXS-86, Sheldrick, G. M. Institut fur Anorganische Chemie der Universitat, Gottingen, F. R. G. (b) Sheldrick, G. M. In "Computing in Crystallography"; Schenk, H.; Olthof-Hazekamp, R.; Van Koningsveld, H.; Bassi, G. C., Eds.; Delft University: Delft, 1978.

14. Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*, Vol. IV, The Kynoch Press: Birmingham, England, 1974, Table 2.2B.

15. Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* 1964, **17**, 781.

16. Cromer, D. T. *International Tables for X-ray Crystallography*, Vol. IV, The Kynoch Press: Birmingham, England, 1974, Table 2.3.1.

17. Gladysz, J. A.; Williams, G. M.; Tam, W.; Johnson, D. L.; Parker, D. W. *Inorg. Chem.* 1979, **18**, 553.

18. Tuleen, D. L.; Bennett, R. H. *J. Heterocyclic Chem.* 1969, **6**, 115.

19. King, R. B. In "Organometallic Syntheses"; Eisch, J. J.; King, R. B., Eds.; Academic Press: New York, 1965; Vol. 1, p 151.

20. Alway, D. G.; Barnett, K. W. *Inorg. Chem.* 1980, **19**, 1533.

21. Albinati, A.; Caseri, W. R.; Pregosin, P. S. *Organometallics* 1987, **6**, 788.

22. (a) Laycock, D. E.; Baird, M. C. *Inorg. Chim. Acta* 1980, **42**, 263. (b) Kreiter, C. G.; Koemn, U. *Z. Naturfosch.* 1983, **38b**, 943. (c) Johnson, L. K.; Angelici, R. J. *Inorg. Chem.* 1987, **26**, 973. (d) Green, M. L. H.; Nagy, P. L. I. *J. Organomet. Chem.* 1963, **1**, 58. (e) Faller, J. W.; Johnson, B. V. *J. Organomet. Chem.* 1975, **88**, 101.

23. Eekhof, J. H.; Hogeveen, H.; Kellog, R. M. *J. Organomet. Chem.* 1978, **161**, 361.

24. (a) Clark, H. C.; Kurosawa, K. *Inorg. Chem.* 1972, **11**, 1275. (b) Deeming, A. J.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc. D* 1970, 598. (c) Deeming, A. J.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* 1973, 1848.

25. Jesson, J. P. In "Transition Metal Hydrides"; Muetterties, E. L., Ed.; Marcel Dekker, Inc.: New York, 1971; p 75 and references therein.

26. Church, M. J.; Mays, M. J. *J. Chem. Soc. A*, 1970, 1938.

27. (a) Owston, P. G.; Rowe, J. M. *Acta Cryst.* 1960, 13, 253. (b) Gregory, U. A.; Jarvis, J. A. J.; Kilbourn, B. T.; Owston, P. G. *J. Chem. Soc. (A)*, 1970, 2770.

28. Miki, K.; Kai, Y.; Yasuoka, N.; Kasai, N. *J. Organomet. Chem.* 1977, 135, 53.

29. (a) Panattoni, C.; Bomberi, G.; Belluco, U.; Baddley, W. H. *J. Am. Chem. Soc.* 1968, 90, 798. (b) Bombieri, G.; Forsellini, E.; Panattoni, C.; Graziani, R.; Bandoli, G. *J. Chem. Soc. (A)* 1970, 1313.

30. Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* 1973, 10, 335.

31. McWeeny, R.; Mason, R.; Towl, A. D. C. *Discuss. Faraday Soc.* 1969, 47, 20.

32. O'Connor, E. J.; Helquist, P. *J. Am. Chem. Soc.* 1982, 104, 1869 and references therein.

33. (a) Karcher, B. A.; Jacobson, R. A. *J. Organomet. Chem.* 1977, 132, 387. (b) Abrahams, S. C. *Quart. Rev.* 1956, 10, 407. (c) Mayerle, J. J. *Inorg. Chem.* 1977, 16, 916.

34. (a) Bartell, L. S.; Higginbotham, H. K. *J. Chem. Phys.* 1965, 42, 851. (b) Wagner, R. S.; Dailey, B. P. *J. Chem. Phys.* 1957, 26, 1588. (c) Momany, F. A.; Bonham, R. A.; Druelinger, M. L. *J. Am. Chem. Soc.* 1963, 85, 3075. (d) Lide, D. R.; Jen, M. *J. Chem. Phys.* 1963, 38, 1504. (e) Bonham, R. A.; Bartell, L. S.; Kohl, D. A. *J. Am. Chem. Soc.* 1959, 81, 4765. (f) Iijima, T. *Bull. Chem. Soc. Jpn.* 1972, 45, 1291. (g) Hilderbrandt, R. L.; Wieser, J. D. *J. Mol. Stuct.* 1973, 15, 27. (h) Tables of Interatomic Distances and Configuration in Molecules and Ions, Chem. Soc. Spec. Publ. no. 11; 1958. (i) International Distances Supplement, Chem. Soc. Spec. Publ. no. 18; 1965.

35. Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* 1983, 395.

36. Moeller, T. In "Inorganic Chemistry; A Modern Introduction"; John Wiley and Sons: New York, 1982; p 70.

37. Boyar, E.; Deeming, A. J.; Arce, A. J.; de Sanctis, Y. *J. Organomet. Chem.* 1984, 276, C45.

38. Boyar, E.; Deeming, A. J.; Henrick, K.; McPartlin, M.; Scott, A. *J. Chem. Soc., Dalton Trans.* 1986, 1431.

39. Adams, R. D.; Selegue, J. P. *J. Organomet. Chem.* 1980, 195, 223.

40. Teller, R. G.; Bau, R. *Struct. and Bonding* 1981, **44**, 1.

41. Churchill, M. R.; Hollander, F. J. *Inorg. Chem.* 1980, **19**, 306.

42. Deeming, A. J. *Adv. Organometal. Chem.* 1986, **26**, 1.

SECTION III. 2,3-DIHYDROTHIOPHENE (2,3-DHT) COMPLEXES OF TUNGSTEN. THE STRUCTURE OF $W(CO)_3$(dppe)(2,3-DHT)

ABSTRACT

Several phosphine-containing tungsten carbonyl complexes of 2,3-dihydrothiophene (2,3-DHT) have been prepared as models for the adsorption of this partly hydrogenated thiophene on hydrodesulfurization (HDS) catalyst surfaces. The X-ray determined structure of $W(CO)_3$(dppe)(2,3-DHT) is also described. In all complexes, the 2,3-DHT ligand is coordinated through the sulfur and not the olefin.

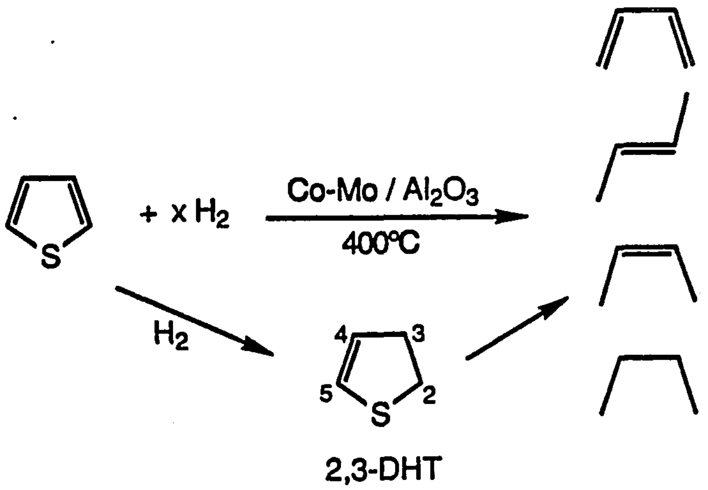
$$W(CO)_4(L\frown L) \xrightarrow[THF]{h\nu} W(CO)_4(L\frown L)(THF) \xrightarrow{2,3\text{-DHT}} \underline{fac}\text{-}W(CO)_3(L\frown L)(2,3\text{-DHT}) \quad 1$$

$$W(CO)_5L \xrightarrow[THF]{h\nu} W(CO)_4(L)(THF) \xrightarrow{2,3\text{-DHT}} \underline{cis}\text{-}W(CO)_4(L)(2,3\text{-DHT}) \quad 2$$

$L\frown L$ = dppe, dmpe; L = PPh_3, PMe_3, PMe_2Ph, $PMePh_2$

INTRODUCTION

Catalytic hydrodesulfurization (HDS) is the process which removes sulfur from thiophene and other sulfur-containing organic compounds in crude oil. Model organometallic complexes of thiophene and thiophene derivatives have been studied in our research group in an effort to elucidate the mechanism of the HDS process.[1] The formation of 2,3-dihydrothiophene (2,3-DHT) has been proposed as the first step in the



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HDS of thiophene.[2] In an effort to examine the coördination modes of this partly hydrodrogenated thiophene, which potentially could coordinate through the olefin or the sulfur on the catalyst surface, a number of its transition metal complexes have been prepared in recent years: $Mn(CO)_3Cl(2,3\text{-DHT})$,[1a] $W(CO)_5(2,3\text{-DHT})$,[3] $[Re(CO)_5(2,3\text{-DHT})]SO_3CF_3$,[3] $Ru(CO)_3Cl_2(2,3\text{-DHT})$,[3] and $PdCl_2(2,3\text{-DHT})_2$. We report in this paper the syntheses of a variety of phosphine substituted tungsten complexes and the first X-ray determined structure of a 2,3-DHT compound.

EXPERIMENTAL SECTION

General Procedures

All reactions were carried out under an atmosphere of prepurified N_2 at room temperature using standard inert atmosphere and Schlenk[4] techniques unless otherwise stated. Tetrahydrofuran (THF) and Et_2O were distilled under N_2 from Na/benzophenone. Pentane, hexanes, MeCN and CH_2Cl_2 were distilled from CaH_2 under N_2.

Trimethylphosphine was prepared by the reaction of methyl Grignard reagent and triphenylphosphite.[5] Diphenylmethylphosphine and PMe_2Ph were obtained from Strem Chemicals and used without further purification. Triphenylphosphine was used as received from SCM Chemicals.

Infrared spectra were obtained using a Perkin Elmer 681 spectrophotometer, and spectra were referenced to the 1944.0 cm^{-1} band of polystyrene. The ^1H data were recorded on a Nicolet NT-300 MHz spectrometer using Me_4Si as the internal reference. Low temperature ^1H NMR spectra were obtained on a Bruker WM 300 MHz instrument. Electron impact mass spectra (EIMS) were obtained on a Finnigan 4000. Fast atom bombardment (FAB, glycerol matrix) mass spectra were obtained using a Kratos MS-50 spectrometer. Photochemical reactions were carried out in a quartz Schlenk tube equipped with a cooling probe using a reactor obtained from Bradford Scientific, Inc., Marblehead, MA.

The following compounds were prepared using methods published in the literature: 2,3-DHT,[3,6] $W(CO)_4(dppe)$,[7] $Mo(CO)_4(dppe)$,[7] $W(CO)_4(dmpe)$,[8] $W(CO)_5(PPh_3)$[9] and $W(CO)_5(PMe_3)$,[10] where dppe = $Ph_2PCH_2CH_2PPh_2$ and dmpe = $Me_2PCH_2CH_2PMe_2$.

Synthesis of $W(CO)_3(dppe)(2,3\text{-}DHT)$, I

A THF (35 mL) solution of $W(CO)_4(dppe)$ (0.29 g, 0.42 mmol) was placed in quartz tube equipped with a water-cooled probe and purged with N_2. The solution was irradiated with 254 nm light for 7.5 h with the progress of the reaction to give $W(CO)_3(dppe)(THF)$ being monitored by IR. A pentane solution of 2,3-DHT[3] (0.36 M, 4.5 mL, 1.6 mmol) was added to the reaction mixture and stirred for 30 min. The volume of solvent was then reduced in vacuo to ~5 mL. Addition of pentane (~10 mL) led to the precipitation of a yellow solid. The mixture was stored at -20 °C for 15 h. The solvent was decanted off and the yellow-green residue dried in vacuo. Compound I was obtained as a yellow-green powder (0.30 g, 95%). FAB MS: 752 (M^+), 724 (M^+-CO), 666 (M^+-DHT), 610 [M^+-(2CO+DHT)], 582 [M^+-(3CO+DHT)], 398 ($dppe^+$). ^1H NMR (C_6D_6): δ 4.92 (m, 1 H, H5), 4.73 (td, 1 H, H4, J_{4-5} = 6.0 Hz, J_{3-4} = 2.1 Hz), 2.32 (t, 2 H, H2, J_{2-3} = 7.9 Hz), 1.97 (tt, 2 H, H3), 2.0-2.18 and 2.36-2.58 (m, 4 H, CH_2), 7.98-6.96 (m, 20 H, Ph). Anal. Calcd for $C_{33}H_{30}O_3P_2SW$: C, 52.68; H. 4.02; S, 4.25. Found: C, 52.52; H, 4.16; S, 3.70. Yellow-green cube-like crystals of I, which readily lost their luster when removed from the mother liquor, were obtained on storing a concentrated THF solution of I at -20 °C for 20 h.

Determination of X-ray Structure of $W(CO)_3(dppe)(2,3\text{-}DHT)\cdot 2THF$

Data collection

Because crystals of the title compound rapidly deteriorated when removed from the parent solution, the chosen crystal was quickly mounted on the end of a glass fiber, then immediately moved to the diffractometer where it was cooled to 165 K. A yellow crystal of $W(CO)_3(dppe)(DHT)\cdot 2THF$ was mounted on the fiber in a random orientation. Preliminary examination and data collection were performed on an Enraf-Nonius CAD4 computer controlled kappa axis diffractometer. The crystal was cooled with an Enraf-Nonius FR-558 low temperature system. Important data collection parameters are summarized in Table 2.

Data reduction

A total of 5229 reflections were collected, of which 4954 were unique and not systematically absent. As a check on crystal and electronic stability, three representative reflections were measured every 60 min. No significant loss of intensity was observed throughout the data collection, so no decay correction was applied.

Lorentz and polarization corrections were applied to the data. The linear absorption coefficient is 32.7 cm^{-1} for MoKα radiation. Intensities of equivalent reflections were averaged. The agreement factors for the averaging of 475 observed and accepted reflections was 4.6% based on intensity and 2.7% based on F_o.

Structure Solution and Refinement

The positions of all 40 non-hydrogen atoms in the tungsten complex were given by a Patterson interpretation method.[11] The remainder of the non-hydrogen atoms (two molecules of THF in the lattice) were located after subsequent least-squares refinement cycles and a difference-Fourier map. Since no empirical absorption correction had been made, the following procedure was used: Following least-squares refinement of all

Table 1. Infrared data for the complexes in THF solvent

Compound	ν(CO), cm^{-1}
$W(CO)_3$(dppe)(2,3-DHT), I	1932(s), 1844(s), 1829(ms, sh)
$Mo(CO)_3$(dppe)(2,3-DHT), II	1936(s), 1851(s), 1835(s, sh)
$W(CO)_3$(dmpe)(2,3-DHT), III	1928(s), 1838(s), 1817(s)
$W(CO)_4(PPh_3)$(2,3-DHT), IV	2020(m), 1845(vs), 1811(s)
$W(CO)_4(PMe_3)$(2,3-DHT), V	2017(m), 1840(s, broad), 1790(ms)
$W(CO)_4(PMePh_2)$(2,3-DHT), VI	2022(ms), 1845(vs), 1818(s)
$W(CO)_4(PMe_2Ph)$(2,3-DHT), VII[a]	2022(m), 1842(s), 1815(ms)
$W(CO)_5$(2,3-DHT), VIII	2080(w), 1937(vs), 1915(s, sh)

[a] In hexanes.

Table 2. Crystal data for $W(CO)_3(dppe)(2,3\text{-DHT})\cdot 2THF$, I

Formula	$WSP_2C_{41}O_5H_{46}$, i.e., $WSP_2O_3C_{33}H_{30}\cdot 2(C_4H_8O)$
Formula weight	896.68
Space group	$P2_1/n$, no. 14
a, Å	13.648(8)
b, Å	16.263(7)
c, Å	17.20(2)
β, deg	93.62(8)
V, $Å^3$	3809(8)
Z	4
d_{calc}, g/cm^3	1.563
Crystal size, mm	0.3 x 0.4 x 0.5
$\mu(MoK_\alpha)$, cm^{-1}	32.74
Data collection instrument	Enraf-Nonius CAD4
Radiation (monochromated in in incident beam)	MoK_α ($\lambda = 0.71073$ Å)
Orientation reflections, number, range (2θ)	25, $24 < 2\theta < 32$
Temperature, °C	-110(5)
Scan method	θ-2θ
Data collection range, 2θ, deg	0-45
Number of unique data, total	4954
with $F_o^2 > 3\sigma(F_o^2)$	4143
Number of parameters refined	169

Table 2. Continued

Absorption correction	numerical
R^a	0.0896
$R_w{}^b$	0.1590
Quality-of-fit indicator[c]	4.4
Largest shift/esd, final cycle	0.01
Largest peak, e/Å^3	4.13

[a] $R = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$.

[b] $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

[c] Quality-of-fit $= [\Sigma w(|F_o| - |F_c|)^2 / (N_{obs} - N_{parameters})]^{1/2}$.

of the non-hydrogen atoms with isotropic thermal parameters, including values of F_{calc} based on hydrogen atoms in calculated positions, a numerical absorption correction was made on the unaveraged data. The data were then again averaged, and refinement was continued.

Although the data set provided a large ratio of observed to unobserved reflections, it was not possible to refine the structure using anisotropic thermal parameters for any but the heavy atoms. In order to aid the refinement process, several constraints were added. Expected carbon-oxygen bond lengths for the CO groups were added as observations in the least-squares calculations, and the phenyl rings were refined as rigid groups. Also, the isotropic thermal parameters for the carbonyl oxygen atoms were restrained to be 1.3 times the isotropic thermal parameters for the attached carbon atoms. The final atomic positional parameters are given in Table 3.

The relatively large errors in the calculated bond lengths and bond angles (see the appropriate tables) arise from the large errors in the cell constants as determined from the 25 orientation reflections. However, the general structure of the complex is sound.

Scattering factors were taken from Cromer and Waber.[12] Anomalous dispersion effects were included in F_c;[13] the values for f' and f" were those of Cromer.[14] Only those reflections having intensities greater than 3.0 times their standard deviation were used in the refinements. Refinement was carried out with the SHELX-76 program package.

Table 3. Table of positional parameters and their estimated standard deviations for $W(CO)_3$(dppe)(2,3-DHT)•2THF, I

Atom	x	y	z	$B(A^2)^{a,b}$
W	0.24027(6)	0.23531(5)	0.21988(4)	1.14(2)
S	0.2589(4)	0.2950(3)	0.3586(3)	1.3(1)
P(1)	0.1226(4)	0.1363(3)	0.2773(3)	1.2(1)
P(2)	0.3582(4)	0.1270(3)	0.2669(3)	1.3(1)
C(1)	0.137(1)	0.314(1)	0.194(1)	1.5(2)*
C(2)	0.226(2)	0.184(1)	0.1173(9)	2.1(2)*
C(3)	0.346(1)	0.307(1)	0.186(1)	2.2(2)*
O(1)	0.077(1)	0.3614(8)	0.1703(8)	1.9(2)*
O(2)	0.223(1)	0.1552(9)	0.0541(8)	2.7(3)*
O(3)	0.407(1)	0.3480(9)	0.1599(9)	2.8(3)*
C(4)	0.195(1)	0.056(1)	0.333(1)	1.0(2)*
C(5)	0.287(1)	0.034(1)	0.291(1)	1.0(2)*
C(10)	0.0431(9)	0.1774(8)	0.3488(6)	1.5(4)*
C(16)	0.038(1)	0.0792(8)	0.2105(7)	1.9(4)*
C(22)	0.4519(9)	0.0845(8)	0.2069(7)	1.5(4)*
C(28)	0.4333(9)	0.1508(8)	0.3569(6)	1.4(4)*
C(6)	0.337(2)	0.380(1)	0.364(1)	1.7(4)*

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[a] Starred atoms were refined isotropically.

[b] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3) * [a^2*B(1,1) + b^2*B(2,2) + c^2*B(3,3) + ab(\cos \gamma)*B(1,2) + ac(\cos \beta)*B(1,3) + bc(\cos \alpha)*B(2,3)]$.

Table 3. Continued

Atom	x	y	z	$B(A^2)^{a,b}$
C(7)	0.304(2)	0.443(1)	0.401(1)	2.0(4)*
C(8)	0.204(2)	0.432(1)	0.432(1)	2.2(4)*
C(9)	0.159(2)	0.361(1)	0.383(1)	1.5(4)*
C(11)	0.0529(9)	0.1614(8)	0.4286(6)	2.3(4)*
C(12)	-0.0118(9)	0.1971(8)	0.4783(6)	2.4(4)*
C(13)	-0.0864(9)	0.2490(8)	0.4483(6)	2.6(5)*
C(14)	-0.0962(9)	0.2650(8)	0.3685(6)	2.5(4)*
C(15)	-0.0315(9)	0.2292(8)	0.3187(6)	1.5(4)*
C(17)	-0.007(1)	0.0072(8)	0.2352(7)	3.2(5)*
C(18)	-0.074(1)	-0.0341(8)	0.1852(7)	2.4(4)*
C(19)	-0.098(1)	-0.0036(8)	0.1105(7)	2.1(4)*
C(20)	-0.054(1)	0.0684(8)	0.0859(7)	2.9(5)*
C(21)	0.014(1)	0.1097(8)	0.1359(7)	1.7(4)*
C(23)	0.5109(9)	0.0204(8)	0.2367(7)	1.9(4)*
C(24)	0.5774(9)	-0.0175(8)	0.1898(7)	1.8(4)*
C(25)	0.5849(9)	0.0086(8)	0.1132(7)	1.7(4)*
C(26)	0.5259(9)	0.0727(8)	0.0834(7)	1.8(4)*
C(27)	0.4594(9)	0.1106(8)	0.1302(7)	1.8(4)*
C(29)	0.4938(9)	0.2197(8)	0.3537(6)	1.1(3)*
C(30)	0.5501(9)	0.2448(8)	0.4200(6)	2.8(5)*
C(31)	0.5459(9)	0.2009(8)	0.4895(6)	2.4(4)*
C(32)	0.4854(9)	0.1320(8)	0.4926(6)	2.7(5)*

Table 3. Continued

Atom	x	y	z	B(A^2)^{a,b}
C(33)	0.4291(9)	0.1070(8)	0.4263(6)	1.8(4)*
0100	0.198(2)	0.016(1)	0.520(1)	4.5(4)*
C101	0.243(2)	-0.060(2)	0.514(1)	3.4(5)*
C102	0.275(2)	-0.082(2)	0.597(2)	4.3(6)*
C103	0.198(2)	-0.040(2)	0.642(1)	3.0(5)*
C104	0.139(2)	0.012(2)	0.587(2)	3.9(6)*
0200	0.757(1)	0.332(1)	0.2110(9)	3.2(3)*
C201	0.808(2)	0.329(2)	0.141(2)	4.6(6)*
C202	0.778(3)	0.254(2)	0.097(2)	6.8(9)*
C203	0.738(3)	0.195(3)	0.162(2)	6.8(9)*
C204	0.702(3)	0.255(2)	0.213(2)	4.6(7)*

Synthesis of $Mo(CO)_3(dppe)(2,3\text{-}DHT)$, II

This synthesis was carried out as described for the W analog starting with $Mo(CO)_4(dppe)$ (0.15 g, 0.25 mmol) in THF (35 mL). The solution was irradiated with 366 nm light for 9 h with the progress of the reaction being monitored by IR, and a pentane solution of 2,3-DHT (0.25 M, 2.0 mL, 0.5 mmol) was added. The volume of the solvent was reduced in vacuo after stirring for 1 h and pentane (40 mL) was added. The mixture was stored at -20 °C overnight. A yellow powder of II was obtained in ~60% yield. This compound was only characterized by its IR and ^1H NMR. ^1H NMR (C_6D_6): δ 4.96 (m, 1 H, H5), 4.79 (td, 1 H, H4, J_{4-5} = 5.8 Hz, J_{3-4} = 2.1 Hz), 2.19 (t, 2 H, H2, J_{2-3} = 8.1 Hz), 1.98 (tt, 2 H, H3), 2.3-2.5 and 2.05-2.18 (m, 4 H, CH_2), 7.34-7.98 (m, 20 H, Ph). The solution NMR of II taken 15 min after dissolution, showed the presence of a large amount of free 2,3-DHT. The formation of $Mo(CO)_4(dppe)$ is also apparent in the NMR. The MS spectrum of a solid sample of II stored at ambient temperature overnight showed a fragmentation pattern which corresponds to $Mo(CO)_4(dppe)$.

