1986

Chemistry of tungsten theocarbyne and thiocarbene complexes: Syntheses and structures of [HB(pz)3](CO)2(CS)W-Au(PR3) complexes, first examples of a semibridging CS ligand

Heesook Park Kim
Iowa State University

Recommended Citation

Kim, Heesook Park, "Chemistry of tungsten theocarbyne and thiocarbene complexes: Syntheses and structures of [HB(pz)3](CO)2(CS)W-Au(PR3) complexes, first examples of a semibridging CS ligand " (1986). *Retrospective Theses and Dissertations*. 8090.
https://lib.dr.iastate.edu/rtd/8090

INFORMATION TO USERS

This reproduction was made from a copy of a manuscript sent to us for publication and microfilming. While the most advanced technology has been used to photograph and reproduce this manuscript, the quality of the reproduction is heavily dependent upon the quality of the material submitted. Pages in any manuscript may have indistinct print. In all cases the best available copy has been filmed.

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

1. Manuscripts may not always be complete. When it is not possible to obtain missing pages, a note appears to indicate this.
2. When copyrighted materials are removed from the manuscript, a note appears to indicate this.
3. Oversize materials (maps, drawings, and charts) are photographed by sectioning the original, beginning at the upper left hand corner and continuing from left to right in equal sections with small overlaps. Each oversize page is also filmed as one exposure and is available, for an additional charge, as a standard 35mm slide or in black and white paper format.*
4. Most photographs reproduce acceptably on positive microfilm or microfiche but lack clarity on xerographic copies made from the microfilm. For an additional charge, all photographs are available in black and white standard 35mm slide format.*

*For more information about black and white slides or enlarged paper reproductions, please contact the Dissertations Customer Services Department.

U·M·I Dissertation Information Service

University Microfilms International
A Bell & Howell Information Company
300 N. Zeeb Road, Ann Arbor, Michigan 48106

8627125

Kim, Heesook Park

CHEMISTRY OF TUNGSTEN THIOCARBYNE AND THIOCARBENE COMPLEXES. SYNTHESES AND STRUCTURES OF (HB(PZ)(3))(CO)(2)(CS)W-AU(PR(3)) COMPLEXES, FIRST EXAMPLES OF A SEMIBRIDGING CS LIGAND

Iowa State University PH.D. 1986

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

PLEASE NOTE:

In all cases this material has been filmed in the best possible way from the available copy. Problems encountered with this document have been identified here with a check mark __√__.

1. Glossy photographs or pages _____
2. Colored illustrations, paper or print ______
3. Photographs with dark background _____
4. Illustrations are poor copy ______
5. Pages with black marks, not original copy ______
6. Print shows through as there is text on both sides of page ______
7. Indistinct, broken or small print on several pages __✓__
8. Print exceeds margin requirements ______
9. Tightly bound copy with print lost in spine _______
10. Computer printout pages with indistinct print ______
11. Page(s) __________ lacking when material received, and not available from school or author.
12. Page(s) __________ seem to be missing in numbering only as text follows.
13. Two pages numbered ______. Text follows.
14. Curling and wrinkled pages ______
15. Dissertation contains pages with print at a slant, filmed as received ________
16. Other ____

____

____

University
Microfilms
International

Chemistry of tungsten thiocarbyne and thiocarbene complexes. Syntheses and structures of $[HB(pz)_3](CO)_2(CS)W\text{-}Au(PR_3)$ complexes, first examples of a semibridging CS ligand

by

Heesook Park Kim

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

Approved:

In Charge of Major Work

For the Major Department

For the Graduate College

Iowa State University
Ames, Iowa

1986

TABLE OF CONTENTS

DEDICATION

To my mother and father

PREFACE

One of the most important developments in organotransition-metal chemistry was the discovery of carbene and carbyne complexes. The growth of carbene and carbyne chemistry has been partially sparked by interest in olefin and acetylene metathesis and Fischer-Tropsch synthesis in which metal carbenes and carbynes are postulated as key intermediates. Another field of interest in organometallic chemistry is that of thiocarbonyls; the similarity of carbon monosulfide (CS) to CO has stimulated much interest in the synthesis and reactivity of CS complexes. The present research includes chemistry of thiocarbyne, η^2-thiocarbene, and thiocarbonyl compounds.

The material in this dissertation is arranged so that a minimum of rewriting is required for preparation of manuscripts for publication. Reported in this dissertation is research on the protonation of $[HB(pz)_3](CO)_2W(\equiv CSMe)$ which produces an unusual η^2-CH(SMe) carbene ligand, whose subsequent reactions with nucleophiles yield metallacyclopropane ring compounds containing W and S. As background for these studies, Section I provides a literature review of η^2-carbene and metallacyclopropane compounds.