Reaction of $W(CO)_3(dppe)(2,3\text{-}DHT)$ with CO

Compound I (20 mg, 0.027 mmol) was placed in a 100 mL Schlenk flask under nitrogen and THF (5 mL) was added. Carbon monoxide was bubbled through for 5 h. The mixture was then sealed under one atmosphere of CO and stirring was continued overnight (12 h). The solvent was removed in vacuo and the residue extracted with benzene. The benzene extract was pumped to dryness. The ^{1}H NMR and IR showed that $W(CO)_4(dppe)$ (14 mg, 76%) was the only organometallic product.

Synthesis of $W(CO)_3(dmpe)(2,3\text{-DHT})$, III

A THF (35 mL) solution of $W(CO)_4(dmpe)$ (0.21 g, 0.47 mmol) was placed in a quartz tube and irradiated with 254 nm light as described for $W(CO)_4(dppe)$. Photolysis was discontinued after 6 h, a pentane solution of 2,3-DHT (0.20 M, 5 mL, 1.0 mmol) was added and the mixture stirred for 30 min. The volume of the solvent was reduced in vacuo and excess hexanes (40 mL) added. The mixture was stored at -20 °C for 7 days. Yellow crystalline solid III (0.15 g, 63%) was obtained after filtration and drying. MS: 504 (M^+), 476 (M^+-CO), 446 [M^+-(2CO+2H)], 418 [(M^+-DHT) or [M^+-(3CO+2H)]], 390 [M^+-(CO+DHT)], 362 [M^+-(2CO+DHT)], 334 [M^+-(3CO+DHT)], 86 (DHT^+, base peak). ^{1}H NMR (C_6D_6): δ 5.75 (td, 1 H, H5, J_{4-5} = 5.7 Hz, J_{3-5} = 2.2 Hz), 5.20 (m, 1 H, H4), 3.00 (t, 2 H, H2, J_{2-3} = 7.9 Hz), 2.32 (tt, 2 H, H3), 0.7-1.5 (m, 4 H, CH_2), 1.37 (d) and 0.91 (d) (12 H, Me, J = 7.5 Hz, J = 6.2 Hz). Anal. Calcd for $C_{13}H_{22}O_3P_2SW$: C, 30.97; H, 4.40; S, 6.35. Found: C, 31.29; H, 4.40; S, 5.81.

Synthesis of $W(CO)_4(PR_3)(2,3\text{-DHT})$, $PR_3 = PPh_3$

A THF (30 mL) solution of $W(CO)_5(PPh_3)$ (0.10 g, 0.17 mmol) was placed in a quartz tube and purged with N_2. The solution was then irradiated with 254 nm light for 2 h while N_2 was still bubbling through it. A pentane solution of 2,3-DHT (0.22 M, 1.8 mL, 0.40 mmol) was added and stirred for 30 min under N_2. The volume of the solvent was reduced to ~2 mL, pentane (20 mL) was added, and the solution was cooled at -20 °C for 3 days. The compound $W(CO)_4(PPh_3)$(2,3-DHT), **IV** (40 mg, 36%) was obtained as a yellow-green powder. MS: 586 [M^+-(2H+2CO)], 558 {[M^+-(2H+3CO)] or (M^+-DHT)}, 530 {[M^+-(2H+4CO)] or [M^+-(DHT+CO)]}, 502 [M^+-(DHT+2CO)], 474 [M^+-(DHT+3CO)], 446 [M^+-(DHT+4CO)], 262 (PPh_3^+), 84 (thiophene, base peak). ^{1}H NMR (C_6D_6): δ 4.99 (td, 1 H, H5, J_{4-5} = 5.8 Hz, J_{3-5} = 2.2 Hz), 4.76 (m, 1 H, H4), 2.41 (t, 2 H, H2, J_{2-3} = 7.9 Hz), 1.83 (tt, 2 H, H3), 7.37-7.31 and 6.90-6.65 (m, Ph). **PR_3=PMe_3.** The synthesis of cis-$W(CO)_4(PMe_3)$(2,3-DHT), **V**, was carried out as described for **IV** starting with $W(CO)_5(PMe_3)$ (0.035 g, 0.088 mmol) in THF (35 mL). The solution was irradiated with 254 nm light for 3 h, after which a pentane solution of 2,3-DHT (0.22 M, 0.45 mL, 0.099 mmol) was added. The solution was stirred for 30 min and the solvent removed in vacuo to give a dark green oil of **V** (~40%). Attempts to crystallize **V** from THF/hexanes gave an oil and some decomposition. MS: 458 (M^+), 400 [M^+-(2CO+2H)], 86 (DHT^+, base peak), 76 (PMe_3^+). ^{1}H NMR (C_6D_6): δ 5.57 (td, 1 H, H5, J_{4-5} = 5.74 Hz, J_{3-5} = 2.2 Hz), 5.07 (m, 1 H, H4), 2.81 (t, 2 H, H2, J_{2-3} = 8.0 Hz), 2.17 (tt, 2 H, H3), 1.09 (d, 9 H, PMe_3, J = 7.2 Hz). The compound cis-$W(CO)_4(PMe_3)_2$ was also formed in this reaction and was not separated from **V**. **PR_3=$PMePh_2$.** A THF (35 mL) solution of $W(CO)_6$ (0.15 g, 0.43 mmol) in a quartz tube equipped with a side arm was purged by bubbling N_2 for 15 min. The solution was then irradiated with 366 nm light for 8 h, the $W(CO)_5$(THF) generated was treated with $PMePh_2$ (0.086 g, 0.43 mmol, 54 μL) and the solution stirred for 30 min. The resulting $W(CO)_5(PMePh_2)$ was irradiated with 254 nm light for 2 h and the solution treated with a pentane solution of 2,3-DHT (0.19 M, 3.0 mL, 0.57 mmol).

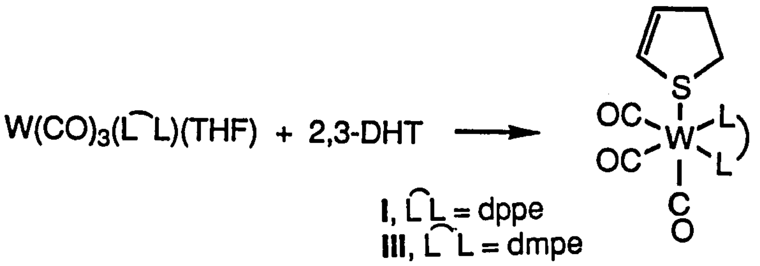
The solution was stirred for 30 min and the solvent reduced in volume to ~5 mL. The mixture was layered with hexanes and stored at -20 °C for 20 h. Compound $W(CO)_4(PMePh_2)(2,3\text{-DHT})$, **VI**, was obtained as a dark green oil (~50%). Some $W(CO)_4(PMePh_2)_2$ was also formed and was not separated. MS: 582 (M^+), 554 (M^+-CO), 524 [M^+-(2CO+2H)], 496 {(M^+-DHT) or [M^+-(3CO+2H)]}, 468 {[M^+-(DHT+CO)] or [M^+-(4CO+2H)]}, 440 [M^+-(DHT+2CO)], 86 (DHT^+, base peak). ^1H NMR (C_6D_6): δ 5.24 (td, 1 H, H5, J_{4-5} = 5.7 Hz, J_{3-5} = 2.2 Hz), 5.00 (m, 1 H, H4), 2.63 (t, 2 H, H2, J_{2-3} = 7.9 Hz), 2.08 (tt, 2 H, H3), 1.90 (d, 3 H, PMe, J = 7.3 Hz), 8.0-7.0 (m, Ph).

PR_3=PMe_2Ph. The compound <u>cis</u>-$W(CO)_4(PMe_2Ph)(2,3\text{-DHT})$, **VII**, was prepared as described above, starting with $W(CO)_6$ (0.14 g, 0.40 mmol) in THF (35 mL). The solution was photolyzed using 366 nm light for 8 h and PMe_2Ph (56.6 μL, 0.40 mmol) was added. After stirring for 30 min, further photolysis using 254 nm light for 4 h was carried out and 1.5 equivalents of a pentane solution of 2,3-DHT was added. Stirring was continued for 30 min, the volume of solvent was reduced to ~5 mL, pentane (~10 mL) was added, and the mixture was stored at -20 °C for 16 h. Compound <u>cis</u>-$W(CO)_4(PMe_2Ph)(2,3\text{-DHT})$, **VII**, was obtained as a dark green oil (~45%). The <u>cis</u>-$W(CO)_4(PMe_2Ph)_2$ was also formed and was not separated from **VII**. MS: 462 [M^+-(2CO+2H)], 434 {(M^+-DHT) or [M^+-(3CO+2H)]}, 378 [M^+-(DHT+2CO)], 350 [M^+-(DHT+3CO)], 86 (DHT^+, base peak). ^1H NMR (C_6D_6): δ 5.22 (td, 1 H, H5, J_{4-5} = 5.8 Hz, J_{3-5} = 2.2 Hz), 4.93 (m, 1 H, H4), 2.58 (t, 2 H, H2, J_{2-3} = 7.9 Hz), 2.02 (tt, 2 H, H3), 1.48 (d, $P\underline{Me_2}Ph$, J = 7.1 Hz), 7.06-6.95 (m, $PMe_2\underline{Ph}$).

RESULTS AND DISCUSSION

Synthesis of *fac*-$W(CO)_3(L\frown L)(2,3\text{-DHT})$ and *cis*-$W(CO)_4(L)(2,3\text{-DHT})$

Reaction of $W(CO)_3(L\frown L)(THF)$, obtained by photolytic decarbonylation of $W(CO)_4(L\frown L)$, with a pentane solution of 2,3-DHT in THF results in the



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formation of the facial sulfur-coordinated 2,3-DHT complexes I and III which are characterized by their IR, MS and elemental analysis. The 3 IR bands of approximately equal intensity observed for compounds I and III are characteristic of facial geometry.[15] While compound I is stable as a solid it slowly loses 2,3-DHT in solution to give $W(CO)_4(dppe)$ and an insoluble tungsten compound. The 2,3-DHT in I is also displaced by CO over a period of 18 h to give $W(CO)_4(dppe)$ in 76% yield. The Mo analog of I, II, was also prepared and found to be very unstable even as a solid at ambient temperature.

Similarly, the reaction of $W(CO)_4(L)(THF)$ with 2,3-DHT in THF results

$$W(CO)_4(L)(THF) \; + \; 2,3\text{-DHT} \longrightarrow \underline{cis}\text{-}W(CO)_4(L)(2,3\text{-DHT}) \qquad 2$$

$$L = PPh_3,\ PMe_3,\ PPh_2Me,\ PPhMe_2$$

in the formation of 2,3-DHT complexes with IR spectra characteristic of bis-substituted tetracarbonyltungsten compounds in which the two substituents are cis to each other.[7,8,10b] These unstable oils slowly decomposed even at -20 °C to give $W(CO)_4(L)_2$, $W(CO)_5(L)$ and an insoluble tungsten precipitate. The mass spectra of all the mono-phosphine substituted complexes of 2,3-DHT show a fragment with an m/e value attributable to $W(CO)_2(L)(\eta^6\text{-thiophene})$ suggesting that the formation of these thiophene compounds from the 2,3-DHT precursors occurs readily in the MS experiments.

NMR and Structural Studies

The ^1H NMR spectrum of I in d_6-benzene solvent shows an upfield shift for the coordinated 2,3-DHT signals (Table 5) in comparison to the signals observed for free 2,3-DHT. Similar shifts to higher fields were observed in the solvents $CDCl_3$, $(CD_3)_2CO$ and CD_3NO_2 for compound I. Such upfield shifts in olefin complexes are generally attributed to the formation of π-olefin complexes.[16] Also, in all the previously reported sulfur-coordinated 2,3-DHT compounds,[3,6] the olefin signals are shifted downfield with respect to the free ligand. An X-ray diffraction study of I was therefore undertaken in an effort to determine the bonding mode of the 2,3-DHT in I. An ORTEP plot of I showing the numbering scheme is given in Figure 1. Selected bond distances and angles are given in Table 4. The X-ray crystal studies show that the 2,3-DHT is coordinated through the sulfur with a W-S bond distance of 2.573(5) Å. Similar W-S bond distances have been reported in the literature: $W(CO)_5[(CH_3S)_2C{=}PPh_2Me]$[2.555(2) Å],[17a] $(CO)_4\overline{W\text{-}[S(\underline{t}\text{-Bu})CH_2CH_2S}(\underline{t}\text{-Bu})]$ [2.565(4) and 2.559(5) Å].[17b] The

Table 4. Selected bond distances (Å) and angles (°) for W(CO)$_3$(dppe)(2,3-DHT), I[a]

Bond Distances (Å)			
W - S	2.573(5)	W - P(1)	2.519(5)
W - C(0)	1.93-1.97	W - P(2)	2.486(6)
S - C(6)	1.75(2)	C(6) - C(7)	1.30(3)
S - C(9)	1.82(2)	C(8) - C(7)	1.52(3)
C(4) - C(5)	1.53(3)	C(8) - C(9)	1.53(3)

Bond Angles (°)			
S - W - P(1)	84.6(2)	W - S - C(9)	114.2(7)
S - W - P(2)	86.6(2)	C(6) - S - C(9)	89(1)
S - W - C(1)	89.7(6)	S - C(6) - C(7)	115(2)
S - W - C(2)	176.7(6)	S - C(9) - C(8)	107(1)
S - W - C(3)	91.1(6)	C(6) - C(7) - C(8)	116(2)
W - S - C(6)	111.8(7)	C(7) - C(8) - C(9)	103(2)

[a] The numbers in parentheses are estimated standard deviations.

Table 5. ^1H NMR chemical shifts of the 2,3-DHT ligand in the complexes in C_6D_6 solvent

Complexes[a]	H5	H4	H3	H2
$W(CO)_3(dppe)L$	4.92	4.73	1.97	2.32
$W(CO)_3(dmpe)L$	5.74	5.18	2.30	2.99
$W(CO)_4(PPh_3)L$	5.24	4.98	2.06	2.66
$W(CO)_4(PPh_2Me)L$	5.23	5.00	2.08	2.63
$W(CO)_4(PPhMe_2)L$	5.21	4.93	2.02	2.58
$W(CO)_4(PMe_3)L$	5.57	5.07	2.17	2.81
$W(CO)_5L$	5.23	4.83	1.87	2.44
L	5.92	5.23	2.23	2.77

[a] L = 2,3-DHT.

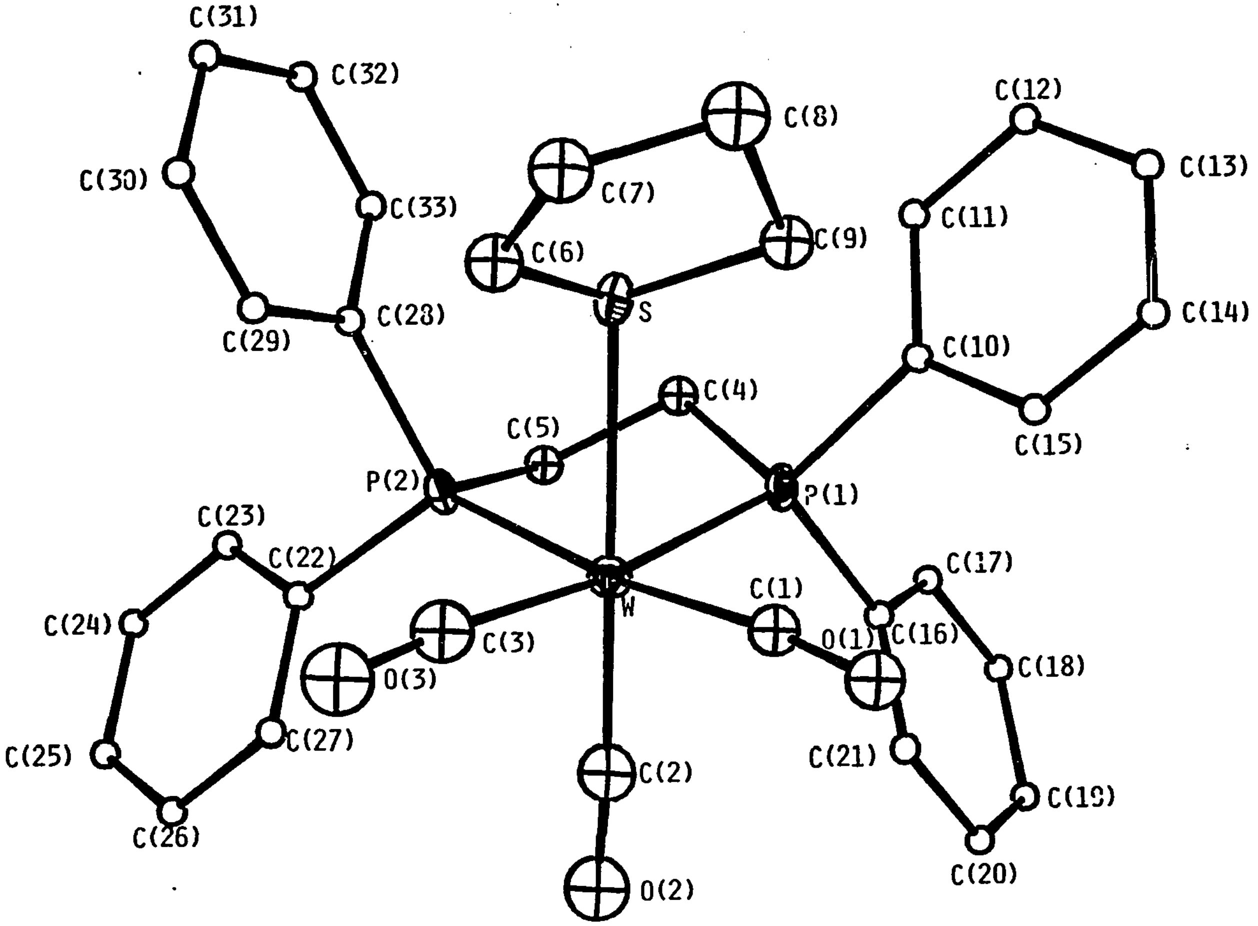

Figure 1. An ORTEP drawing of the $W(CO)_3(dppe)(2,3\text{-DHT})$, I

W-C6 and W-C7 distances of 3.61 Å and 4.64 Å indicate there is no interaction between the W and the olefin bond. The C6-C7 bond distance of 1.30(3) Å is comparable to reported C=C distances.[18] The C8 atom of the 2,3-DHT ligand is in the plane defined by S, C6 and C7.

While it is apparent that the 2,3-DHT is coordinated through the sulfur in the solid state, it is possible that in solution there is an equilibrium between sulfur- and olefin-coordinated forms. A temperature dependent ^1H NMR study of I in d_8-toluene was, therefore, carried out over the temperature range of 22 to -90 °C. With the exception of H2, which remained a triplet, the signals corresponding to 2,3-DHT in I are broadened with no distinct splitting at low temperature (-80 °C). Also, in comparison to the ambient temperature spectrum, the low temperature spectra of I show a further upfield shift (~0.2 ppm). However, there are no new signals which may be attributed to a distinctly different coordination mode for the 2,3-DHT. Due to the instabilities of I and III over long acquisition times, efforts to obtain evidence for an olefin coordinated form of 2,3-DHT by the use of W-^{13}C coupling were unsuccessful. Compound I does not react with $[Me_3O]BF_4$; methylation of the sulfur might be expected if the 2,3-DHT were coordinated through the olefin.

Other phosphine-substituted 2,3-DHT complexes were prepared in an attempt to understand the observed high field chemical shifts of the olefinic protons in I. Although trends in their ^1H NMR spectra (Table 5) are not completely understood, it appears that shielding of the 2,3-DHT by the phenyl rings of the phosphines in these compounds is primarily responsible for the upfield shifts observed. The solvent also probably plays a role since the 2,3-DHT protons in $W(CO)_5$(2,3-DHT) are downfield in $CDCl_3$ [δ 6.19 (H5), 5.87 (H4), 3.53 (H2), 2.96 (H3)] as compared with those in C_6D_6.

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REFERENCES

(1) (a) Lesch, D. A.; Richardson, Jr., J. W.; Jacobson, R. A.; Angelici, R. J. J. Am. Chem. Soc. 1984, 106, 2901. (b) Huckett, S. C.; Sauer, N. N.; Angelici, R. J. Organometallics 1987, 6, 591. (c) Spies, G. H.; Angelici, R. J. J. Am. Chem. Soc. 1985, 107, 5569. (d) Sauer, N. N.; Angelici, R. J. Organometallics 1987, 6, 1146. (e) Spies, G. H.; Angelici, R. J. Organometallics 1987, 6, 1897. (f) Hachgenei, J. W.; Angelici, R. J. Angew. Chem. Int. Ed. Engl. 1987, 26, 909. (g) Hachgenei, J. W.; Angelici, R. J. Organometallics 1988, accepted for publication. (h) Hachgenei, J. W.; Angelici, R. J. J. Organomet. Chem. 1988, in press.

(2) (a) Angelici, R. J. Acc. Chem. Res. 1988, accepted for publication. (b) Markel, E. J.; Schrader, G. L.; Sauer, N. N.; Angelici, R. J. J. Catal. 1988, submitted for publication. (c) Devanneaux, J.; Maurin, J. J. Catal. 1981, 69, 202. (d) Zdrazil, M. Collect. Czech. Chem. Commun. 1975, 40, 3491. (e) Desikan, P.; Amberg, C. H. Can. J. Chem. 1964, 42, 843.

(3) Sauer, N. N.; Angelici, R. J. Inorg. Chem. 1987, 26, 2126.

(4) (a) Shriver, D. F.; Drezdon, M. A. "The Manipulation of Air Sensitive Compounds". 2nd Edition, John Wiley and Sons: New York, 1986. (b) Herzog, S.; Dehnert, J.; Luhder, K. "Technique of Inorganic Chemistry", Jonassen, H. B. Ed., Interscience: New York, 1969, Vol. VII.

(5) Gibson, V. C.; Graimann, C. E.; Hare, P. M.; Green, M. L. H. J. Chem. Soc., Dalton Trans. 1985, 2025.

(6) Sauer, N. N.; Angelici, R. J.; Huang, Y. C. J.; Trahanovsky, W. S. J. Org. Chem. 1986, 51, 113.

(7) Grim, S. O.; Briggs, W. L.; Barth, R. C.; Tolman, C. A.; Jesson, J. P. Inorg. Chem. 1974, 13, 1095.

(8) (a) Darensbourg, D. J.; Kump, R. L. Inorg. Chem. 1978, 17, 2680. (b) Schenk, W. A.; Müller, H. Chem. Ber. 1982, 115, 3618.

(9) Wang, S. J.; Angelici, R. J. Inorg. Chem. 1988, in press.

(10) (a) Mathieu, R.; Lenzi, M.; Poilblanc, R. Inorg. Chem. 1970, 9, 2030. (b) Koemm, U.; Kreiter, C. G.; Strack, H. J. Organomet. Chem. 1978, 148, 179.

(11) Sheldrick, G. M. SHELXS-86, Institut fur Anorganische Chemie der Universitat, Gottingen, F.R.G.

(12) Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography," Vol. IV, The Kynoch Press: Birmingham, England, 1974, Table 2.2B.

(13) Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781.

(14) Cromer, D. T. "International Tables for X-ray Crystallography," Vol. IV, The Kynoch Press: Birmingham, England, 1974, Table 2.3.1.

(15) (a) Schenk, W. A.; Müller, H. *Chem. Ber.* **1982**, *115*, 3618. (b) Birdwhistell, K. R.; Tonker, T. L.; Templeton, J. L. *J. Am. Chem. Soc.* **1987**, *109*, 1401.

(16) (a) Laycock, D. E.; Baird, M. C. *Inorg. Chim. Acta* **1980**, *42*, 263. (b) Kreiter, C. G.; Koemm, U. *Z. Naturfosch.* **1983**, *38b*, 943. (c) Johnson, L. K.; Angelici, R. J. *Inorg. Chem.* **1987**, *26*, 973. (d) Green, M. L. H.; Nagy, P. L. J. *J. Organomet. Chem.* **1963**, *1*, 58. (e) Faller, J. W.; Johnson, B. V. *J. Organomet. Chem.* **1975**, *88*, 101.

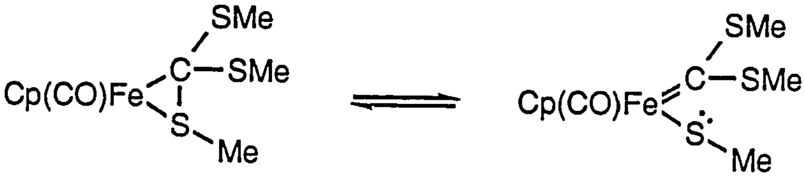
(17) (a) Pickering, R. A.; Jacobson, R. A.; Angelici, R. J. *J. Am. Chem. Soc.* **1981**, *103*, 817. (b) Reisner, G. M.; Bernal, I.; Dobson, G. R. *J. Organomet. Chem.* **1978**, *157*, 23.

(18) (a) Kuchitsu, K.; Fukuyama, T.; Morino, Y. *J. Mol. Struct.* **1968**, *1*, 463. (b) Costain, C. C.; Stoichoff, B. P. *J. Chem. Phys.* **1959**, *30*, 777.

SECTION IV. A RAPID EQUILIBRIUM BETWEEN THE METALLATHIACYCLOPROPANE, $Cp(CO)\overline{Fe[C(S}Me)(SMe)_2]$, AND ITS CARBENE-MERCAPTIDE FORM

ABSTRACT

The compound $Cp(CO)\overline{Fe[C(S}Me)(SMe)_2]$ (I) was obtained by photolysis of $CpFe(CO)_2[C(SMe)_3]$ (II) and reaction of $\{CpFe(CO)(MeCN)[=C(SMe)_2]\}PF_6$ (III) with NaSMe. Temperature-dependent ^1H NMR studies of I suggest that it is in rapid equilibrium with a carbene-mercaptide form $CpFe(CO)(SMe)$-$[=C(SMe)_2]$, Z. The existence of the carbene-mercaptide form (Z) is supported by the reaction of I with 2 equivalents of the phosphines, PMe_3 and PMe_2Ph, to give $CpFe(CO)(SMe)(PR_3)$ and the ylide $(MeS)_2C=PR_3$. Further support is obtained from the reaction of I with $[Me_3O]BF_4$ to give the dimethyl sulfide iron carbene complex $\{CpFe(CO)(SMe_2)[=C(SMe)_2]\}BF_4$.



I

Z

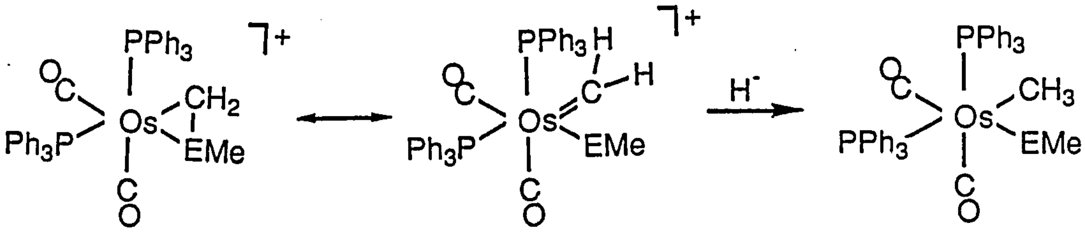
INTRODUCTION

A variety of heteroatom-containing metallacyclopropane complexes of the form A (eq. 1) where X = OR, SR, NR_2, PR_2 exist in the literature.[1]

A B

1

However, there are no cases where there is direct evidence for the existence of the carbene form B in which the C-X bond is cleaved. Headford and Roper;[2a] Collins and Roper[2b,c] suggested that the reactive intermediate in the reaction (eq. 2) of $NaBH_4$ and the metallacyclopropane,



1 2 3

2

where E = S, Se, Te

1, to give 3 is the carbene resonance form 2; however, there were no other results which would support their interesting proposal.

We present in this paper the synthesis, characterization and reactions of $Cp(CO)\overline{Fe[C(S}Me)(SMe)_2]$ which indicate that the compound is in rapid equilibrium with the carbene-mercaptide of the general type B.

EXPERIMENTAL SECTION

General Procedures

All reactions were carried out under an atmosphere of prepurified N_2 at room temperature using standard inert atmosphere and Schlenk techniques[3,4] unless otherwise stated. Tetrahydrofuran (THF) and Et_2O were distilled under N_2 from Na/benzophenone. Hexanes, MeCN and CH_2Cl_2 were distilled from CaH_2 under N_2.

Trimethylphosphine was prepared by the reaction of methyl Grignard reagent and triphenylphosphite.[1h] Diphenylmethylphosphine and PMe_2Ph were obtained from Strem Chemicals and used without further purification. Triphenyl phosphite, $[Me_3O]BF_4$ and HBF_4/Et_2O were used as received from Aldrich Chemical Co. Trimethyl phosphite was distilled from sodium metal under N_2.

Infrared spectra were obtained using a Perkin Elmer 681 spectrophotometer, and spectra were referenced to the 1944.0 cm^{-1} band of polystyrene. The ^1H and $^{13}C\{H\}$ NMR data were recorded on a Nicolet NT-300 MHz spectrometer using Me_4Si as the internal reference. The temperature dependent ^1H NMR spectra were obtained on a Bruker WM 300 MHz instrument. Electron impact mass spectra (EIMS) were obtained on a Finnigan 4000 instrument. Fast atom bombardment (FAB, glycerol matrix) mass spectra were obtained using a Kratos MS-50 spectrometer.

Photochemical reactions were carried out with a 254 nm light source in a quartz Schlenk tube equipped with a cooling probe using a reactor obtained from Bradford Scientific, Inc., Marblehead, MA.

The complexes $CpFe(CO)_2[C(SMe)_3]$ (II),[5] $\{CpFe(CO)_2[=C(SMe)_2]\}PF_6$[6a] and $\{CpFe(CO)(MeCN)[=C(SMe)_2]\}PF_6$ (III)[6b] were prepared according to literature methods.

Preparation of $Cp(CO)\overline{Fe[C(S}Me)(SMe)_2]$, I

A hexanes (35 mL) solution of $CpFe(CO)_2[C(SMe)_3]$ (II) (0.12 g, 0.36 mmol) was placed in a quartz tube equipped with a water-cooled probe and purged with N_2. The solution was irradiated with 254 nm light for 90 min. The volume of the solution was reduced to 10 mL in vacuo and transferred onto a column of alumina (adsorption, 80-200 mesh, 1 x 15 cm). A brownish yellow-green solution, the second band, was eluted with hexane/Et_2O (5:1). The solvent was removed in vacuo giving $Cp(CO)\overline{Fe[C(S}Me)(SMe)_2]$ (I), as a brownish yellow-green oil (0.080 g, 65%). Satisfactory elemental analyses could not be obtained because of the instability of the compound.

Synthesis of I from $\{CpFe(CO)(MeCN)[=C(SMe)_2]\}PF_6$ and NaSMe

Irradiation of a solution of $\{CpFe(CO)_2[=C(SMe)_2]\}PF_6$[6a] (0.10 g, 0.23 mmol) in MeCN (35 mL) at 254 nm for 2 h led to the formation of $\{CpFe(CO)(MeCN)[=C(SMe)_2]\}PF_6$,[6b] as established by the IR spectrum of the solution. After removal of the solvent in vacuo, the reddish product was extracted with THF (20 mL) and filtered through Celite on a glass frit. A THF solution of NaSMe, generated by slowly bubbling MeSH through a suspension of NaH (57% in mineral oil, 0.012 g, 0.28 mmol) in THF (20 mL) for 30 min,[5] was added to the filtrate and stirred for 60 min. The resulting solution was worked up as described in the photolytic preparation of I from II. I was obtained as an oil in 30% yield. The major impurity in I generated by this reaction was $Cp_2Fe_2(CO)_2(SMe)_2$.[7]

Reaction of Cp(CO)$\overline{\text{Fe[C(S}}$Me)(SMe)$_2$] and [Me_3O]BF_4

To a stirred solution of I (0.050 g, 0.16 mmol) dissolved in freshly distilled CH_2Cl_2 (20 mL) was added [Me_3O]BF_4 (0.028 g, 0.18 mmol). Stirring was continued for 45 min after which KPF_6 (~1.0 g) was added. After 1 h, the mixture was filtered through anhydrous $MgSO_4$ on a glass frit. The filtrate was layered with Et_2O (100 mL) and stored at -20 °C for one week. This led to the isolation of {CpFe(CO)(SMe_2)[=C(SMe)$_2$]}PF_6, IV, (0.049 g, 74%) as dark red crystals. Anal. Calcd for $C_{11}H_{17}F_6FeOPS_3$: C, 28.59; H, 3.71; S, 20.08. Found: C, 28.57; H, 3.65; S, 20.05.

Reaction of Cp(CO)$\overline{\text{Fe[C(S}}$Me)(SMe)$_2$] and PMe_3

To I (0.060 g, 0.20 mmol) dissolved in freshly distilled hexane (10 mL) was added PMe_3 (0.030 g, 0.39 mmol, 40 μl). The solution was stirred for 2 h with the progress of the reaction being monitored by IR. The two bands corresponding to I were replaced by a single band at 1940 cm^{-1} (vs). The mixture was treated with one equivalent of HBF_4/Et_2O solution. This resulted in the precipitation of a thick lavender oil. The supernatant was transferred onto a column of alumina (1 x 15 cm) and eluted with dry Et_2O. The brownish-yellow oily product CpFe(CO)(PMe_3)-(SMe), V, eluted in the second band in ~45% yield. Compound V decomposes within 3 h in $CDCl_3$ solution. Owing to its instability satisfactory elemental analyses could not be obtained. However, its methylated product was characterized and analyzed as described in the following synthetic procedure. The lavender oil was extracted with CH_2Cl_2 and layered with hexanes and stored at -20 °C for 3 days. A reddish-yellow oily-solid, $[(MeS)_2CHPMe_3]BF_4$, **VII**, was obtained and characterized by ^1H NMR and FAB MS (see Tables 2 and 4). The ylide precursor, $(MeS)_2C{=}PMe_3$, **VI**, to the cationic product **VII** was observed prior to the addition of HBF_4 in a reaction in d_6 benzene monitored by ^1H NMR (Table 2).

As described above, I (0.060 g, 0.18 mmol) was treated with PMe_2Ph (0.12 g, 0.90 mmol, 0.13 mL). Two hours of stirring led to the formation of $CpFe(CO)(PMe_2Ph)(SMe)$, **VIII**, which was also isolated by chromatography. It was characterized spectroscopically (Tables 1, 2, and 4) by comparison with **V**.

Reaction of $CpFe(CO)(SMe)(PMe_3)$ and $[Me_3O]BF_4$

To a stirred CH_2Cl_2 (20 mL) solution of **V** (0.045 g, 0.16 mmol) obtained from the reaction of I and PMe_3, $[Me_3O]BF_4$ (0.028 g, 0.18 mmol) was added. Stirring was continued for 10 min after which KPF_6 (~1.0 g) was added. The mixture was filtered through anhydrous $MgSO_4$ on a glass frit after 1 h. The filtrate was layered with Et_2O (100 mL) and stored at -20 °C for 3 days. The yellow powder obtained upon filtration was redissolved in acetone, layered with Et_2O and stored at -20 °C for one week. Golden needle-like crystals of $[CpFe(CO)(PMe_3)(SMe_2)]PF_6$, **IX** (0.062 g, 87%), were obtained upon filtration and drying in vacuo. Anal. Calcd for $C_{11}H_{20}F_6FeOPS$: C, 30.58; H, 4.66. Found: C, 30.50; H, 4.54.

Table 1. Infrared spectra of the complexes in hexanes

Complex	ν(CO), cm^{-1}
$Cp(CO)\overline{Fe[C(S}Me)(SMe)_2]$ (I)[a]	1949 (m), 1938 (s)
$Cp(CO)_2Fe[C(SMe)_3]$ (II)[b]	2025 (s), 2014 (m), 1978 (s), 1968 (m)
$\{Cp(CO)Fe(MeCN)[=C(SMe)_2]\}PF_6$[c] (III)	1997 (s)
$\{CpFe(CO)(SMe_2)[=C(SMe)_2]\}PF_6$ (IV)[d]	1985 (s)
$CpFe(CO)(PMe_3)(SMe)$ (V)	1940 (s)
$(MeS)_2C{=}PMe_3$ (VI)	
$[(MeS)_2CHPMe_3]BF_4$ (VII)	
$CpFe(CO)(PMe_2Ph)(SMe)$ (VIII)	1942 (s)
$[Cp(CO)Fe(SMe_2)(PMe_3)]PF_6$ (IX)[d]	1973 (s)
$\{CpFe(CO)[P(OPh)_3][=C(SMe)_2]\}PF_6$ (X)[d,e]	1985 (s)
$\{CpFe(CO)[P(OMe)_3][=C(SMe)_2]\}PF_6$ (XI)[d,e]	1981 (s)

[a] In CH_2Cl_2: 1924 cm^{-1}.

[b] Ref. 5.

[c] In CH_3CN.

[d] In CH_2Cl_2.

[e] Ref. 6.

Table 2. ^1H NMR spectra complexes in C_6D_6 (δ)

Complex	C_5H_5	Other resonance
I	4.27	2.22 (6H, SMe), 1.38 (3H, SMe)
II[a]	4.89	2.24 (9H, SMe)
III[b,c]	5.03	3.23 (6H, SMe), 2.44 (3H, MeCN)
IV[d,e]	4.96	3.20 (6H, SMe), 1.6-2.6 (V, br, SMe_2)
V	4.20 (d, J_{PH} = 1.2 Hz)	2.02 (d, J_{PH} = 1.3 Hz, 3H, SMe) 1.01 (d, J_{PH} = 9.8 Hz 9H Me)
VI		2.15 (d, J_{PH} = 1.1 Hz, 6H, SMe), 0.94 (d, J_{PH} = 12.2 Hz, 9H, PMe_3)
VII[d]		4.60 (d, J_{PH} = 12.9 Hz, 1H, CH), 2.38 (6H, SMe), 1.99 (d, J_{PH} = 13.9 H_2, 9H, PMe_3)
VIII	4.12	2.02 (6H, SMe); 1.46 (d, J_{PH} = 9.4 Hz, 6H, PMe_2Ph), 7.05 (m, Ph)
IX[f]	5.25 (d, J_{PH} = 1.5 Hz)	2.50 (6H, SMe_2), 1.72 (d, J_{PH} = 10.5 Hz, 9H, PMe_3)
X[f]	5.20 (d, J_{PH} = 1.1 Hz)	3.07 (6H, SMe), 7.27 (m, 15H, $P(OPh)_3$)
XI[f]	5.22 (d, J_{PH} = 1.2 Hz)	3.19 (6H, SMe), 3.77 (d, J_{PH} = 11.5 Hz, 9H, $P(OMe)_3$)

[a] In CD_2Cl_2.

[b] In CD_3CN.

[c] Ref. 11.

[d] In $CDCl_3$.

[e] At 80 °C the broad SMe_2 signal becomes fairly sharp. The SMe_2 is observed as two sharp signals at -20 °C (2.40 and 1.81 ppm).

[f] In $(CD_3)_2CO$.

Table 3. ^{13}C NMR spectra in C_6D_6 (δ)

Complex	C_5H_5	CO	Other resonances
I	79.94	216.03	70.67 [$\underline{C}(SMe)_3$], 21.51 (coordinated SMe) 20.00 (uncoordinated SMe)
II[a]	89.66	216.18	59.72 [$\underline{C}(SMe)_3$], 19.27 (SMe)
III[b]	85.0	216.4	321.2 [$\underline{C}(SMe)_2$], 28.1 (SMe) 136.1 (br, CH_3CN), 4.2 (CH_3CN)
VI[c,d]	85.20	215.52	318.53 [$\underline{C}(SMe)_2$], 28.96 (SMe), 24.12 (SMe_2), 22.62 (SMe_2)
V	82.54	220.90	16.70(SMe), 18.52 (d, J_{PC} = 121.4 H_2, PMe_3)

[a] In CD_2Cl_2.

[b] Ref. 6.

[c] In $CDCl_3$.

[d] At -30 °C.

Table 4. Mass spectra

Complex	Observed masses
I	302 (M^+), 274 [base peak, (M^+-CO)], 153 [$C(SMe)_3$]
II	348 (M^+-SMe), 153 {base peak, [$C(SMe)_3$]}
IV[a]	317 (M^+), 289 (M^+-CO), 255 [base peak, (M^+-SMe_2)]
V	272 (M^+), 244 [base peak, (M^+-CO)], 197 [M^+-(CO+SMe)]
VII[a]	183 (M^+), 167 (M^+-CH_4), 136 (M^+-SMe), 107 (M^+-PMe_3)
VIII	334 (M^+), 306 (M^+-CO), 259 [M^+-(CO+SMe)], 138 (base peak, $PMePh_2^+$)
IX[a]	287 (M^+, base peak), 225 (M^+-SMe_2), 197 [M^+-(CO+SMe_2)]

[a] FAB MS.

Reaction of $\{CpFe(CO)(SMe_2)[=C(SMe)_2]\}PF_6$ (IV) with $P(OR)_3$; R = Ph, Me

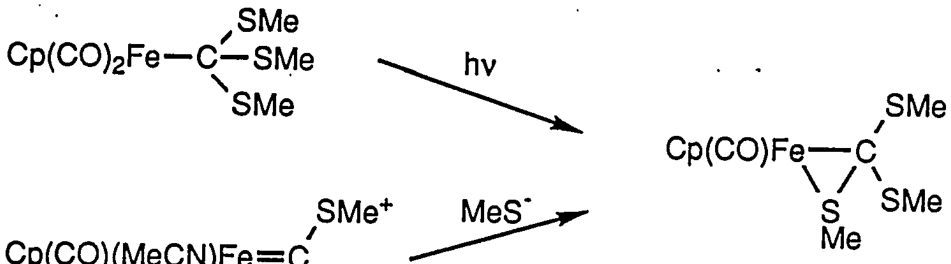
To an acetone (10 mL) solution of IV (0.038 g, 0.082 mmol) was added $P(OPh)_3$ (92 µL, 0.47 mmol). The solution was heated to 40 °C for 6 h and the solvent was removed in vacuo. A proton NMR spectrum of the reaction mixture in acetone indicated that $\{CpFe(CO)[P(OPh)_3][=C(SMe)_2]\}PF_6$ (X)[6] was the only product formed. A reaction in d^6-acetone monitored by ^1H NMR showed that the formation of **X** was quantitative.

Similarly, a reaction of IV (0.034 g, 0.074 mmol) and $P(OMe)_3$ (50 µl, 0.42 mmol) at 40 °C went to completion in 2 h. The $\{CpFe(CO)[P(OMe)_3][=C(SMe)_2]\}PF_6$, **XV**, was formed in 72% yield based on a ^1H-NMR monitored reaction in d_6-acetone. There was evidence for the formation of other unidentified minor products.

RESULTS AND DISCUSSION

Synthesis of $\mathrm{Cp(CO)\overline{Fe[C(S}Me)(SMe)_2]}$, I

Photolysis of $CpFe(CO)_2[C(SMe)_3]$[5] in hexanes produces a brownish solution which upon chromatography gives I as a brownish yellow-green oil in 65% yield. Compound I, in which both the carbon and a sulfur are coordinated to the iron, can also be obtained but in lower yield (30%) from the reaction of $\{CpFe(CO)(MeCN)[=C(SMe)_2]\}PF_6$[6] and NaSMe. In the latter reaction it is not known whether SMe^- initially displaces the MeCN



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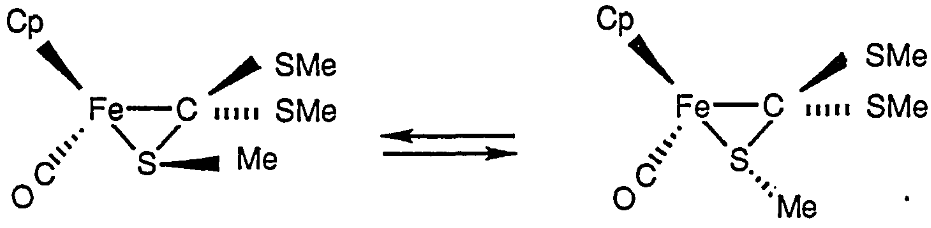
I

ligand to form the carbene-mercaptide $CpFe(CO)(SMe)[=C(SMe)_2]$ which rapidly closes the ring to form I or SMe^- first adds to the carbene carbon to give $CpFe(CO)(MeCN)[C(SMe)_3]$ which forms I by intramolecular displacement of the MeCN. NMR studies of the reaction show no evidence for any intermediates.