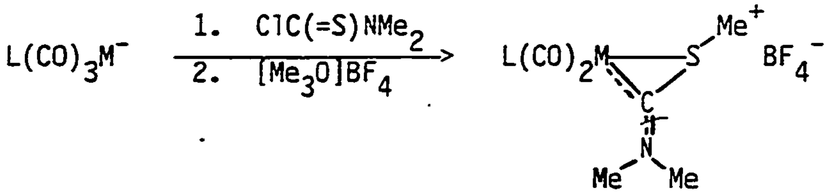
Sections II, III, and IV are composed of articles which have been submitted for journal publication. These sections include results of this dissertation research concerning reactivities of $[HB(pz)_3](CO)_2W(\equiv CSMe)$, $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]^+$, and $[HB(pz)_3](CO)_2W(CS)^-$.

References and figures apply only to those contained within that section.

SECTION I. η^2-CARBENE AND S, O, P, AND N CONTAINING METALLACYCLOPROPANE COMPOUNDS

η^2-CARBENE LIGANDS

As compared with η^1-carbenes, η^2-carbene complexes are rare. One example is the [η^2-C(SMe)(NMe$_2$)] carbene ligand, which is prepared by methylation of the thiocarboxamido moiety, η^2-C(S)(NMe$_2$), according to eq 1.[1] An X-ray structural investigation of (PPh$_3$)(CO)$_3$Mn[η^2-C(NMe$_2$)(SMe)]$^+$ shows that the $C_{carbene}$-S distance in the η^2-carbene compound (1.78 Å) is 0.1 Å longer than that of the analogous η^1-carbene compound $(CH_3NC)_2Pt[=C(SEt)(NHCH_3)]_2^{2+}$.[2] Thus, it seems that in the η^2-carbene complex there is less C-S π bonding and more metal-carbon π bonding than in the η^1-carbene compound. The reduction of C-S π bonding is probably due to S-coordination to the metal which would make less electron density available for π-bonding to the C.

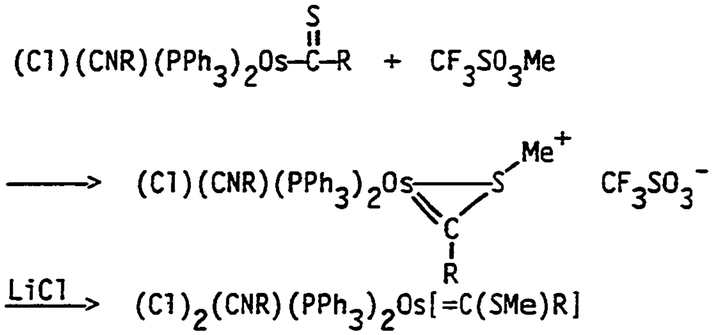


(1)

L = (CO)(PPh$_3$); M = Mn

L = Cp ; M = Mo

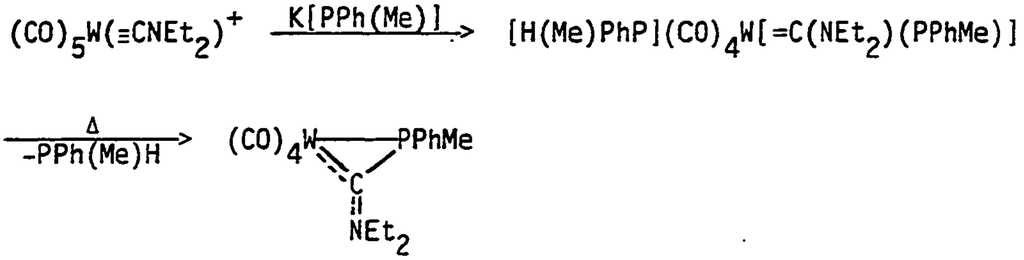
Another η^2-thiocarbene compound is prepared by methylation of an η^2-thioacyl compound, according to eq 2.[3] Subsequent conversion of the η^2-carbene to an η^1-carbene occurs by addition of Cl$^-$ (eq 2).[3]



(2)

$R = 4\text{-}C_6H_4CH_3$

Addition of $K[PPh(Me)]$ to $(CO)_5W(\equiv CNEt_2)^+$ yields among other products a carbene complex $[H(Me)PhP](CO)_4W[=C(NEt_2)(PPhMe)]$, which upon thermolysis eliminates the trans phosphine ligand to give a metallacyclic carbene complex (eq 3).[4] The $C_{carbene}$-N distance,

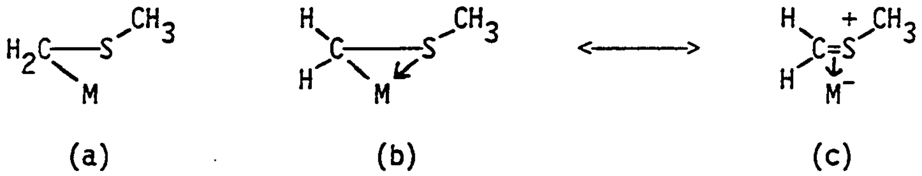


(3)