The mass spectrum of I, which is moisture and air sensitive, shows a parent ion peak (M^+) at m/e = 302 and a base peak at m/e = 274 corresponding to M^+-CO. Other fragments of the molecule such as $[C(SMe)_3]$ (m/e = 153) and CpFe (m/e = 121) are also observed. The infrared spectrum of I shows two bands (Table 1) which suggests the presence of two isomers. The ambient temperature ^1H NMR spectrum (CD_2Cl_2) of I, however, displays three signals at 4.52, 2.33, and 1.90 corresponding to the Cp, terminal and bridging SMe protons, respectively. While isomers C and D (eq. 4) are not apparent in the ambient temperature ^{1}H NMR spectrum, the



C D 4

low temperature (-90 °C, Fig. 1) spectrum shows two Cp(a,b) and six methyl signals (c-h) expected for these two isomers (eq 4). The two forms of I, which differ by the up or down position of the Fe-coordinated SMe group are assigned to signals a, c, f, h and b, d, e, g. Although it is not possible to assign each of these sets of signals to C or D, one of them is in slight excess (52:48 ratio) as determined from integrations of the spectra. Signals g and h correspond to the Fe-coordinated SMe groups of the two forms. Four signals (c-f) are observed for the uncoordinated SMe groups because each isomer has two inequivalent uncoordinated SMe groups. The four uncoordinated SMe signals become two broad signals on warming to -70 °C and become a single line at -39 °C. Also the two Cp signals, a and b, observed at 4.54 and 4.48 ppm at -90 °C coalesce to give a single line at -75 °C.

The rate of interconversion between forms C and D was calculated by simulating the broadened Fe-coordinated SMe signals at various temperatures. A two-site exchange program, based on the original work of

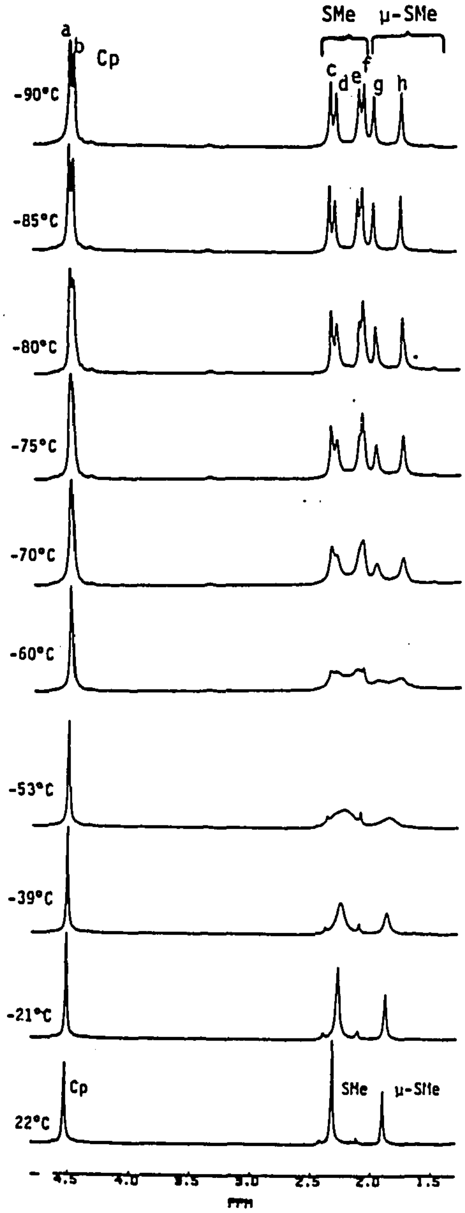
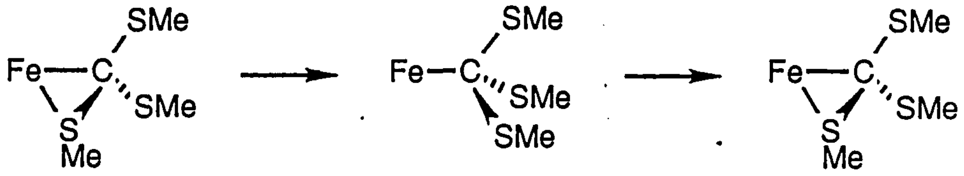


Figure 1. Variable temperature ^1H NMR spectra of $Cp(CO)\overline{Fe[C(S}Me)(SMe)_2]$, I, in CD_2Cl_2

Gutowsky and Holm,[8] and run on a Nicolet 1280 computer was used to calculate the rate (k) from observed line width and peak positions. A line width of 0.6 Hz was observed for the non-exchange-broadened peaks. The $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ (Table 5) were determined from an Erying plot using rate constants for the exchange process obtained at temperatures between 198 and 252 K (-75 and -21 °C).[9]

The rate constants for the process involving the coalesence of the Fe-coordinated SMe signals were also calculated using the approximate expression, $\Delta G^{\ddagger} = (19.14\ T_C)(9.97 + \log T_C/dv)$[9] where Tc = coalescence temperature, dv = the peak separation, and found to be the same within experimental error as that found from the line-fitting procedure above. This indicates that the signals coalesce by one process or the less likely possibility that two processes are occurring at the same rate at all temperatures.

In order to account for the temperature-dependent NMR results, one may consider the various fluxional processes which might occur in the metallathiocyclopropane ring in I. One possible process involves initial cleavage of the Fe-S bond (eq 5) to give an intermediate in which rapid



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rotation around the Fe-C bond would make all of the SMe groups equivalent. Thus, one would expect the 6 SMe signals at -90° to coalesce

Table 5. Rate constants and activation parameters for the interconversion of isomers C and D of $\mathrm{Cp(CO)\overline{Fe[C(S}Me)(SMe)_2]}$ in CD_2Cl_2[a]

T (K)	k^b (sec^{-1})	$\Delta G^{\ddagger c,d}$ (kJ mol^{-1})
198	6.85×10^1	40.9
203	1.04×10^2	41.3
213	2.0×10^2	42.0
220	3.77×10^2	42.6
234	1.02×10^3	43.7
252	2.17×10^3	45.1

[a] Concentration = 0.20 M.

[b] $k = 1/\tau$.

[c] $\Delta H^\ddagger = 25.44 \pm 0.97$ kJ mol^{-1}; $\Delta S^\ddagger = -77.91 \pm 4.45$ J mol^{-1} K^{-1}.

[d] $\Delta G^\ddagger$ is the same within experimental error when calculated from the peak separation of the SMe, $C(SMe)_2$ or Cp signals.

to one line at 22 °C. Their observed coalesence to two lines means that this process does not explain the NMR results.

A second possible process is that involving inversion at the sulfur of the Fe-coordinated SMe group. Abel and coworkers[10] have reviewed related inversions of coordinated sulfur groups (M-$\ddot{S}$(R)R')) and noted a number of factors contribute a to observed $\Delta G^{\ddagger}$ values which range from 20 kJ mol^{-1} to >90 kJ mol^{-1}. Such an inversion in I would average the Fe-coordinated SMe signals but it would leave the uncoordinated SMe groups inequivalent. Thus, one would expect to find 3 SMe peaks at the high temperature limit. The observed 2 peak SMe region at 22 °C means that this process does not account for the NMR results.

A third possible process is a rotation of the entire η^2-C(SMe)$_3$ unit in I about an axis through the Fe and perpendicular to the C-S bond similar to what has been suggested for $(PMe_3)_4W-(\eta^2-CH_2PMe_2)H$[1h] and $Cp_2Zr[\eta^2-CHR(SR)]$.[11] This rotation does not, however, make the uncoordinated SMe groups equivalent, as observed in the spectrum of I at 22 °C.

While none of the above 3 processes account for the observed coalesences, a combination of the latter two processes, inversion at the Fe-coordinated SMe and rotation of the η^2-C(SMe)$_3$ unit occurring at the same rates at all temperatures would account for the equal rates of coalesence of the Cp, the Fe-coordinated SMe, and uncoordinated SMe signals. Although it is not possible to rigorously exclude this possibility, it is unlikely that these two quite different processes would have the sames rates and activation parameters.

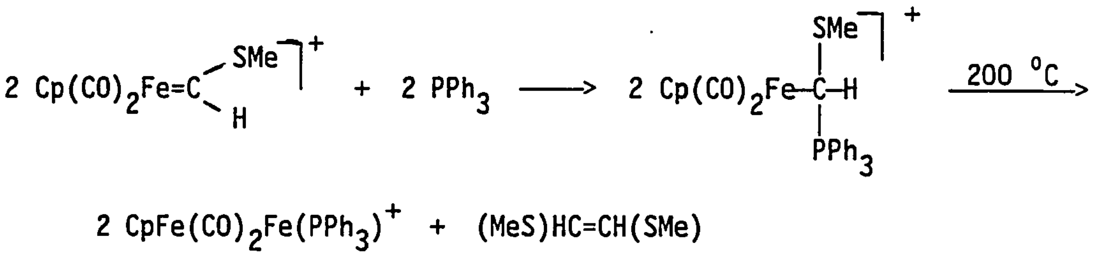
The mechanism which best accounts for the NMR results is that which involves cleavage of the C-S bond in isomers C and D to give the carbene-mercaptide complex Z, followed by rapid rotation around the Fe-SMe bond and around the Fe-C(SMe)$_2$. That rotation around the Fe = C(SMe)$_2$ bond is likely to be rapid is supported by many studies of carbene complexes,[12] particularly those of heteroatom carbenes. This mechanism would account for the coalesence of the two Cp peaks, the two Fe-coordinated SMe peaks and the 4 uncoordinated SMe peaks all at the same rate. In the ^{13}C NMR spectrum of I in C_6D_6 at ambient temperature, a distinct signal for the carbon in the η^2 $\underline{C}(SR_3)$ unit is observed at 70 ppm. This is characteristic of a saturated carbon and is similar to that (61.79 and 71.69 ppm) observed in $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)_2]$.[13] There is no evidence for a carbene carbon of form Z, which would be expected in the region 200-250 ppm, as observed for $Cp(CO)_2Fe[{=}CH(SMe)]^+$, $Cp(CO)P[P(OPh)_3]Fe[{=}CH(SMe)]^+$ and $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]^+$.[13,14] Therefore, the equilibrium in eq 6 must lie far to the left and Z would be present only as a short-lived intermediate.

I Z

6

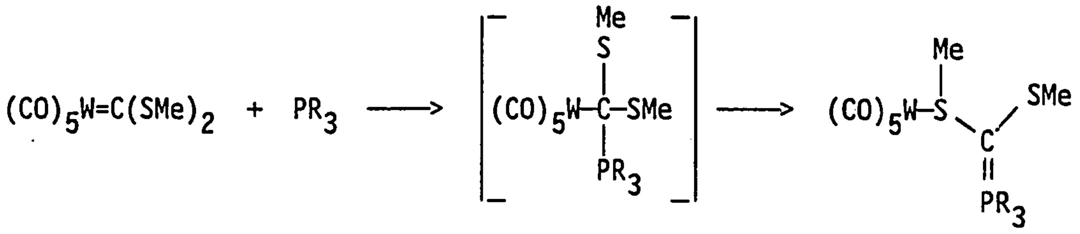
Reactions of $Cp(CO)\overline{Fe[C(S}Me)(SMe)_2]$, I

To explore the possibility that the carbene-mercaptide form (Z) of I would react as a carbene, we studied reactions of I with phosphines. Phosphines are known to react with carbenes[15] and perhaps the most closely related example is that (eq 7) of $Cp(CO)_2Fe{=}C(H)(SMe)^+$ with PPh_3 to form $Cp(CO)_2Fe{-}C(H)(SMe)(PPh_3)^+$,[16] which upon heating to 200 °C releases the olefin and forms the phosphine substituted complex.



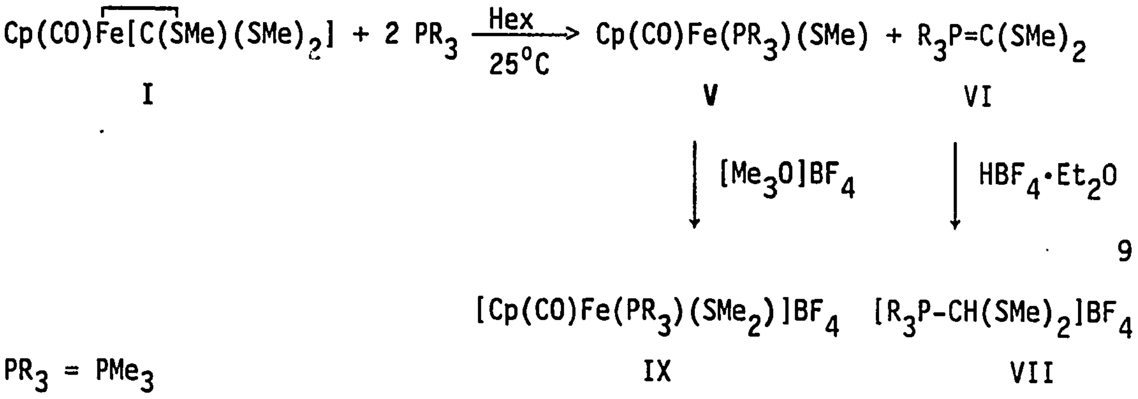
$$2\ Cp(CO)_2Fe{=}C(SMe)(H)^+ + 2\ PPh_3 \longrightarrow 2\ Cp(CO)_2Fe{-}C(SMe)(H)(PPh_3)^+ \xrightarrow{200\ ^{\circ}C} 2\ CpFe(CO)_2Fe(PPh_3)^+ + (MeS)HC{=}CH(SMe) \qquad 7$$

A tungsten dithiocarbene complex $(CO)_5W{=}C(SMe)_2$ also reacts with phosphines PR_3, presumably via a ylide intermediate[17]



$$(CO)_5W{=}C(SMe)_2 + PR_3 \longrightarrow \left[(CO)_5W{-}C(SMe)(SMe)(PR_3)\right] \longrightarrow (CO)_5W{-}S(Me){-}C(SMe){=}PR_3 \qquad 8$$

Reaction of I with nucleophilic phosphines requires 2 h and leads to the formation of V and the corresponding ylide (eq. 9).

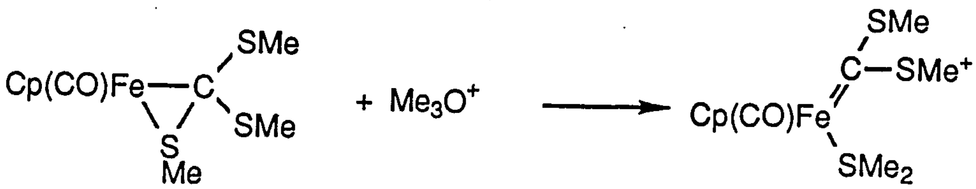


$$\begin{tikzcd} \underset{\text{I}}{Cp(CO)\overline{Fe[C(S}Me)(SMe)_2]} + 2\ PR_3 \arrow[r, "Hex", "25^{\circ}C"'] & \underset{\text{V}}{Cp(CO)Fe(PR_3)(SMe)} \arrow[d, "{[Me_3O]BF_4}"] + \underset{\text{VI}}{R_3P{=}C(SMe)_2} \arrow[d, "HBF_4\cdot Et_2O"] \\ & \underset{\text{IX}}{[Cp(CO)Fe(PR_3)(SMe_2)]BF_4} \quad \underset{\text{VII}}{[R_3P{-}CH(SMe)_2]BF_4} \end{tikzcd} \qquad 9$$

$PR_3 = PMe_3$

Compound **V** was characterized by its IR, ^1H and ^{13}C NMR, and MS (PR_3 = PMe_3). While **V** was too unstable for an elemental analysis, its methylated derivative, **IX**, was analyzed correctly. The ylide product $Me_3P{=}C(SMe)_2$ (**VI**) was observed in a reaction monitored by ^1H NMR and obtained as the tetrafluoroborate salt (**VII**). By analogy with reactions 7 and 8 the reaction of I with PMe_3 can be thought to occur via PMe_3 attack at the carbene carbon of the carbene mercaptide complex Z to give a $CpFe(CO)(SMe)[C(SMe)_2PMe_3]$ intermediate. Subsequent substitution of the $Me_3PC(SMe)_2$ group by a second PMe_3 results in the formation of the final products. The reaction of I with one equivalent of phosphine does not go to completion. Also, I does not react to any appreciable extent under the same conditions with less basic phosphines such as $PMePh_2$.

While compound I reacts as a carbene, presumably because of its rapid interconversion to the carbene-mercaptide form Z, we sought to determine whether the SMe group of this form could be alkylated as has been observed for other mercaptide complexes.[18] Compound I reacts with $[Me_3O]BF_4$ in 30 min to give a reddish solution from which $\{CpFe(CO)(SMe_2)[{=}C(SMe)_2]\}PF_6$ (**IV**) is isolated, after anion exchange, as a dark red crystalline solid. King and Bisnette[7] reported that the reaction of $CpFe(CO)_2SMe$ with MeI



10

I

IV

proceed rapidly (15 min) to give $CpFe(CO)_2(SMe_2)^+$. It is to be expected that a similar reaction with Me_3O^+ would be even faster. However, reaction (10) requires 30 min, presumably because the reactive form of I which is the carbene-mercaptide $CpFe(SMe)(CO)[=C(SMe)_2]$, Z is present in small concentration as a result of equilibrium (6) lying far to the left.

Compound **IV** was characterized by its IR, MS, ^1H and ^{13}C NMR as well as elemental analysis. The coordinated dimethylsulfide is seen as a broad signal spanning nearly one ppm in the ambient temperature ^1H NMR spectrum. On cooling to -20 °C, the methyl groups of the coordinated sulfide are observed as two sharp signals (Fig. 2). At 80 °C the methyl groups are observed as a fairly sharp singlet. At low temperature the methyl groups of the sulfide are diastereotopic and as a result they occur as 2 singlets. At higher temperature there is a rapid inversion at the sulfur which makes the methyl groups equivalent on the NMR time scale. A similar inversion was observed by Kuhn and Schumann[19] in the $CpFe(CO)(SMe_2)(L)^+$ complexes, where L = PPh_3, CN^-. A $\Delta G^\ddagger = 54.9 \pm 0.6$ kJ mol^{-1} (T_c = 296) is obtained for the activation energy of the exchange process in **IV**[20] using the approximate expression previously described.[9] This compares well with the values obtained for $[CpFe(CO)(SMe_2)(PPh_3)]BF_4$, 53.7 ± 2.0 kJ mol^{-1} (T_c = 273 K) and $CpFe(CO)(SMe_2)(CN)$, 60.2 ± 3.3 kJ mol^{-1} (T_c = 286 K).[21]

Further confirmation of the structure of compound **IV** was obtained from its reaction with $P(OPh)_3$ at 40 °C in acetone for 5 h to give an orange solution from which $\{CpFe(CO)[P(OPh)_3][=C(SMe)_2]\}PF_6$, **X**, was

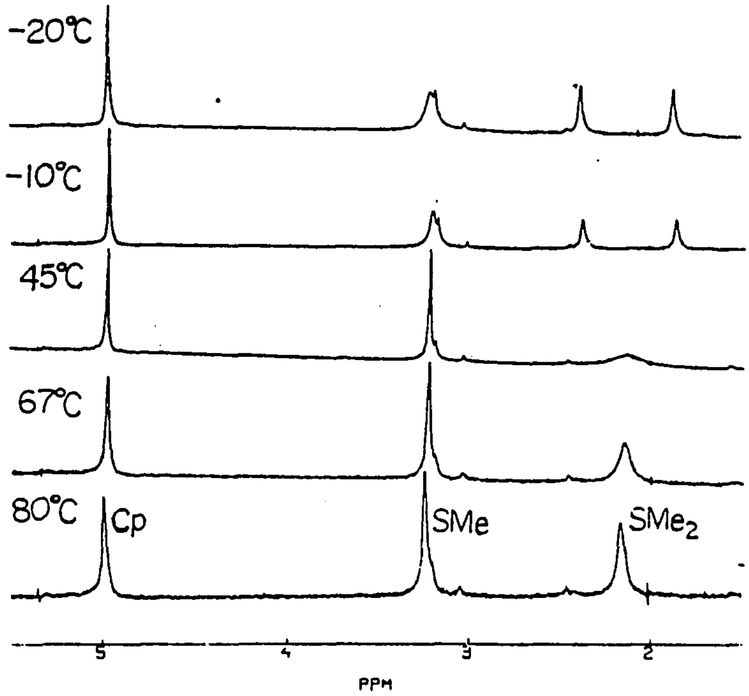


Figure 2. Temperature-dependent ^1H NMR spectra of {CpFe(CO)(SMe_2)[=C(SMe)$_2$]}PF_6, IV, in $CDCl_3$

isolated. The $P(OMe)_3$ analog was obtained from the reaction of **IV** and $P(OMe)_3$. Both of the phosphite-carbene complexes had been prepared previously[6] and identified by their characteristic spectra.

The alkylation of the SMe group in **I** to give $\{CpFe(CO)(SMe_2)[=C(SMe)_2]\}PF_6$, **IV** (eq 11) clearly shows that **I** reacts as if the carbene-mercaptide form of **I** is present in its reactions.

CONCLUSION

We have shown that the temperature dependent ^1H NMR spectra of $Cp(CO)\overline{Fe[C(S}Me)(SMe)_2]$ are best interpreted as indicating a rapid equilibrium between the metallathiacyclopropane and the carbene mercaptide Z (eq 6). Supporting evidence for the carbene-mercaptide form is found in the reactions of I with PR_3 to give free ylide and phosphine iron complex (eq 10) and with Me_3O^+ to give the dimethyl sulfide complex $CpFe(CO)(SMe_2)[=C(SMe)_2]^+$, IV as in equation 10.

With this evidence for the carbene-mercaptide form of compound I, one asks whether other complexes with similar ligands show evidence for such a form:

11

King and Bisnette,[22a] de Gill and Dahl[22b] have reported the synthesis of $Cp(CO)_2\overline{M(CH_2S}Me))$ (M = Mo, W) by both photolysis and pyrolysis of $CpM(CO)_3(CH_2SMe))$. Unsuccessful attempts were also made by King and Bisnette at the synthesis of the iron analog. A series of Ni, Pd and Pt compounds with the general formula $(PPh_3)\overline{MCl[CH_2S}Me]$ have been reported.[23] In contrast to the uncoordinated SMe groups in I, the hydrogens on the carbon of the metallacyclopropane in all of these compounds are inequivalent at ambient temperature. There is also no evidence for a carbene mercaptide form of $Cl\overline{Pt(PPh_3)(CH_2S}Me)$. Unlike I, it reacts with PPh_3 to displace the sulfur and give an alkyl complex $ClPt(PPh_3)_2[CH_2(SMe)]$.[23] In addition, $Cl\overline{Pd(PPh_3)(CH_2S}Me)$ reacts with alkyl halides to give a halogen exchanged product, $\mathrm{I\overline{Pd(PPh_3)(CH_2S}Me)}$24 no alkylation of the sulfur occurs.

It is well documented in the literature[25] that α-heteroatom carbenes tend to be more stable than alkyl-, aryl- and hydrogen-substituent carbenes because of the stabilizing effect which results from the interaction of the carbene carbon and the lone electron pairs on the heteroatoms. It is, therefore, understandable why the metallathiacyclopropane, I, in which such stabilizing groups (SMe) are present is more likely to show evidence for a carbene-mercaptide form than the hydrogen-substituted analogs. Other metallathiacyclopropane complexes which are most likely to be in equilibrium with a carbene-mercaptide form (eq. 11) are also those where the carbene R substituents are stabilizing heteroatom groups.

ACKNOWLEDGMENT

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REFERENCES

(1) (a) Omae, I. *Coord. Chem. Rev.* **1979**, 28, 97 and references therein. (b) Paul, W.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1983**, 22, 316. (c) Werner, H. *Angew. Chem., Int. Ed. Engl.* **1983**, 22, 927. (d) Davidson, J. G.; Barefield, E. K.; Van Derveer, D. G. *Organometallics* **1985**, 4, 1178. (e) Adams, H.; Bailey, N. A.; Cahill, P.; Rogers, D.; Winter, M. J. *J. Chem. Soc., Chem. Commun.* **1983**, 831. (f) Young, S. J.; Olmstead, M. M.; Knudsen, M. J.; Schore, N. E. *Organometallics* **1985**, 4, 1432. (g) Etienne, M.; Choukroun, R.; Basso-Bert, M.; Dahan, F.; Gervais, D. *Nouv. J. Chim.* **1984**, 8, 531. (h) Gibson, V. C.; Graimann, C. E.; Hare, P. M.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1985**, 2025. (j) Barefield, E. K.; Sepelak, D. J. *J. Am. Chem. Soc.* **1979**, 101, 1096. (k) Lindner, E.; Neese, P.; Hiller, W.; Fawzi, R. *Organometallics* **1986**, 5, 2030.

(2) (a) Headford, C. E. L.; Roper, W. R. *J. Organomet. Chem.* **1983**, 244, C53. (b) Collins, T. J.; Roper, W. R. *J. Chem. Soc., Chem. Commun.* **1977**, 901. (c) Collins, T. J.; Roper, W. R. *J. Organomet. Chem.* **1978**, 159, 73.

(3) Shriver, D. F.; Drezdon, M. A. "The Manipulation of Air Sensitive Compounds", 2nd ed.; John Wiley and Sons: New York, 1986.

(4) Herzog, S.; Dehnert, J.; Luhder, K. "Technique of Inorganic Chemistry", H. B. Jonassen, Ed., Interscience: New York, 1969; Vol. VII.

(5) McCormick, F. B.; Angelici, R. J. *Inorg. Chem.* **1981**, 20, 4108.

(6) (a) McCormick, F. B.; Angelici, R. J. *Inorg. Chem.* **1979**, 18, 1231. (b) McCormick, F. B.; Angelici, R. J. *J. Organomet. Chem.* **1981**, 205, 79.

(7) King, R. B.; Bisnette, M. B. *Inorg. Chem.* **1965**, 4, 482.

(8) Gutowsky, H. S.; Holm, C. H. *J. Chem. Phys.* **1956**, 25, 1228.

(9) (a) Günther, H. *NMR Spectroscopy*; John Wiley and Sons: New York, 1980; Chapter VIII. (b) Espenson, J. H. *Chemical Kinetics and Reaction Mechanisms*; McGraw-Hill Book Company; New York, 1981; Chapter 6. (c) Drago, R. S. *Physical Methods in Chemistry*; W. B. Sanders: Philadelphia, 1977; Chapter 8.

(10) Abel, E. W.; Bhargava, S. K.; Orrell, K. G.. *Prog. Inorg. Chem.* **1984**, 32, 1.

(11) (a) Ward, A. S.; Mintz, E. A.; Ayers, M. R. Organometallics 1986, 5, 1585. (b) Mintz, E. A.; Ward, A. S.; Tice, D. S. Organometallics 1985, 4, 1308. (c) Kim, H. P.; Angelici, R. J. Organometallics 1986,

(12) (a) Hoffmann, P. in "Transition Metal Carbene Complexes", Verlag Chemie: Weinheim, 1983, p. 113. (b) Brookhart, M.; Nelson, G. O. J. Am. Chem. Soc. 1977, 99, 6099. (c) Brandt, S.; Helquist, P. J. Am. Chem. Soc. 1979, 101, 6473. (e) O'Connor, J.; Brandt, S.; Helquist, P. J. Am. Chem. Soc. 1987, 109, 3739. (f) Brookhart, M.; Tucker, J. R.; Flood, T. C.; Jensen, J. J. Am. Chem. Soc. 1980, 102, 1203. (g) Brookhart, M.; Tucker, J. R.; Husk, G. R. J. Am. Chem. Soc. 1981, 103, 979. (h) Brookhart, M.; Humphrey, M. B.; Kratzer, H. J.; Nelson, G. O. J. Am. Chem. Soc. 1980, 102, 7802. (i) McCormick, F. B.; Angelici, R. J. Inorg. Chem. 1979, 18, 1231 and references therein. (j) McCormick, F. B.; Angelici, R. J. Inorg. Chem. 1981, 20, 1111.

(13) Kim, H. P.; Angelici, R. J. Organometallics 1986, 5, 2489.

(14) Yu, Y. S.; Angelici, R. J. Organometallics 1983, 2, 1583.

(15) (a) Bodnar, T.; Cutler, A. J. J. Organomet. Chem. 1981, 213, C31. (b) Casey, C. P.; Miles, W. H.; Tukada, H.; O'Connor, J. M. J. Am. Chem. Soc. 1982, 104, 3761.

(16) Yu, Y. S.; Angelici, R. J. Organometallics 1983, 2, 1018.

(17) Pickering, R. A.; Jacobson, R. A.; Angelici, R. J. J. Am. Chem. Soc. 1981, 103, 817.

(18) (a) Treichel, P. M.; Schmidt, M. S.; Koehler, S. D. J. Organomet. Chem. 1983, 258, 209. (b) Schenck, W. A.; Schwietzke, T. Organometallics 1983, 2, 1905. (c) Angelici, R. J.; Gingerieh, R. G. W. Organometallics 1983, 2, 89.

(19) Kuhn, N.; Schuman, H. J. Organomet. Chem. 1984, 276, 55.

(20) Sandstrom, J. "Dynamic NMR Spectroscopy", Academic Press: New York, 1982.

(21) Kuhn, N.; Schuman, H. Inorg. Chim. Acta 1986, 116, L11.

(22) (a) King, R. B.; Bisnette, M. B. Inorg. Chem. 1965, 4, 486. (b) de Gill, E. R.; Dahl, L. F. J. Am. Chem. Soc. 1969, 91, 3751.

(23) (a) Yoshida, G.; Kurosana, H.; Okawara, R. J. Organomet. Chem. 1976, 113, 85. (b) Miki, K.; Kai, Y.; Yasuoka, N.; Kasai, N. J. Organomet. Chem. 1977, 135, 53. (c) Miki, K.; Kai, Y.; Yasuoka, N.; Kasai, N. Bull. Chem. Soc. Jpn. 1981, 54, 3639. (d) Chong, K. S.;

Retting, S. J.; Storr, A.; Trotter, J. Can. J. Chem. 1980, 58, 1080. (e) McPherson, H. D.; Wardell, J. L. Inorg. Chim. Acta 1979, 35, L353. (f) Yoshida, G.; Matsumura, Y.; Okawara, R. J. Organomet. Chem. 1975, 92, C53.

(24) McPherson, H. D.; Wardell, J. L. Inorg. Chim. Acta 1984, 81, 39.

(25) (a) Cardin, D. J.; Cetinkaya, B.; Lappert, M. F. Chem. Rev. 1972, 72, 545. (b) O'Connor, E. J.; Helquist, P. J. Am. Chem. Soc. 1982, 104, 1869. (c) Knors, C.; Kuo, G.; Lauher, J. W.; Eigenbrof, C.; Helquist, P. Organometallics 1987, 6, 988 and references therein. (d) Glavee, G. N.; Su, Y.; Jacobson, R. A.; Angelici, R. J. Inorg. Chim. Acta, submitted for publication.

(26) Clark, G. R.; Headford, C. E. L.; Marsden, K.; Roper, W. R. J. Organomet. Chem. 1982, 231, 335.

(27) (a) Rathke, J. W.; Muetherties, E. L. J. Am. Chem. Soc. 1975, 97, 3272. (b) Karsch, H. H.; Klein, H. F.; Schmidbaur, H. Angew. Chem., Int. Ed. Engl. 1975, 14, 637. (c) Werner, H.; Gotzig, J. Organometallics 1983, 2, 547.

(28) (a) Adams, H.; Bailey, N. A.; Cahill, P.; Rogers, D.; Winter, M. J. J. Chem. Soc., Dalton Trans. 1986, 2119. (b) Adams, H.; Bailey, N. A.; Osborn, V. A.; Winter, M. J. J. Chem. Soc., Dalton Trans. 1986, 2127.

SECTION V. REACTIONS OF $CpFe(CO)_2(=\overline{COCH_2CH_2O})^+$, $CpFe(CO)_2[=C(SMe)_2]^+$, AND RELATED CARBENE COMPLEXES WITH REDUCING AGENTS AND NUCLEOPHILES.

THE STRUCTURE OF $\{CpFe(CO)_2[=C(SMe)_2]\}PF_6$

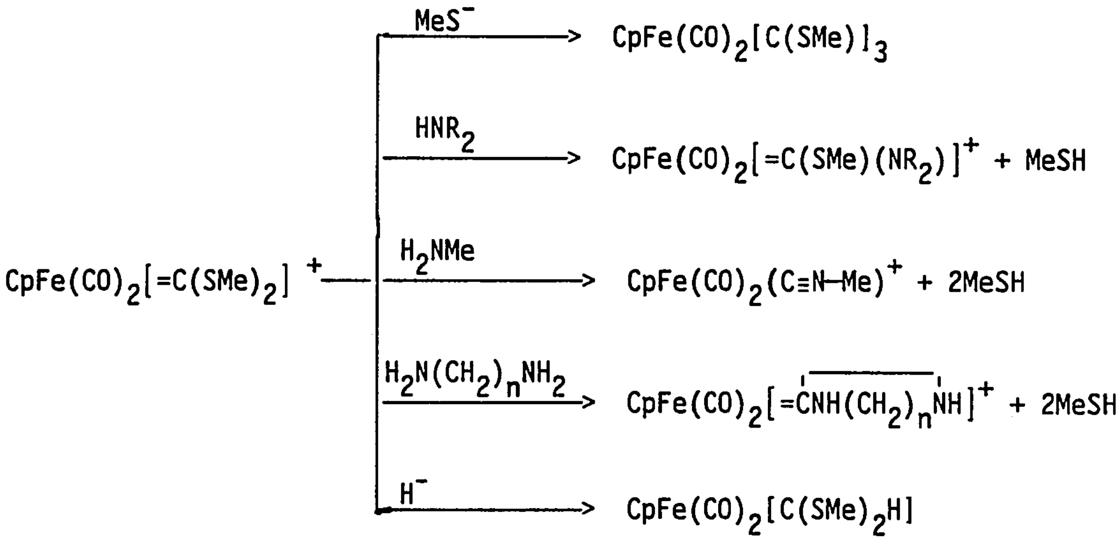
ABSTRACT

The reduction of $CpFe(CO)_2(=\overline{COCH_2CH_2O})^+$ (I) with one equivalent of sodium naphthalenide (NaNp) yields $[CpFe(CO)_2]_2$ (II), CO_2 and C_2H_4. The same reduction of $CpFe(CO)_2[=C(SMe)_2]^+$ (X), however, gives II, $CpFe(CO)_2[C(SMe)_3]$ (XII), $Cp\overline{Fe(CO)[C(S}Me)(SMe)_2]$ (XIII) and $[CpFe(CO)(SMe)]_2$. Small amounts (0.1 equivalent) of NaNp catalyze reactions of I and X with phosphines to give a mixture of CO- and carbene-substituted products, $CpFe(CO)(L)(=\overline{COCH_2CH_2O})^+$, $CpFe(CO)_2(L)^+$, $CpFe(CO)(L)_2^+$ and $CpFe(CO)(L)[=C(SMe)_2]^+$ ($L = PMePh_2$); a mechanism involving radical intermediates is proposed for the reactions. Complex I reacts with anions (I^-, Cl^-, MeO^-, NCS^-, $PhCH_2S^-$) to give the ring-opened alkoxycarbonyl complexes $CpFe(CO)_2[C(=O)OCH_2CH_2X]$. With oxidizing agents such as Me_3NO, the dioxycarbene ligand in I is converted to ethylene carbonate, $O=\overline{COCH_2CH_2O}$. An X-ray diffraction study of X shows the carbene moiety to be planar with the SMe groups in a syn and anti conformation. The plane of the carbene ligand is oriented "crosswise" with respect to the CO groups.

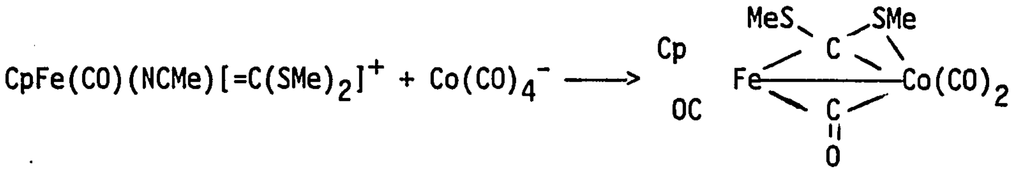
INTRODUCTION

Transition metal carbene complexes are important in reactions leading to carbon-carbon bond formation in organic synthesis [1] and in metal catalyzed reactions such as polymerization of alkenes [2a], olefin cyclopropanation [2b], Fischer-Tropsch synthesis [2c], and olefin metathesis [3]. Consequently, there is a great deal of interest in their reaction chemistry. The $CpFe(CO)_2(carbene)^+$ complexes ($Cp=\eta^5-C_5H_5$) are one such class of compounds which have received considerable attention in the quest to generate stable, isolable and yet reactive carbene complexes [4-28]. These complexes are of two general types: those with at least one heteroatom, e.g., O, S, N or P, directly bonded to the carbene carbon and those without. The latter type, with alkyl, aryl, or hydrogen substituents bonded to the carbene carbon, are generally unstable even at low temperatures. As a result they either decompose giving the transition metal olefin complex along with other products [4,11,12] or react with unactivated olefins to form cyclopropanes [7-10,14,25]. They also readily undergo addition at the carbene carbon with phosphines and other nucleophiles [4,5,11,12].

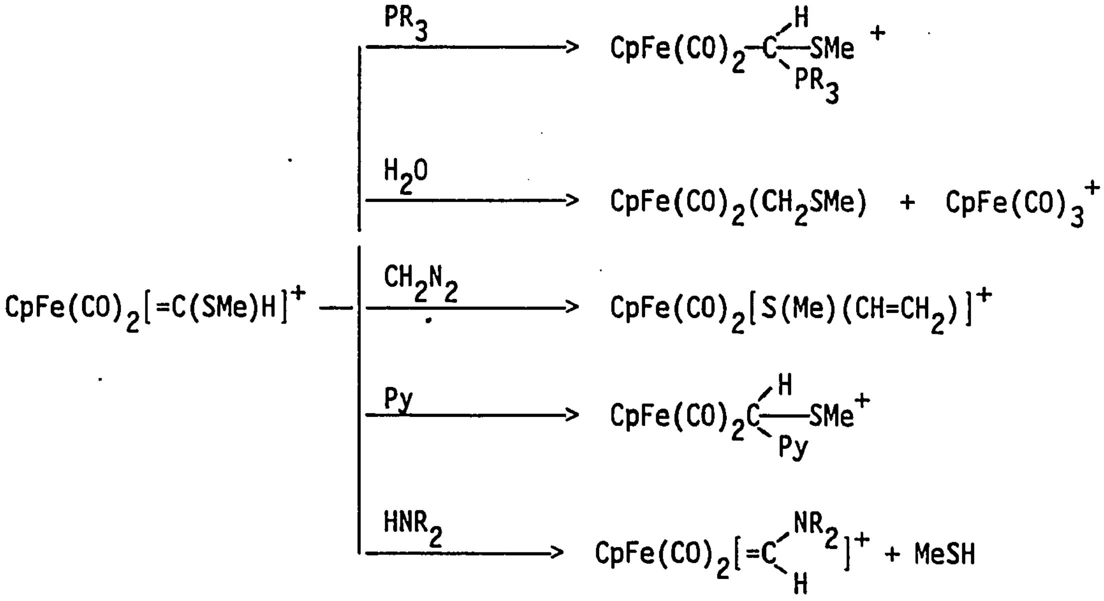
In contrast, α-heteroatom carbenes tend to be more stable and often may be isolated at ambient temperature [15-17,20-22,24]. The stability of these complexes is attributed to the interaction of the carbene carbon with a lone electron pair on the heteroatom. Coupling of the carbene moiety in these systems to give olefinic products [20,26] and reactions with olefins to give free cyclopropanes [27] are relatively rare.


CpFe(CO)2[=C(SMe)2] +
MeS⁻
CpFe(CO)2[C(SMe)]3
HNR2
CpFe(CO)2[=C(SMe)(NR2)]+ + MeSH
H2NMe
CpFe(CO)2(C≡N—Me)+ + 2MeSH
H2N(CH2)nNH2
CpFe(CO)2[=CNH(CH2)nNH]+ + 2MeSH
H⁻
CpFe(CO)2[C(SMe)2H]

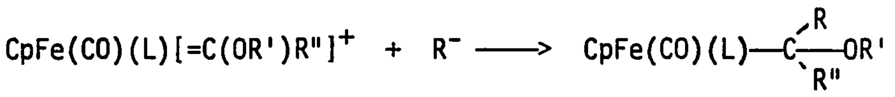
1


CpFe(CO)(NCMe)[=C(SMe)2]+ + Co(CO)4⁻
Cp
OC
MeS
SMe
C
Fe
Co(CO)2
C
O

2


CpFe(CO)2[=C(SMe)H]+
PR3
CpFe(CO)2—C(H)(SMe)(PR3) +
H2O
CpFe(CO)2(CH2SMe) + CpFe(CO)3+
CH2N2
CpFe(CO)2[S(Me)(CH=CH2)]+
Py
CpFe(CO)2C(H)(SMe)(Py)+
HNR2
CpFe(CO)2[=C(NR2)(H)]+ + MeSH

3



$$\mathrm{CpFe(CO)(L)[{=}C(OR')R'']^{+}} + \mathrm{R^{-}} \longrightarrow \mathrm{CpFe(CO)(L){-}C(R)(R'')(OR')} \qquad 4$$

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

R^- = H^-, Me^-, Ph^-; R' = Me, Et; R" = Me, Et, c-C_3H_5, $CH(Me)_2$.

However, these complexes undergo a variety of other reactions as illustrated by equations 1 [15-18], 2 [23], 3 [19,20], and 4 [6,9b,13,28].

Despite the wide range of reactivity which has been observed for the $CpFe(CO)_2(carbene)^+$ complexes, there are no reports, to our knowledge, of studies involving reducing agents such as Na-amalgam or sodium naphthalenide. We report in this paper the X-ray-determined structure of $\{CpFe(CO)_2[=C(SMe)_2]\}PF_6$ and its reactions with reducing agents. Reactions of $[CpFe(CO)_2(=\overline{COCH_2CH_2O})]PF_6$ and other α-heteroatom carbenes are also described.

EXPERIMENTAL

General Procedures

All reactions were carried out under an atmosphere of prepurified N_2 at room temperature using standard inert atmosphere [29] and Schlenk [30] techniques unless otherwise stated. Tetrahydrofuran (THF) and Et_2O were distilled under N_2 from Na/benzophenone. Hexanes, MeCN and CH_2Cl_2 were distilled from CaH_2 under N_2.

Solutions of sodium naphthalenide (NaNp) were prepared by stirring 1:1 molar ratios of sodium metal and naphthalene in THF [31]. These solutions were standardized using a standard potassium hydrogenphthalate solution. The $[N(n\text{-}Bu)_4]PF_6$ was prepared by a published procedure [32]. Diphenylmethylphosphine and PMe_2Ph were obtained from Strem Chemicals and used without further purification. Triphenylphosphine was used as received from SCM Chemicals.

Infrared spectra were obtained using either a Perkin Elmer 281 or 681 spectrophotometer, and spectra were referenced to the 1944.0 cm^{-1} band of polystyrene. The ^1H and ^{13}C NMR data were recorded on a Nicolet NT-300 MHz spectrometer using Me_4Si as the internal reference. The ^{31}P NMR spectra were obtained on a Bruker WM 300 MHz instrument. The ^{31}P signals which are upfield of the H_3PO_4 external reference are given as negative values. Electron impact mass spectra (EIMS) and GC-MS spectra were obtained on a Finnigan 4000. Fast atom bombardment (FAB, glycerol matrix) mass spectra were obtained using a Kratos MS-50 spectrometer.

Cyclic voltammograms were recorded with a Bioanalytical System CV-1B cyclic voltagraph in a conventional three electrode cell at 25°C. A stationary platinum disk (3.1 mm^2) was used as the working electrode, and platinum wire served as the auxiliary electrode. The reference electrode was Ag/AgCl (3.0 M NaCl) and measurements were made in MeCN (0.1 M $[N(n\text{-}Bu)_4]PF_6$). All solutions were deoxygenated by purging with argon and kept under an atmosphere of argon throughout the measurements. Photochemical reactions were carried out with a 254 nm light source in a quartz schlenk tube equipped with a cooling probe using a reactor obtained from Bradford Scientific, Inc., Marblehead, MA.

The complexes $[CpFe(CO)_2(=\overline{COCH_2CH_2O})]PF_6$ (**I**) [21], $[CpFe(CO)(PPh_3)(=\overline{COCH_2CH_2O})]PF_6$ (**IIIb**) [22], $\{CpFe(CO)_2[=C(SMe)_2]\}PF_6$ (**X**) [16], $Cp_2Fe_2(CO)_2(SMe)_2$ (**XI**) [33], $CpFe(CO)_2[C(SMe)_3]$ (**XII**) [18a], $Cp(CO)\overline{Fe[C(S}Me)(SMe)_2]$ (**XIII**) [18b], $[CpFe(CO)_2(=\overline{CSCH_2CH_2S})]PF_6$ (**XV**) [22], and $\{CpFe(CO)_2[=C(SMe)(NMe_2)]\}PF_6$ (**XVIII**) [15] were prepared according to literature methods. The $[CpFe(CO)_2(PMePh_2)]PF_6$ (**Va**) [34], $[CpFe(CO)(PMePh_2)_2]PF_6$ (**IV**) [34], and $[CpFe(CO)(PMePh_2)(=\overline{COCH_2CH_2O})]PF_6$ (**IIIa**) [22] were prepared by using slight modifications (see below) of the syntheses reported for their PPh_3 analogs.

Preparation of $[CpFe(CO)_2(PMePh_2)]PF_6$, Va

To a stirred acetone (30 ml) solution of $[CpFe(CO)_3]PF_6$ (0.71 g, 2.0 mmol), $PMePh_2$ (0.81 g, 4.0 mmol, 0.75 ml) was added. The mixture was stirred for 15 min; then the volume was reduced to ~5.0 ml under reduced pressure. Addition of Et_2O (80 ml) resulted in the precipitation of a yellow-green solid. The solvent was decanted from the residue which was dissolved in a minimum amount of acetone. Crystallization from acetone/Et_2O gave **Va** (0.97 g) in 93% yield. ^1H NMR(CD_3CN): δ 5.34 (d,

J_{PH} = 1.6 Hz, Cp), 2.35 (d, J_{PH} = 10.6 Hz, Me), 7.56 (m, Ph). ^{31}P NMR(CD_3CN): δ 49.91.

Preparation of $[CpFe(CO)(PMePh_2)_2]PF_6$, IV

Irradiation of a CH_2Cl_2 (35 ml) solution of **Va** (1.1 g, 2.1 mmol) and $PMePh_2$ (1.2 g, 6.0 mmol, 1.1 ml) with 254 nm light for 4 h led to the formation of **IV**. Crystallization in CH_2Cl_2/hexane at -20°C gave **IV** (0.98 g) in 70% yield. ^1H NMR(CD_3CN): δ 4.88 (t, J_{PH} = 1.6 Hz, Cp), 1.41 (pseudo-triplet, J_{PH} = 4.9 Hz, Me), 7.65-7.02 (m, Ph). ^{31}P NMR(CD_3CN): δ 47.34. Anal. Calc. for $C_{32}H_{31}F_6FeOP_3$: C, 55.35; H, 4.50. Found: C, 54.97; H, 4.49%.

Preparation of $[CpFe(CO)(PMePh_2)(=\overline{COCH_2CH_2O})]PF_6$, IIIa

To a cooled (0°C) suspension of **Va** (0.39 g, 0.75 mmol), NaBr (0.060 g, 0.60 mmol) and $BrCH_2CH_2OH$ (2 ml) was added ethylene oxide (8 ml). The mixture was stirred for 18 h, and the solvent was removed under reduced pressure. The residue was washed with three 10-ml portions of Et_2O and then extracted with CH_2Cl_2. The extract was filtered through anhydrous $MgSO_4$ on a glass frit. The filtrate was concentrated under vacuum, Et_2O was added and solution allowed to stand at -20°C overnight resulting in the formation of crystals of **IIIa** (0.36 g) in 86% yield. ^1H NMR (CD_3CN): δ 4.98 (d, J_{PH} = 1.7 Hz, Cp), 4.50 m and 4.21 m (OCH_2), 2.20 (d, J_{PH} = 9.9 Hz, Me), 7.27-7.54 (m, Ph). ^{31}P NMR(CD_3CN): δ 55.69. Anal. Calc. for $C_{22}H_{22}F_6FeO_3P_2$: C, 46.67; H, 3.92. Found: C, 46.45; H, 3.81%.

Reduction of $[CpFe(CO)_2(=\overline{COCH_2CH_2O})]PF_6$, I

To a stirred THF (40 ml) solution of I (0.12 g, 0.31 mmol), 0.30 M NaNp (1.0 ml, 0.30 mmol) was added; the pale yellow solution instantly turned red. After stirring for 1 h the reddish solution became purple. The solvent was removed under reduced pressure. The naphthalene was removed by sublimation into a trap under dynamic vacuum at 25°C. The remaining purple residue was dissolved in Et_2O and chromatographed on a 1 x 6 cm column of alumina (adsorption, 80-200 mesh). Elution with a 1:1 mixture of hexane/Et_2O, followed by evaporation of the solution to dryness gave $[CpFe(CO)_2]_2$ (II) in 70% yield. ^1H NMR ($CDCl_3$): δ 4.76 (s, Cp). ^{13}C NMR (CD_2Cl_2): δ 88.80 (Cp), 215.86 (CO). Mass spec: 354 (M^+). A GC-MS analysis of the gaseous products formed in this reaction gave the following m/e: 44 and 28, 27 and 26. (This reaction was carried out under He.) These peaks correspond to carbon dioxide and ethylene, respectively. In an effort to find out if any intermediates were formed enroute to the formation of II, the above reaction was repeated using I (0.060 g, 0.15 mmol) and 0.24 ml of 0.58 M NaNp in a 100 ml Schlenk flask connected directly to an IR cell by teflon tubing as described by Gladysz and coworkers [35]. By periodically drawing some of the solution from the reaction vessel into the IR cell, the reaction was monitored. The results are described in the Results and Discussion section.

NaNp-catalyzed Substitution of I

To a THF (20 ml) solution of I (0.13 g, 0.33 mmol) and $PMePh_2$ (0.52 g, 2.6 mmol, 0.48 ml), 0.1 equivalent of NaNp (0.11 ml of an 0.34 M solution) was quickly added with stirring. The pale yellow solution immediately became intense yellow. The volume of the solution was quickly reduced to 5 ml under vacuum and hexanes were added with stirring. This resulted in the precipitation of a yellow solid. The solvent was decanted from the yellow residue which was then washed with two 10-ml portions of Et_2O. The residue was then extracted with CH_2Cl_2 (20 ml) and filtered through anhydrous $MgSO_4$ on a glass frit. After reduction of the filtrate volume to ~4 ml under vacuum, it was layered with 20 ml of Et_2O and stored at -20°C overnight. After filtering and drying, 0.16 g of a yellow solid was obtained. The ^1H NMR of this solid in CD_3CN indicated that it was composed of $[CpFe(CO)(PMePh_2)(=\overline{COCH_2CH_2O})]PF_6$ (**IIIa**) and $[CpFe(CO)(PMePh_2)_2]PF_6$ (**IV**) in 72% and 21% yields, respectively; there was also q trace amount of **Va**. Similar results were obtained using PPh_3 as the phosphine.

Reaction of **I** with PR_3

A CH_2Cl_2 (10 ml) solution of **I** (0.050 g, 0.12 mmol) and $PMePh_2$ (0.20 g, 1.0 mmol, 0.19 ml) was stirred for 60 min. The volume of the solvent was reduced to ~2 ml under vacuum, and hexanes (~40 ml) were added with stirring. The solvent was decanted, and the residue was washed with Et_2O and then extracted with CH_2Cl_2. The CH_2Cl_2 solution was filtered through anhydrous $MgSO_4$ on a glass frit. Hexanes were added to precipitate a yellow solid (65 mg). The ^1H NMR spectrum of the solid in CD_3CN indicated the following compounds were present: $[CpFe(CO)(PMePh_2)(=\overline{COCH_2CH_2O})]PF_6$ (**IIIa**) (73%), $[CpFe(CO)_2(PMePh_2)]PF_6$ (**Va**) (12%) and $[CpFe(CO)(PMePh_2)_2]PF_6$ (**IV**) (6%). When **I** and $PMePh_2$ were reacted for 18 h, **IV** was isolated as the only product in 85% yield.

The reaction of **I** (0.060 g, 0.15 mmol) and PPh_3 (0.33 g, 1.2 mmol) in CH_2Cl_2 (20 ml) was performed as described above for the analogous $PMePh_2$ reaction. In this case, $[CpFe(CO)_2(PPh_3)]PF_6$ (**Vb**) and $[CpFe(CO)(PPh_3)(=\overline{COCH_2CH_2O})]PF_6$ (**IIIb**) were the only products observed after a 12 h reaction time. No further reaction occurred after 24 h.

Reaction of $[CpFe(CO)(PMePh_2)(=\overline{COCH_2CH_2O})]PF_6$, IIIa, and $PMePh_2$

To a stirred solution of **IIIa** (0.15 g, 0.26 mmol) in CH_2Cl_2 (10 ml) was added $PMePh_2$ (0.050 g, 1.8 mmol, 0.34 ml). After 20 h, the volume of the solvent was reduced to ~5 ml under vacuum, and hexanes (50 ml) were added with stirring. This resulted in the precipitation of a yellow solid. The solvent was decanted from the residue which was then washed with two 10-ml portions of Et_2O. The residue was extracted with two 10-ml portions of CH_2Cl_2 and the extract was filtered through anhydrous $MgSO_4$ on a glass frit. The volume of the CH_2Cl_2 extract was reduced to ~4 ml and then layered with Et_2O (20 ml) and stored at -20°C overnight. Yellow crystals of **IV** were formed; 0.16 g (87%).

Reaction of I with [PPN]Cl and Other Anions

When a stirred solution of **I** (66 mg, 0.17 mmol) in CH_2Cl_2 (10 ml) was treated with [PPN]Cl (96 mg, 0.17 mmol), the pale yellow solution of **I** instantly became golden. The IR(CH_2Cl_2) spectrum displayed bands at 2037 (vs), 1985 (vs), and 1635 (m) cm^{-1}, suggesting the presence of $CpFe(CO)_2[C(=O)OCH_2CH_2Cl]$, **VIa** [$^1H$ NMR (CD_3CN): δ 5.03 (s, Cp), 4.14 (t, J = 5.6 Hz, CH_2), 3.64 (t, J = 5.6 Hz, CH_2)]. Addition of CF_3SO_3H (15 μl, 0.17 mmol) to this solution resulted in the formation of a pale yellowish powdery suspension. Removal of the solvent under vacuum produced 0.16 g of a yellow solid. ^1H NMR and IR spectra of the solid product showed it to be $[CpFe(CO)_3]CF_3SO_3$ (54 mg, 92%). IR(CH_3CN): 2125 (vs), 2073 (vs) cm^{-1}. ^1H NMR (CD_3CN): δ 5.77 (s, Cp).

The reaction of I (24 mg, 0.060 mmol) and $[N(n\text{-}Bu)_4]I$ (23 mg, 0.060 mmol) in CH_2Cl_2 (10 ml), followed by CF_3SO_3H, yielded very similar results to that of [PPN]Cl. The analogous reactions of I with NaOMe (in MeOH), $NaSCH_2Ph$ (in THF) and [PPN]SCN, followed by CF_3SO_3H gave the same types of IR and NMR spectra as observed in the reaction of [PPN]Cl.

Reaction of $[CpFe(CO)_2(=\overline{CSCH_2CH_2S})]PF_6$, **XV** with NaSMe

To a stirred THF (20 ml) solution of NaSMe prepared by slowly bubbling MeSH through a suspension NaH (50% in mineral oil, 14 mg, 0.29 mmol), **XV** (0.12 g, 0.28 mmol) was added. The mixture was stirred for 15 min, and the solvent was removed under reduced pressure. The residue was extracted with hexane and the extract was filtered through Celite on a glass frit. Removal of solvent in vacuo led to the isolation of $CpFe(CO)_2[\overline{C(SMe)SCH_2CH_2S}]$, **XVII**, as a yellow solid (0.060 g, 65%). Further purification of **XVII** by column chromatography on alumina led to decomposition. Its elemental analysis was not obtained. ^1H NMR (C_6D_6): δ 4.34 (s, Cp), 3.16 (m, SCH_2), 2.81 (m, SCH_2), 2.21 (s, SMe). MS: 328 (M^+), 300 (M^+-CO), 272 (M^+-2CO), 151 {$[\overline{C(SMe)SCH_2CH_2S}]$, base peak}, 121 (CpFe). When **XVII** was treated with 1 eq $HBF_4 \cdot Et_2O$, **XV** was regenerated quantitatively.

Reaction of I with Me_3NO

To a stirred solution of I (0.050 g, 0.13 mmol) in CH_2Cl_2 (20 ml), Me_3NO (0.010 g, 0.20 mmol) was added. An instantaneous color change from pale yellow to red was observed. The IR spectrum taken in CH_2Cl_2 showed bands at 2040 (m), 1993 (m, sh), 1973 (s), 1810 (s), and 1773 (mw) cm^{-1}. The reddish solution slowly decomposed to give a dark brown residue which showed no IR bands in the carbonyl region. The IR of the supernatant showed bands at 1973 (s, broad), 1810 (s), 1773 (mw) cm^{-1}. The ^1H NMR spectrum of the supernatant showed signals at δ 4.78 and 4.52. The IR bands at 1810 and 1773 cm^{-1} and the NMR signal at 4.52 are characteristic of ethylene carbonate (**VIII**). In an attempt to capture $CpFe(CO)_2^+$ as $CpFe(CO)_2I$, $[Bu_4N]I$ (1 equivalent) was quickly added to the reaction mixture after the Me_3NO addition; however, no $CpFe(CO)_2I$ was detected.

When a suspension of iodosobenzene (0.050 g, 0.25 mmol) and I (0.020 g, 0.060 mmol) was stirred for 3 days, ethylene carbonate was the only new product identified.

Similarly, the reaction of I (0.020 g, 0.040 mmol) and freshly distilled H_2O (10 drops) in CH_2Cl_2 yielded ethylene carbonate in 7 days.

Reduction of $\{CpFe(CO)_2[=C(SMe)_2]\}PF_6$, **X**

The reduction of **X** was achieved by the method used in the reduction of I. A solution of **X** (0.040 g, 0.10 mmol) in THF (20 ml) was treated with one equivalent of NaNp in THF. An instantaneous color change from greenish-yellow to dark red was observed. The solvent was removed under reduced pressure, and the residue extracted with hexanes. The extract was filtered through Celite on a glass frit, and the solvent was removed under vacuum. The IR, ^1H and ^{13}C NMR, and mass spectra of the resulting reduction residue were obtained. Similar reactions were carried out at 60°C, 0°C, -30°C, and -60°C. Reactions were also performed at 25°C on solutions containing (0.080 g, 0.19 mmol), (0.12 , 0.29 mmol), and (0.20 g, 0.47 mmol) of **X**. Analysis of the spectroscopic data showed that the hexanes extracts of all the reduction reactions consisted of the following compounds: $Cp_2Fe_2(CO)_4$ (II). $Cp_2Fe_2(CO)_2(SMe)_2$ (XI) {^1H NMR (CD_2Cl_2): δ 4.35 (Cp), 1.27 (SMe). ^{13}C NMR (CD_2Cl_2): δ 216.69 (CO), 81.24 (Cp), 16.51 (SMe). Mass spec: 392 (M^+)}. $CpFe(CO)_2[C(SMe)_3]$ (XII) {^1H NMR (CD_2Cl_2): δ 4.89 (Cp), 2.24 (SMe). ^{13}C NMR (CD_2Cl_2): δ 89.66 (Cp), 19.27 (SMe), 59.72 [$\underline{C}(SMe)_3$]. Mass spec: 348 (M^+-SMe), 153 (base peak, $C(SMe)_3$)}, and $CpF\overline{e(CO)[C(S}Me)(SMe)_2$ (**XIII**) {^1H NMR (C_6D_6): δ 4.27 (Cp), 2.22 (6H, SMe), 1.38 (3H, SMe). ^{13}C NMR (C_6D_6): δ 216.03 (CO), 79.94 (Cp), 70.67 [$\underline{C}(SMe)_3$], 21.51 (coordinated SMe), 20.00 (uncoordinated SMe). Mass spec: 274 (base peak, M^+-CO)}.

NaNp-catalyzed Substitution of X

This reaction was carried out in the same way as the NaNp-catalyzed substitution of I described above starting with X (0.20 g, 0.47 mmol) and $PMePh_2$ (0.74 g, 3.7 mmol, 0.69 ml). The ^1H NMR spectrum of the yellow, solid product (0.298 g) confirmed the presence of $[CpFe(CO)(PMePh_2)_2]PF_6$, $[CpFe(CO)_2(PMePh_2)]PF_6$ and $\{CpFe(CO)(PMePh_2)[=C(SMe)_2]\}PF_6$ (**XIV**) in 32%, 48%, and 18% yields, respectively. ^1H NMR (CD_3CN) for **XIV**: δ 5.10 (d, J_{PH} = 1.5 Hz, Cp), 2.81 (s, SMe), 2.26 (d, J_{PH} = 9.6 Hz, Me), 7.44-7.23 (m, Ph). This ^1H NMR spectrum is very similar to that of $\{CpFe(CO)(PPh_3)$-$[=C(SMe)_2]\}PF_6$ [15b].

Reaction of **X** with $PMePh_2$

To a stirred solution of **X** (0.030 g, 0.080 mmol) in CH_2Cl_2 (10 ml), $PMePh_2$ (0.12 g, 0.60 mmol, 0.11 ml) was added. After stirring for 2 h, the solvent was reduced to ~2 ml under vacuum and hexanes (~40 ml) were added with stirring. The solvent was decanted off, and the residue was crystallized from CH_2Cl_2/hexane to give 0.040 g of a brownish yellow solid. The ^1H NMR spectrum indicated the presence of the following compounds: $[CpFe(CO)(PMePh_2)_2]PF_6$ (64%), $[CpFe(CO)_2(PMePh_2)]PF_6$ (13%), and $\{CpFe(CO)(PMePh_2)[=C(SMe)_2]\}PF_6$ (3.8%).

Reaction of $[CpFe(CO)_2(=\overline{CSCH_2CH_2S})]PF_6$, **XV** with $PMePh_2$

A CH_2Cl_2 (10 ml) solution of **XV** (0.030 g, 0.070 mmol) and $PMePh_2$ (0.11 g, 0.54 mmol, 0.10 ml) was stirred for 15 min. The solvent was removed under reduced pressure, and the residue was washed several times with Et_2O. The residue was extracted with CH_2Cl_2 and filtered through anhydrous $MgSO_4$ on a glass frit. The product in the filtrate was crystallized from CH_2Cl_2/hexane affording 0.35 g of $[CpFe(CO)(PMePh_2)(=\overline{CSCH_2CH_2S})]PF_6$ (**XVI**) (85 %). ^1H NMR (CD_2Cl_2): δ 5.05 (d, J_{PH} = 1.7 Hz, Cp), 3.72 m and 3.36 m (SCH_2), 2.23 (d, J_{PH} = 10.9 Hz, Me), 7.56-7.25 (m, Ph). Trace amounts of **IV** and **Va** were also produced in this reaction and were not separated from **XVI**.

Preparation of $Cp^*Fe(CO)_2[C(SMe)_3]$, **XIX**

Compound **XIX** was prepared as described for **XII** [18a] starting with 0.026 g (0.62 mmol) of 57% NaH in mineral oil and 0.13 g (0.26 mmol) of $\{Cp^*Fe(CO)_2[=C(SMe)_2]\}PF_6$ [18c] in THF (40 ml). The THF was removed under reduced pressure after stirring for 2 h and the residue extracted with hexanes. Compound **XIX** was isolated from the hexanes solution upon removal of the solvent as yellow platelets (0.097 g, 92%). ^1H NMR (C_6D_6): δ 1.53 (15H, C_5Me_5), 2.20 (9H, SMe). ^{13}C NMR (C_6D_6): δ 96.73 ($\underline{C}_5Me_5$), 218.40 (CO), 58.89 [$\underline{C}(SMe)_3$], 18.68 (SMe), 9.26 (C_5Me_5). Mass spec: 400 (M^+), 372 (M^+-CO), 353 (M^+-SMe), 344 (M^+-2CO), 153 {base peak, [$C(SMe)_3$]}. Anal. Calc. for $C_{16}H_{22}FeO_2S_3$: C, 48.02; H, 6.04. Found: C, 48.11; H, 6.20.

Synthesis of {$CpRu(CO)_2[=C(SMe)_2)$}PF_6, **XX**

To a stirred solution of $CpRu(CO)_2[C(S)SMe]$ [23c] (0.85 g) in CH_2Cl_2 (20 ml) cooled to 0°C, CH_3SO_3F (0.24 ml) was added. Stirring was continued for 1 h after which KPF_6 (~2.0 g) was added and the mixture stirred for an additional 30 min. The mixture was treated with excess hexanes to precipitate products. The solvent was removed and the residue was then washed with three 20-ml portions of Et_2O. The residue was extracted with CH_2Cl_2 (20 ml) and filtered through Celite on a glass frit. The extract was layered with hexanes and stored at -20°C for 3 days. **XX** (0.092 g, 72%) was obtained as a yellow crystalline solid. ^1H NMR (CD_2Cl_2): δ 5.64 (Cp), 3.08 (6H, SMe). ^{13}C NMR (CD_2Cl_2): δ 89.95 (Cp), 194.62 (CO), 283.39 [$\underline{C}(SMe)_2$], 30.79 (SMe). Anal. Calc. for $C_{10}H_{11}F_6O_2PS_2Ru$: C, 25.37; H, 2.34; S, 13.55. Found: C, 25.58; H, 2.57; S, 13.70.

Reduction of {$CpRu(CO)_2[=C(SMe)_2]$}PF_6

Sodium naphthalenide (0.18 ml of 0.34 M solution, 0.060 mmol) was added to a stirred THF (10 ml) solution of {$CpRu(CO)_2[=C(SMe)_2]$}PF_6 (0.030

g, 0.060 mmol). The color of the solution changed instantly from gold to red. The mixture was allowed to stir for 30 min and the solvent removed in vacuo. The residue was first extracted with hexanes and then with Et_2O. The hexane extract contained $CpRu(CO)_2[C(SMe)_3]$ (XXI), {^1H NMR (C_6D_6): δ 4.64 (Cp), 2.18 (9H, SMe). ^{13}C NMR (C_6D_6): δ 92.16 (Cp), 200.82 (CO), 53.56 [$\underline{C}(SMe)_3$], 19.10 (SMe). Mass spec: 376 (M^+), 361 (M^+-Me), 348 (M^+-CO), 320 (M^+-2CO), 153 [(base peak), $C(SMe)_3$]} and $[CpRu(CO)(SMe)]_2$ [36a] {Mass spec: 483 (M^+), 468 (M^+-Me), 456 (M^+-CO), 428 (M^+-2CO)}. The Et_2O extract was mainly $[CpRu(CO)_2]_2$ [36b] {Mass spec: 446 (M^+), 390 (M^+-2CO), 362 (M^+-3CO), 334 (M^+-4CO), 223 [$CpRu(CO)_2$, (1/2 M^+)], 195 (1/2 M^+-CO), 167 (1/2 M^+-2CO).

Preparation of $CpRu(CO)_2[C(SMe)_3]$, XXI

Sodium hydride (0.026 g, 0.62 mmol), 57% in mineral oil, was washed with three 10-ml portions of hexanes and dried in vacuo. It was then dissolved in THF (40 ml) and MeSH slowly bubbled through the solution until H_2 evolution ceased [18a]. To this stirred solution, XX (0.21 g, 0.44 mmol) was added. The solvent was removed in vacuo after stirring for 30 min, and the residue was extracted with Et_2O and filtered through Celite on a glass frit. Removal of solvent led to the isolation of XXI (0.14 g, 84%) as a light yellow powder. Anal. Calc. for $C_{11}H_{14}O_2S_3Ru$: C, 35.18; H, 3.76; S, 25.62. Found: C, 35.12; H, 3.61; S, 25.36.

Preparation of $CpRu(CO)_2[C(SMe)_2(SPh)]$ XXII

Sodium hydride (0.014 g 0.26 mmol), 57% in mineral oil, was placed in a 100 ml Schlenk flask and washed with three 10-ml portions of hexanes.

The residue was dried in vacuo and dissolved in THF (40 ml). To this stirred solution was added PhSH (25 μl, 0.24 mmol). **XX** (0.097 g, 0.20 mmol) was added after 30 min and stirring continued for 15 min. The solvent was removed in vacuo and the residue extracted with Et_2O; the extract was filtered through Celite on a glass frit. Hexanes were added to the extract and the mixture concentrated and stored at -20°C for 3 days. Tiny yellow needle-like crystals of **XXII** (0.050 g, 60%) were isolated. ^1H NMR $[(CD_3)_2CO]$: δ 5.50 (Cp), 1.84 (6H, SMe), 7.31 (m, 5H, SPh). ^{13}C NMR (CD_2Cl_2): δ 91.72 (Cp), 200.52 (CO), 57.49 [$\underline{C}(SMe)_2(SPh)$], 19.00 (SMe), 138.36, 136.77, 134.76 (SPh). Mass spec: 438 (M^+), 423 (M^+-Me), 215 [$C(SMe)_2(SPh)$]. Anal. Calc. for $C_{16}H_{16}O_2S_3Ru$: C, 43.92; H, 3.69; S, 21.98. Found: C, 43.52; H, 3.72; S, 22.02.

Synthesis of $\{CpRu(CO)(MeCN)[=C(SMe)_2]\}PF_6$, XXIII

Compound **XXIII** was prepared by irradiation of **XX** (0.11 g, 0.24 mmol) in MeCN (30 ml) for 2 h. The solvent was removed in vacuo and the residue washed with several portions of Et_2O. The residue was then extracted with CH_2Cl_2 (25 ml) and filtered through Celite on a glass frit. The extract was reduced in volume to ~10 ml in vacuo, layered with hexanes and stored at -20°C. **XXIII** (0.83 g, 81%) was isolated as a red crystalline solid. ^1H NMR (CD_3CN): δ 5.24 (Cp), 3.02 (6H, SMe), 2.34 (3H, MeCN). Anal. Calc. for $C_{11}H_{14}F_6NOPS_2Ru$: C, 27.16; H, 2.90. Found: C, 27.25; H, 2.86.

STRUCTURE DETERMINATION

A single crystal with approximate dimensions of 0.20 x 0.10 x 0.05 mm was mounted on a glass fiber and subsequently placed on a goniometer head. Ten reflections ($10.5 < 2\theta < 34°$) were centered on a SYNTEX $P2_1$ four-circle diffractometer and indexed using an automatic indexing program (BLIND) [37]; the results indicated a centered monoclinic space group. A total of 6119 reflections (2 octants of data) were collected using an ω-step scan technique within a 2θ sphere of 50° and corrected for Lorentz-polarization effects. Since the absorption coefficient was comparatively low, an absorption correction was not applied. Independent reflections (760) with $I \geq 3\sigma(I)$ were retained for use in subsequent calculations. The estimated variance in each intensity was calculated by $\sigma(I)^2 = C_T + C_B + (0.03\ C_T)^2 + (0.03\ C_B)^2$, where C_T and C_B represent the total background counts, respectively, and the factor 0.03 is an estimate of non-statistical errors.

The position of the iron atom in the unit cell was obtained from an analysis of the Patterson map. The remaining non-hydrogen atoms were located from successive structure factor and electron density map calculations. The crystal data and atomic and thermal parameters for the non-hydrogen atoms are given in Tables 2 and 3, respectively. The positional and anisotropic thermal parameters for the non-hydrogen atoms were refined by a combination of block matrix/full matrix least squares calculations [38]. The positional parameters of the hydrogen atoms were calculated and included but were not varied during the refinement; they were all given a fixed isotropic temperature factor of 6.0 Å^2. The

Table 1. Infrared spectra of complexes in CH_2Cl_2

Complex	ν(CO) cm^{-1}
$[CpFe(CO)_2(=\overline{COCH_2CH_2O})]PF_6$ (I)	2070(s), 2024(s)
$Cp_2Fe_2(CO)_4$ (II)[a]	2006(m), 1963(s), 1794(s)
$[CpFe(CO)(PMePh_2)(=\overline{COCH_2CH_2O})]PF_6$ (IIIa)	1992(s)
$[CpFe(CO)(PPh_3)(=\overline{COCH_2CH_2O})]PF_6$ (IIIb)	1994(s)
$[CpFe(CO)(PMePh_2)_2]PF_6$ (IV)	1968(s, broad)
$[CpFe(CO)_2(PMePh_2)]PF_6$ (Va)	2053(s), 2010(s)
$[CpFe(CO)_2(PPh_3)]PF_6$ (Vb)	2055(s), 2010(s)
$CpFe(CO)_2[C(=O)OCH_2CH_2Cl]$ (VIa)	2037(vs), 1985(vs), 1635(m)
$CpFe(CO)_2(=\overline{C(H)OCH_2CH_2O})$ (VII)[a]	2026(s), 1970(s)
$O=\overline{COCH_2CH_2O}$ (VIII)	1810(s), 1773(m)
$\{CpFe(CO)_2[=C(SMe)_2]\}PF_6$ (X)	2072(s), 2030(s)
$Cp_2Fe_2(CO)_2(SMe)_2$ (XI)[a]	1962(s)
$CpFe(CO)_2[C(SMe)_3]$ (XII)[a]	2025(s), 2014(m), 1978(s), 1968(m)
$Cp\overline{Fe(CO)[C(S}Me)(SMe)_2]$ (XIII)[a]	1949(m), 1938(s)
$\{CpFe(CO)(PMePh_2)[=C(SMe)_2]\}PF_6$ (XIV)	1969(s)
$[CpFe(CO)_2(=\overline{CSCH_2CH_2S})]PF_6$, (XV)	2077(s), 2038(s)
$[CpFe(CO)(PMePh_2)(=\overline{CSCH_2CH_2S})]PF_6$ (XVI)	1982(s, broad)
$CpFe(CO)_2[\overline{C(SMe)SCH_2CH_2S}]$ (XVII)[a]	2030(s), 1976(vs)
$\{CpFe(CO)_2[=C(SMe)(NMe_2)]\}PF_4$ (XVIII)	2046(s), 2001(s)

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[a] In hexanes solvent.

Table 1. Continued

Complex	ν(CO) cm^{-1}
$Cp^*Fe(CO)_2[C(SMe)_3]$ (XIX)	2010(s), 1994(w), 1954(vs), 1945(w)
$\{CpRu(CO)_2[=C(SMe)_2]\}PF_6$ (XX)	2070(s), 2027(2)
$CpRu(CO)_2[C(SMe)_3]$ (XXI)	2040(s), 2032(m), 1984(vs), 1974(ms)
$CpRu(CO)_2[C(SMe)_2(SPh)]$ (XXII)[b]	2034(s), 1973(s)
$\{CpRu(CO)(MeCN)[=C(SMe)_2]\}PF_6$ (XXIII)[c]	1993(s)

[b] In THF.

[c] In CH_3CN.

Table 2. Crystal data for $\{CpFe(CO)_2[=C(SMe)_2]\}PF_6$ (X)

Compound	$\{CpFe(CO)_2[=C(SMe)_2]\}PF_6$
Formula	$C_{10}H_{11}F_6FeO_2PS_2$
Formula weight	428.15
Crystal system	monoclinic
Space group	C2/c
a (Å)	32.91 (1)
b (Å)	6.790 (3)
c (Å)	14.509 (4)
β (°)	105.48 (3)
V (Å^3)	3124 (2)
Z	8
$\mu(MoK_\alpha)$ (cm^{-1})	13.83
ρ (calculated) g/cm^3	1.82
Temperature, °C	20
Diffractometer	SYNTEX $P2_1$
Monochromator	oriented graphite
Radiation	MoK_α (λ = 0.71069 Å)
Reflections measured	hkl, $hk\bar{l}$ (6119 reflections)
Scan type	ω-step scan
Independent reflections observed ($I > 3\sigma_I$)	760
Min, max, 2θ (degree)	0°, 50°
Max no. of parameters refined	115
R (conventional)	0.080
Rw	0.084

Table 3. Atomic positional parameters (X 10^4) and equivalent isotropic thermal parameters[a] (A^2 x 10^3) for {$CpFe(CO)_2[=C(SMe)_2]$}PF_6 (X)

Atom	x	y	z	$\bar{U}$
Fe	6071 (1)	644 (6)	373 (3)	32
S68	6832 (2)	-1052 (10)	1880 (5)	37
S67	6762 (2)	-2665 (12)	43 (5)	45
O9	6455 (6)	3868 (30)	-1614 (14)	77
O10	6256 (6)	2508 (33)	-1285 (13)	70
C1	5473 (10)	-29 (61)	-459 (22)	76
C2	5446 (8)	1400 (51)	182 (39)	115
C3	5600 (8)	662 (69)	1104 (24)	80
C4	5728 (8)	-1252 (50)	1006 (28)	76
C5	5666 (10)	-1770 (54)	616 (35)	108
C6	6585 (5)	-1102 (33)	713 (15)	20
C7	6466 (9)	-2430 (43)	-1181 (16)	51
C8	7271 (8)	-2681 (45)	2019 (16)	47
C9	6318 (10)	2521 (48)	1116 (23)	69
C10	6195 (8)	1717 (39)	-635 (23)	47
P4[b]	2500	2500	5000	37
P5[c]	5000	-5035 (18)	-2500	59
F41	2306 (4)	768 (25)	4290 (9)	55
F42	2749 (5)	938 (24)	5753 (11)	63
F43	2106 (4)	2338 (28)	5451 (11)	64
F51[c]	5000	-2652 (49)	-2500	114
F52[c]	5000	-7418 (50)	-2500	114
F53	4564 (6)	-5021 (29)	-2905 (13)	114
F54	4955 (6)	-5015 (30)	-1443 (14)	114

[a] $\bar{U} = 1/3\ \Sigma\ U_{ii} \times 10^3$ where the temperature factors are defined as $\exp(-2\pi^2\ \Sigma h_i h_j a_i^* a_j^* U_{ij})$.

[b] Occupies special position d in the space group C2/c with atomic multiplicity of 0.50.

[c] Occupies special position e with atomic multiplicity of 0.50.

conventional residual index ($R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$) was 0.080; the function minimized in the least squares refinement was $\Sigma w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F)$. The PF_6^- was found to be disordered and undoubtedly contributed to the somewhat higher residual index, and the smaller number of observed reflections than expected, and relatively large errors in the distances and angles.

RESULTS AND DISCUSSION

Structure of $\{CpFe(CO)_2[=C(SMe)_2]\}PF_6$ (X)

A perspective view of X showing the numbering scheme and thermal elipsoids is given in Fig. 1. The positional parameters, and selected angles and distances are listed in Tables 3 and 4, respectively.

The iron in X is in a slightly distorted octahedral geometry with the cyclopentadienyl ring occupying one face. The L-Fe-L angles 94.7°, 92.1°, and 93.1° for the carbene and two CO ligands are similar to those found in $[CpFe(CO)_2(CS)]PF_6$ [39], $CpFe(CO)_2[C(PPh_3)(=CHPh)]BF_4$ [40], and $CpFe(CO)_2[=\overline{CC(CH_3)S(O)OC}H_2]$ [41] which also have the piano stool geometry. The Fe-C(carbene) bond distance 2.02 (2) Å is somewhat longer than Fe=C bond lengths (1.91-2.00 Å) in other Fe-carbene complexes such as $\{CpFe(CO)_2[=C(H)(SPh)]\}PF_6$ [42b], $\{CpFe(CO)_2[=C(Me)(SMe)]\}PF_6$ [42b], $[CpFe(CO)_2(C_7H_6)]PF_6$ [42c], and $[CpFe(CO)_2(C_{11}H_{18})]PF_6$ [42c] but shorter than typical Fe-C(sp^3) bonds (2.08-2.10 Å) [42]. This suggests relatively weak π-bonding between Fe and the carbene carbon; on the other hand, there is significant π-bonding between the carbene carbon and the sulfur atoms. This is evident from the C6-S67 and C6-S68 distances (1.65 and 1.67 Å, respectively), which are much shorter than known S-C(alkyl) distances (range: 1.80-1.84) [42], and the S67-C7 and S68-C8 distances (1.79 Å) in X. Pi-bonding between the carbene carbon and the sulfur atoms was previously proposed based on the inequivalence of the methyl groups (C7 and C8) in the carbene ligand in ^1H and ^{13}C NMR spectra of the complex [15]. The ambient temperature solution ^1H NMR spectrum of X shows a single line for the two methyl groups; however, on cooling to -55°C two

Table 4. Selected bond distances (Å) and angles (°) for $\{CpFe(CO)_2[=C(SMe)_2]\}PF_6$ (X)

Fe-C1	2.07 (3)	C6-Fe-C9	93. (1)
Fe-C2	2.07 (3)	C6-Fe-C10	94.7 (9)
Fe-C3	2.10 (3)	C9-Fe-C10	92. (1)
Fe-C4	2.08 (3)	C6-S68-C8	105. (1)
Fe-C5	2.08 (4)	C6-S67-C7	110. (1)
Fe-C6	2.02 (2)	Fe-C6-S68	113. (1)
Fe-C9	1.73 (3)	Fe-C6-S67	130. (1)
Fe-C10	1.78 (3)	S68-C6-S67	117. (1)
S67-C6	1.65 (2)	Fe-C9-O9	175. (2)
S68-C6	1.67 (2)	Fe-C9-O10	176. (2)
S67-C7	1.79 (2)		
S68-68	1.78 (3)		
C9-O9	1.18 (4)		
C10-O10	1.15 (4)		

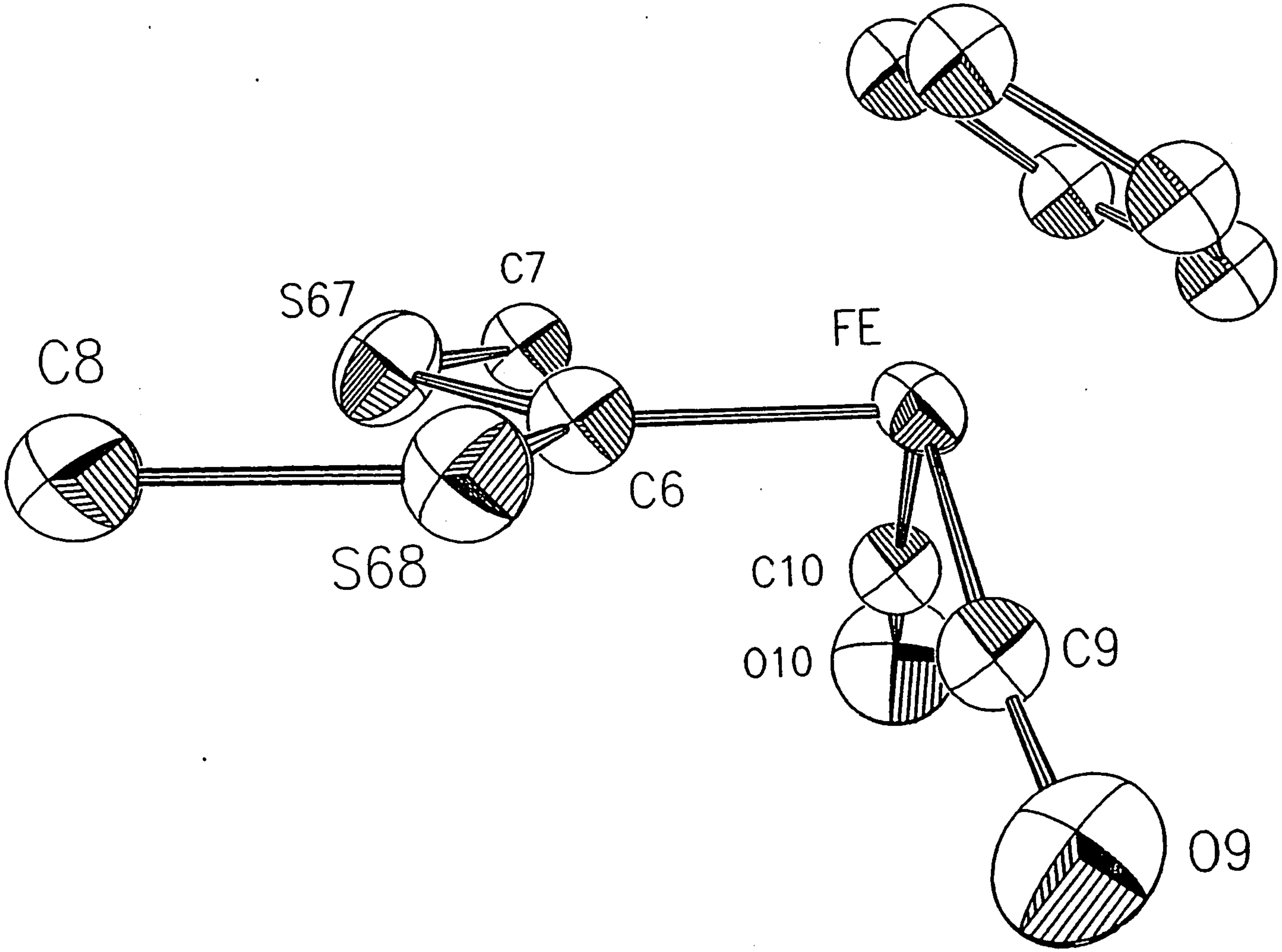
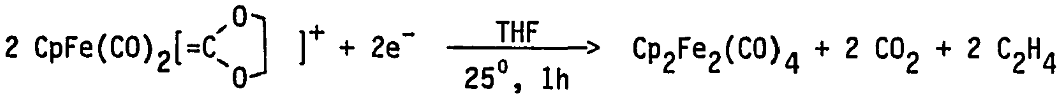


Figure 1. ORTEP diagram of $CpFe(CO)_2[=C(SMe)_2]^+$, X showing the orientation of the carbene ligand

sharp singlets are observed. The two singlets coalesce upon warming at -2.5°C [15]. In other thiocarbene complexes such as $\{PtCl[=C(SEt)_2](PPh_3)_2\}$, $\{PtI[=C(SMe)_2](PPh_3)_2\}I$ and $\{PtI[=C(SEt)_2](PPh_3)_2\}I$ [43], NMR studies also indicate the presence of syn and anti R groups, as in X. The dithiomethyl carbene ligand in X is essentially planar with the plane of the carbene moiety 90° (Fig. 1) from that predicted by frontier orbital arguments for the simplest carbene ($:CH_2$) [44] and observed in $Cp_2Ta(CH_3)(=CH_2)$ and $Cp_2Ta(CH_2Ph)[=C(H)Ph]$ [45a,b], $CpMn(CO)_2[=C(F)Ph]$ [45c], $CpFe(CO)_2[=C(H)Ph]^+$ [7,9] and $CpFe(CO)_2[=C(H)SPh]^+$ [42b]. Similar deviations from the so-called "upright" orientation for the carbene moiety have been observed in $CpM(CO)_2$(carbene) (M = Mn, Re) [46] and other $CpFe(CO)_2(\text{carbene})^+$ complexes [42b,c]. The "crosswise" or "orthogonal" conformation of the carbene moiety in $CpFe(CO)_2[=C(Me)SMe]^+$ [42b] was rationalized on the basis of nonbonded interactions between the Cp ligand and either of the two substituents on the carbene center. The long Fe-C6 distance in X suggests Fe-to-carbene pi bonding is relatively weak, and it is likely that steric or possibly crystal packing forces determine the orientation of the carbene ligand.

Reactions of $[CpFe(CO)_2(=\overline{COCH_2CH_2O})]PF_6$, I

Reducing agents such as sodium amalgam and sodium naphthalenide react immediately with I to give II (70%), CO_2 and ethylene (eq. 5). The



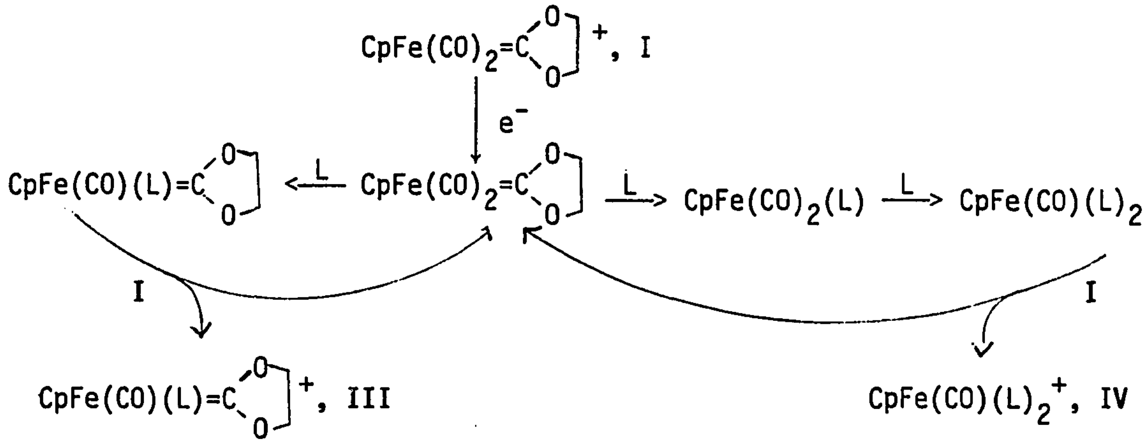
$$2\ CpFe(CO)_2[=C\overset{O}{\underset{O}{\langle}}]^+ + 2e^- \xrightarrow[25^0,\ 1h]{THF} Cp_2Fe_2(CO)_4 + 2\ CO_2 + 2\ C_2H_4 \qquad 5$$

I II

formation of II was established by comparing its infrared and ^1H NMR spectra with those of the authentic compound. The presence of CO_2 and ethylene was established by GC-MS. It is apparent from reactions monitored by IR spectroscopy at 25°C and 0°C that the reduction leading to the formation of the products indicated in eq. 5 goes through some intermediate(s), the exact nature of which is(are) not known. They appear to be fairly long-lived as evident from the IR bands observed at 2035 (ms), 2008 (ms), 1975 (s) and 1950 (s) cm^{-1} which appear within the first minute of reaction and gradually diminish over a period of 60 min as bands corresponding to the final product II appear. An examination of the NaNp reduction product within 5 min after reduction at 4 K showed it to be esr silent. The non-existence of a long-lived odd electron product is further supported by the CV of I, which shows an irreversible reduction wave. Though II is obtained in good yield, it is clear from its CV that it is not the initial product of the reduction. Also, coupling of the cyclic dioxocarbene unit to give the alkoxyolefin, $\overline{OCH_2CH_2O}C=\overline{COCH_2CH_2O}$, similar to what has been observed by Bianchini and coworkers [26] in the formation of tetrathiafulvalene from a cyclic dithiocarbene, does not occur presumably because the fragmentation of the cyclic dioxycarbene intermediate to give CO_2 and ethylene is faster [47]. Work done by Borden and Hoo [48a] and Feller and coworkers [48b] suggests that the fragmentation of the cyclic dioxocarbene to CO_2 and ethylene proceeds via a diradical intermediate.

If I is only partially reduced using 0.1 equivalent of NaNp in the presence of PPh_3 and $PMePh_2$, $[CpFe(CO)(L)(=\overline{COCH_2CH_2O})]PF_6$ (72%),

$[CpFe(CO)(L)_2]PF_6$ (21%) and trace amounts of $[CpFe(CO)_2(L)]PF_6$ (L = $PMePh_2$) are formed instantaneously. The reactions presumably proceed by an electron-catalyzed process (Scheme I). Carbene metal radical complexes such as $Fe(CO)_3[=\overline{CN(Me)CH_2CH_2N}(Me)]_2^{\ddagger}$ [49a], $(CO)_5\bar{Cr}-\dot{C}(OMe)Ph$ [49b], $Cr(CO)_4[=\overline{CN(Et)CH_2CH_2N}(Et)]_2^{\ddagger}$ [49c) have been reported in the literature. It is, therefore, reasonable to postulate a radical intermediate in the reaction described in Scheme I. Reductive CO

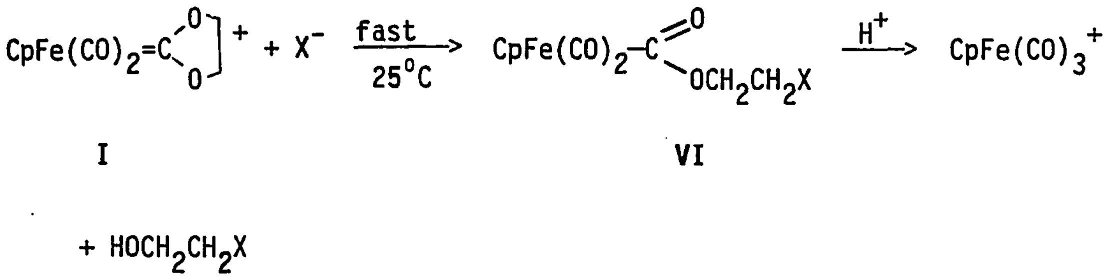


Scheme I

substitution reactions of this kind have been reported both in cases where the radical intermediate is unstable and where it is stable enough to be characterized spectroscopically [50,51]. It is presumed, in view of what is known from the reduction of I, that the cyclic dioxo-carbene liberated in the formation of **IV** decomposes to CO_2 and ethylene. The proposed scheme is supported by the reaction of $CpFe(CO)_2(PMePh_2)^+$ (**Va**) with $PMePh_2$ in the presence of catalytic quantities of NaNp (0.1 equivalent), which leads to the substitution of an additional phosphine in **Va** to give **IV**.

Further support for Scheme I is provided by the reactions of III and IV with $PMePh_2$ in the presence of NaNp (0.1 equivalent) which do not lead to further substituted products.

Reaction of I with various anions (eq. 6) leads to the formation of an ester as a result of the opening of the carbene ring via an attack at one of the methylene carbons. These esters, which have only been characterized by IR and ^1H NMR spectroscopy, are unstable and readily decompose in solution to give $[CpFe(CO)_2]_2$, II [52]. However, if the ester formed (eq. 6) is immediately treated with CF_3SO_3H, $CpFe(CO)_3^+$ is



I

VI

6

(6)

$X^- = I^-, Cl^-, MeO^-, NCS^-, PhCH_2S^-$

isolated in 92% yield (X = Cl) [53]. Unlike I, $\{CpFe(CO)_2[=\overline{CSCH_2CH_2S}]\}PF_6$ (XV) does not react with (PPN)I in CH_2Cl_2 at 25°C but does react with NaSMe to give $CpFe(CO)_2[\overline{C(SMe)SCH_2CH_2S}]$. In the presence of hydrides such as $LiAlH_4$ and $Li[Al(t\text{-}BuO)_3H]$, XV slowly decomposes whereas I reacts to give a mixture of unstable products, probably $CpFe(CO)_2[\overline{C(H)OCH_2CH_2O}]$ (VII), and $CpFe(CO)_2C(O)CH_2CH_3$.

With Me_3NO, I reacts instantaneously to give ethylene carbonate $[O{=}\overline{COCH_2CH_2O}$, VIII] and unidentified organometallic compounds. Iodosobenzene (C_6H_5IO) undergoes a similar reaction to give VIII; however, this reaction is very slow and no evidence for a carbonyl containing organometallic product was seen. Ethylene carbonate is also generated by the reaction of I and H_2O at an extremely slow rate.

The reaction of I with phosphines at ambient temperature results in the formation of $[CpFe(CO)(L)(=\overline{COCH_2CH_2O})]PF_6$ (73%), $[CpFe(CO)_2(L)]PF_6$ (12%) and $[CpFe(CO)(L)_2]PF_6$ (6%) in 1 h (L = $PMePh_2$), at a much slower rate than the NaNp-catalyzed reaction (Scheme I). A complete conversion of IIIa to IV is observed in 24 h. With PPh_3, $[CpFe(CO)(L)(\overline{OCH_2CH_2O})]PF_6$ and $[CpFe(CO)_2(L)]PF_6$ are the only products formed from I, and no further reaction is observed in 24 h. A GC-MS analysis of the vapor phase of the reaction of IIIa and $PMePh_2$ showed it to contain CO_2, CO and ethylene. Though reactions monitored by ^1H NMR and ^{31}P NMR indicate the presence of some intermediates, it has not been possible to elucidate the reaction path.

Reactions of $\{CpFe(CO)_2[=C(SMe)_2]\}PF_6$, X

In contrast to the reduction of I, the instantaneous reaction of $CpFe(CO)_2[=C(SMe)_2]^+$ with sodium naphthalenide leads to the formation of

$$\underset{\textbf{X}}{CpFe(CO)_2[=C(SMe)_2]^+} + e^- \longrightarrow \underset{\textbf{II}}{Cp_2Fe_2(CO)_4} + \underset{\textbf{XI}}{Cp_2Fe_2(CO)_2(SMe)_2} + \qquad 7$$

$$\underset{XII}{CpFe(CO)_2[C(SMe)_3]} + \underset{XIII}{Cp\overline{Fe(CO)[C(S}Me)(SMe)_2]}$$

II (19%), **XI** (5%), **XII** (37%) and **XIII** (39%) with some decomposition to insoluble materials. Compounds **II**, **XI**, **XII**, and **XIII** have been reported previously [18,34,54] and were identified here by their IR, MS and NMR spectra. Although no spectroscopic evidence exists for the radical "$CpFe(CO)_2[=C(SMe)_2]$" as the initial product in the reduction (eq. 7), its intermediacy can be used to explain the formation of the observed reduction products. The $Cp_2Fe_2(CO)_4$ probably results from the direct decomposition of the radical intermediate with loss of the carbene[$:C(SMe)_2$]. The formation of **XII** may occur by MeS• transfer from one "$CpFe(CO)_2[=C(SMe)_2]$" radical to another because it is the favored product when high concentrations of **X** ($\geq 2.4 \times 10^{-2}$ M) and lower temperatures ($\leq 0°C$) are used. Fast addition of NaNp tends to favor the formation of **XIII** probably because it leads to a high concentration of "$CpFe(CO)_2[=C(SMe)_2]$" in which a CO is readily displaced by THF. Reaction of this THF adduct with MeS• present in solution apparently results in the formation of **XIII**. This postulate is supported by the reduction of $\{CpFe(CO)(MeCN)[=C(SMe)_2]\}PF_6$ with NaNp in the presence of MeSSMe which leads to the formation of **XIII** in 70% yield. While it may be argued that the NaNp reacts with MeSSMe to generate the MeS^- which reacts with $\{CpFe(CO)(MeCN)[=C(SMe)_2]\}PF_6$ to yield **XIII**, it is important to note that the reaction of NaSMe and $\{CpFe(CO)(MeCN)[=C(SMe)_2]\}PF_6$ gives **XIII** in only 30% yield, which suggests the MeSSMe reaction proceeds predominately through a reduced MeCN complex.

In contrast to the complex reduction of **X** in eq. 7, a 0.1 equivalent of NaNp instantly catalyzes the reaction of **X** with $PMePh_2$ to form the phosphine substitution products $CpFe(CO)(PMePh_2)[=C(SMe)_2]^+$ (**XIV**, 17.8%), $[CpFe(CO)_2(PMePh_2)]^+$, (**Va**, 32.3%) and $[CpFe(CO)(PMePh_2)_2]PF_6$ (**IV**, 48.5%). The NaNp catalyzed reaction can be envisaged as occurring via radical intermediates similar to those proposed for phosphine substitution in I (Scheme I). However, the major product in the NaNp catalyzed phosphine substitution in I is $[CpFe(CO)(PMePh_2)(=\overline{COCH_2CH_2O})]PF_6$ (IIIa) whereas **IV** and **Va** are the major products in **X**. The reaction of **X** with $PMePh_2$ in the absence of NaNp at 25°C takes nearly 2 h resulting in the following product distribution: **XIV** (3.8%), **Va** (13%) and **IV** (64%).

Reactions of Other $CpFe(CO)_2(carbene)^+$ and $CpRu(CO)_2(carbene)^+$ Complexes

Reduction of $\{CpFe(CO)_2[=\overline{CSCH_2CH_2S}]\}PF_6$ (**XV**) with NaNp in THF leads predominately to decomposition with formation of a small quantity of II and other unidentified products; this compares with the 70% yield of II obtained in the reduction of I (eq. 5). The reaction of **XV** with $PMePh_2$ at 25°C over a period of 15 min, leads to the formation of $\{CpFe(CO)(PMePh_2)-[=\overline{CSCH_2CH_2S}]\}PF_6$ (**XVI**) in 85% yield.

The $\{CpFe(CO)_2[=C(SMe)(NMe_2)\}PF_6$ complex does not react with $PMePh_2$ at 25°C; in the presence of NaNp, it slowly decomposes with the formation of a small quantity of II and other unidentified compounds.

Reaction of $\{Cp^*Fe(CO)_2[=C(SMe)_2]\}PF_6$ with NaSMe at 25°C leads to the formation of $Cp^*Fe(CO)_2[C(SMe)_3]$, **XIX**. Compound **XIX** has IR and NMR properties similar to those of $CpFe(CO)_2[C(SMe)_3]$ [18a].

Reduction of $\{CpRu(CO)_2[=C(SMe)_2]\}PF_6$ (**XX**) with NaNp in THF occurs instantly to give $[CpRu(CO)_2]_2$, $[CpRu(CO)(SMe)]_2$ and $CpRu(CO)_2[C(SMe)_3]$.

There is no evidence for the formation of $Cp(CO)\overline{Ru[C(S}Me)(SMe)_2]$ in this reaction. Compound **XX** also reacts with NaSMe and NaSPh to give $CpRu(CO)_2[C(SMe)_3]$ and $CpRu(CO)_2[C(SMe)_2(SPh)]$, respectively.

CONCLUSION

The α-heteroatom carbenes **I**, **X**, **XV**, **XX** examined in this paper are all readily reduced by NaNp to give unstable primary products which undergo rapid decomposition. The $[CpFe(CO)_2(=\overline{COCH_2CH_2O})]PF_6$ (I) product decomposes cleanly to give **II**, CO_2 and ethylene. In contrast, its sulfur analog, **XV**, yields mainly insoluble sulfides and only small quantities of **II**, but no CS_2. The reduction of $\{CpFe(CO)_2[=C(SMe)_2]\}PF_6$ (**X**) gives a mixture of products: **XI**, **XII**, **XIII** and **II**. Both **I** and **X** undergo phosphine substitution which is catalyzed by NaNp.

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REFERENCES

1. (a) Cardin, D. J.; Cetinkaya, B.; Doyle, M. J.; Lappert, M. F. Chem. Soc. Rev. 1973, 2, 99. (b) Casey, C. P. In "Reactive Intermediates", M. Jones and R. A. Moss, Eds; Wiley: New York, 1981; Vol. 2, p 135. (c) Casey, C. P. In "Reactive Intermediates", M. Jones and R. A. Moss, Eds; Wiley: New York, 1985, 3, 109. (d) Casey, C. P. CHEMTECH 1979, 378. (e) Dotz, K. H. In "Transition Metal Carbene Complexes", Verlag Chemie: Weinheim, 1983. (f) Hoffmann, P. In "Transition Metal Carbene Complexes", Verlag Chemie: Weinhem, 1983, p 113.

2. (a) Turner, H. W.; Schrock, R. R. J. Am. Chem. Soc. 1982, 104, 2331. (b) Brookhart, M.; Studabaker, W. B. Chem. Rev. 1987, 87, 411. (c) Herrmann, W. A. Angew. Chem. Int. Ed. Engl. 1982, 21, 117.

3. (a) Grubbs, R. H. Prog. Inorg. Chem. 1978, 24, 1. (b) Cross, R. J. Catalysis 1982, 5, 382.

4. Jolly, P. W.; Pettit, R. J. Am. Chem. Soc. 1966, 88, 5044.

5. Green, M. L. H.; Ishaq, M.; Whiteley, R. N. J. Chem. Soc. (A) 1967, 1508.

6. Green, M. L. H.; Mitchard, L. C.; Swamwick, M. G. J. Chem. Soc. (A) 1971, 794.

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

8. (a) Brandt, S.; Helquist, P. J. Am. Chem. Soc. 1979, 101, 6473. (b) O'Connor, E. J.; Brandt, S.; Helquist, P. J. Am. Chem. Soc. 1987, 109, 3739.

9. (a) Brookhart, M.; Tucker, J. R.; Flood, T. C.; Jensen, J. J. Am. Chem. Soc. 1980, 102, 1203. (b) Brookhart, M.; Tucker, J. R.; Husk, G. R. J. Am. Chem. Soc. 1981, 103, 979.

10. Brookhart, M.; Humphrey, M. B.; Kratzer, H. J.; Nelson, G. O. J. Am. Chem. Soc. 1980, 102, 7802.

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

12. Casey, C. P.; Miles, W. H.; Tukada, H.; O'Connor, J. M. J. Am. Chem. Soc. 1982, 104, 3761.

13. (a) Brookhart, M.; Tucker, J. R.; Husk, G. R. J. Am. Chem. Soc. 1983, 105, 258. (b) Kuo, G.; Kerber, R. C.; Helquist, P. Organometallics 1984, 3, 806.

14. (a) Casey, C. P.; Miles, W. H.; Tukada, H. *J. Am. Chem. Soc.* 1985, **107**, 2924. (b) Casey, C. P.; Miles, W. H. *Organometallics* 1984, **3**, 808.

15. McCormick, F. B.; Angelici, R. J. *Inorg. Chem.* 1979, **18**, 1231 and references therein. (b) McCormick, F. B.; Angelici, R. J. *J. Organomet. Chem.* 1981, **205**, 79.

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

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

18. (a) McCormick, F. B.; Angelici, R. J. *Inorg. Chem.* 1981, **20**, 4108. (b) Glavee, G. N.; Angelici, R. J. *J. Am. Chem. Soc.*, submitted for publication. (c) Choi, M.-G.; Angelici, R. J., manuscript in preparation.

19. Yu, Y. S.; Angelici, R. J. *Organometallics* 1983, **2**, 1583.

20. Yu, Y. S.; Angelici, R. J. *Organometallics* 1983, **2**, 1018.

21. Motschi, H.; Angelici, R. J. *Organometallics* 1982, **1**, 343.

22. Singh, M. M.; Angelici, R. J. *Inorg. Chem.* 1984, **23**, 2691.

23. (a) Matachek, J. R.; Angelici, R. J. *Organometallics* 1982, **1**, 1541. (b) Fenske, R. F.; Haller, K. J.; Schugart, K. A.; Matachek, J. R.; Angelici, R. J. *Organometallics* 1984, **3**, 1038. (c) Matachek, J. R.; Angelici, R. J. *Inorg. Chem.* 1986, **25**, 2877.

24. Boland-Lussier, B. E.; Hughes, R. D. *Organometallics* 1982, **1**, 635.

25. Kerber, R. C.; O'Connor, I. J.; Kuo, G.; Kremer, K. A. M.; Helquist, P. *J. Am. Chem. Soc.* 1982, **104**, 6119.

26. Bianchini, C.; Meli, A.; Scapacci, G. *Organometallics* 1985, **4**, 264.

27. Goddard, W. A.; Carter, E. A. *J. Am. Chem. Soc.* 1986, **108**, 4746 and references therein.

28. (a) Brookhart, M.; Studabaker, W. B.; Husk, G. R. *Organometallics* 1985, **4**, 943. (b) *Organometallics* 1987, **6**, 1141.

29. Shriver, D. F.; Drezdon, M. A. "The Manipulation of Air Sensitive Compounds," 2nd Edition, John Wiley and Sons: New York, 1986.

30. Herzog, S.; Dehnert, J.; Luhder, K. "Technique of Inorganic Chemistry", H. B. Jonassen, Ed., Interscience: New York, 1969, Vol. VII.

31. Paul, D. E.; Lipkin, D.; Weissman, S. I. J. Am. Chem. Soc. 1956, 78, 116.

32. Lind, Jr., J. E.; Abdel Rahim, H. A. A.; Rudich, S. W. J. Phys. Chem. 1966, 70, 3610.

33. (a) Ahmad, M.; Bruce, R.; Knox, G. R. J. Organomet. Chem. 1966, 6, 1. (b) King, R. B.; Bisnette, M. B. Inorg. Chem. 1965, 4, 482.

34. Johnson, B. V.; Ouseph, P. J.; Hseih, J. S.; Steinmetz, A. L.; Shade, J. E. Inorg. Chem. 1979, 18, 1796.

35. Gladysz, J. A.; Williams, G. M.; Tam, W.; Johnson, D. L.; Parker, D. W.; Selover, J. C. Inorg. Chem. 1979, 18, 553.

36. (a) Killops, S. D.; Knox, S. A. R. J. Chem. Soc., Dalton Trans. 1978, 1260. (b) Humphries, A. P.; Knox, S. A. R. J. Chem. Soc., Dalton Trans. 1975, 1710.

37. Jacobson, R. A. J. Appl. Crystallogr. 1976, 9, 115.

38. Lapp, R. L.; Jacobson, R. A. "ALLS, A General Crystallographic Least-Squares Program", USDOE report, ISU, Ames, Iowa (1979).

39. Richardson, J. W.; Angelici, R. J.; Jacobson, R. A. Inorg. Chem. 1987, 26, 452.

40. Ye Kolobova, N.; Skripkin, V. V.; Alexandrov, G. G.; Struchkov, Yu T. J. Organomet. Chem. 1979, 169, 293.

41. Churchill, M. R.; Wormald, J. J. Am. Chem. Soc. 1971, 93, 354.

42. (a) O'Connor, E. J.; Helquist, P. J. Am. Chem. Soc. 1982, 104, 1869 and references therein; (b) Knors, C.; Kuo, G.; Lauher, J. W.; Eigenbrot, C.; Helquist, P. Organometallics 1987, 6, 988. (c) Riley, P. E.; Davis, R. E.; Allison, N. T.; Jones, W. M. J. Am. Chem. Soc. 1980, 102, 2458.

43. (a) Dobrzynski, E. D.; Angelici, R. J. Inorg. Chem. 1975, 14, 1513. (b) Farrar, D. H.; Harris, R. O.; Walker, A. J. J. Organomet. Chem. 1977, 124, 125.

44. Schilling, B. E. R.; Hoffmann, R.; Lichtenberger, D. L. J. Am. Chem. Soc. 1979, 101, 585.

45. (a) Guggenberger, L. J.; Schrock, R. R. J. Am. Chem. Soc. 1975, 97, 6578. (b) Schrock, R. R.; Messerle, L. W.; Wood, C. D.; Guggenberger, L. J. J. Am. Chem. Soc. 1978, 100, 3793. (c) Fischer, E. O.; Kleine, W.; Schambeck, W.; Schubert, U. Z. Naturf., Sect B 1982, 36, 1575.

46. (a) Fontana, S.; Schubert, U.; Fischer, E. O. J. Organomet. Chem. 1978, 146, 39. (b) Malisch, W.; Blau, H.; Schubert, U. Angew Chem. Int. Ed. Engl. 1980, 19, 1020. (c) Malish, W.; Blau, H.; Schubert, U. Chem. Ber. 1983, 116, 690.

47. Lemal, D. M.; Gosselink, E. F.; McGregor, S. D. J. Am. Chem. Soc. 1966, 88, 582.

48. (a) Borden, W. T.; Hoo, L. H. J. Am. Chem. Soc. 1978, 100, 6274. (b) Feller, D.; Davidson, E. R.; Borden, W. T. J. Am. Chem. Soc. 1981, 103, 2558.

49. (a) Lappert, M. F.; MacQuitty, J. J.; Pye, P. L. J. Chem. Soc., Chem. Comm. 1977, 411. (b) Krusic, P. J.; Klabunde, U.; Casey, C. P.; Block, T. P. J. Am. Chem. Soc. 1976, 98, 2015. (c) Lappert, M. F.; McCabe, R. W.; MacQuitty, J. M.; Pye, P. L.; Riley, P. I. J. Chem. Soc., Dalton Trans. 1980, 90.

50. (a) Geiger, W. E.; Conelly, N. G. Adv. Organomet. Chem. 1984, 23, 1. (b) Adv. Organomet. Chem. 1985, 24, 87. (c) Geiger, W. D. Prog. Inorg. Chem. 1985, 33, 275. (d) Richmond, M. G.; Kochi, J. K. Inorg. Chem. 1986, 25, 656.

51. (a) Schroeder, N. C.; Angelici, R. J. J. Am. Chem. Soc. 1986, 108, 3688. (b) Donovan, B. T.; Geiger, W. E. J. Am. Chem. Soc. 1988, 110, 2335.

52. (a) King, R. B.; Bisnette, M. B.; Fronzaglia, A. J. Organomet. Chem. 1966, 5, 341. (b) Busetto, L.; Angelici, R. J. Inorg. Chim. Acta 1968, 2, 391.

53. (a) Bowen, D. H.; Green, M.; Grove, D. M.; Moss, J. R.; Stone, F. G. A. J. Chem. Soc., Dalton Trans. 1974, 1189. (b) Game, C. H.; Green, M.; Moss, J. R.; Stone, F. G. A. J. Chem. Soc., Dalton Trans. 1974, 351. (c) Miessler, G. L.; Kim, S.; Jacobson, R. A.; Angelici, R. J. Inorg. Chem. 1987, 26, 1690.

54. King, R. B. "Organometallic Synthesis", J. J. Eisch and R. B. King, Academic Press: New York, 1965, 114.

GENERAL SUMMARY

The research described in Part I of this dissertation shows that 2,3-dihydrothiophene (2,3-DHT), a proposed intermediate in the catalytic hydrodesulfurization (HDS) of thiophene, reacts with transition metal compounds to give the sulfur-coordinated complexes. It is also demonstrated that 2,3-DHT reacts with metal hydrides to give metallacyclopropane complexes which upon protonation yield tetrahydrothiophene (THT). These studies provide a reasonable model for the hydrogenation of 2,3-DHT to THT on HDS catalysts.

In Part II of this dissertation, chemical and spectroscopic evidence for the existence of a novel equilibrium between a metallathiacyclopropane and its carbene-mercaptide form is discussed. The reduction of a number of α-heteroatom stabilized cyclopentadienyldicarbonyliron carbenes to give unstable initial products which decompose to give mixtures of organic and organometallic products is also described. In addition, it is shown that the dithiocarbene, $\{CpFe(CO)_2[=C(SMe)_2]\}PF_6$, and $CpFe(CO)_2(\overline{COCH_2CH_2O})^+$ undergo phosphine substitution which is catalyzed by reducing agents.

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