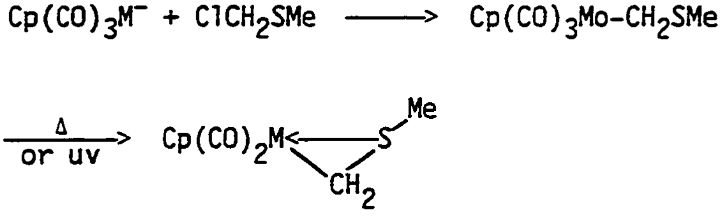
1.28(1) Å;[4a] is close to that (1.28(2) Å) in $(PPh_3)(CO)_3Mn[\eta^2\text{-}C(NMe_2)(SMe)]^+$,[2] and significantly shorter than C-N single bond distances ($N\text{-}CH_3$ = 1.49(3) Å, 1.54(3) Å) in $(PPh_3)(CO)_3Mn[\eta^2\text{-}C(NMe_2)(SMe)]^+$.[2] This suggests some π-interaction between the C and N.

η^2-CH_2SMe LIGANDS

A number of transition metal compounds containing the CH_2SMe ligand have been prepared;[5] three coordination modes are possible for the CH_2SMe group, as shown below.[6] The CH_2SMe group can form a σ complex bonding only through the C atom as in (a) or an η^2-complex containing both the metal-carbon σ bond and a sulfur donor bond as in (b). The (a) and (b) bonding modes can be differentiated by the pattern of the methylene protons in their ^1H NMR spectra; the two methylene protons in (a) are equivalent but nonequivalent in (b). The (c) type of bonding is a possible resonance form of the η^2-bonding mode for the CH_2SMe group. It is impossible to establish the contribution of resonance forms (b) and (c) to the bonding in η^2-CH_2SMe complexes; however, a S-CH_2 distance which is shorter than the S-CH_3 distance suggests a contribution of the type (c) resonance structure.



Reaction of metal anion and $ClCH_2SMe$ Treatment of $NaMo(CO)_3Cp$ with $ClCH_2SMe$ at room temperature gives the η^1, σ-bonded CH_2SMe compound $Cp(CO)_3Mo(CH_2SMe)$. Upon heating or ultraviolet irradiation, this complex loses CO to give $Cp(CO)_2Mo(\eta^2$-$CH_2SMe)$ with CH_3SCH_2 group bonded to the metal atom through the C and S atoms (eq 4).[7] The analogous $(CO)_4Mn(\eta^2\text{-}CH_2SMe)$ can also be prepared by reaction of $Mn(CO)_5^-$ and $ClCH_2SMe$.[7b] An X-ray diffraction study of $Cp(CO)_2Mo(\eta^2\text{-}CH_2SMe)$ shows that the CH_2SMe moiety is best represented by the (b) type of coordination mode [$CH_2\text{-}S$ = 1.78(1) Å, $S\text{-}CH_3$ = 1.82(1) Å)].[8]

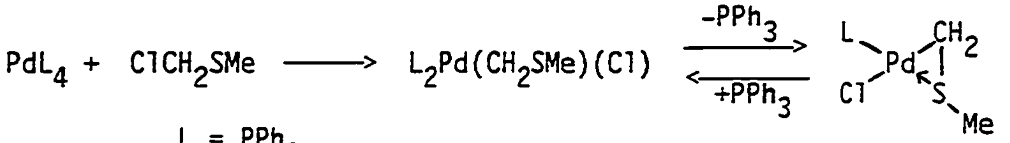


(4)

M = Mo, W

Similarly, the reaction of $[Me_2Ga(N_2C_3HR_2)(OCH_2CH_2NMe_2)]Mo(CO)_3^-$, R = H, Me, with $ClCH_2SMe$ produces the corresponding $\eta^2\text{-}CH_2SMe$ compound.[9] The $CH_2\text{-}S$ distances in the complexes, R = H, Me, are 1.744 Å and 1.756 Å, respectively; whereas the $S\text{-}CH_3$ distance is 1.804 Å and 1.802 Å, respectively. The shorter $CH_2\text{-}S$ distance suggests a contribution of the (c) type of resonance structure.

<u>Oxidative addition of $ClCH_2SMe$</u> The oxidative addition of $ClCH_2SMe$ to $Pd(PPh_3)_4$ affords an $\eta^1\text{-}CH_2SMe$ compound. Repeated crystallization of the η^1 compound in CH_2Cl_2 and diethyl ether affords the $\eta^2\text{-}CH_2SMe$ compound through loss of PPh_3 in accordance with equilibrium shown below (eq 5).[10] An X-ray diffraction study of



(5)

L = PPh_3

$(PPh_3)(Cl)Pd(\eta^2\text{-}CH_2SMe)$ shows that the CH_2SMe group, bonded to the Pd atom through both C and S atoms, forms a metallacyclic three-membered ring.[11] The $S\text{-}CH_2$ bond distance, 1.756(6) Å, is slightly shorter than that of the $S\text{-}CH_3$ bond distance, 1.807(7) Å.

Treatment of the $\eta^1\text{-}CH_2SMe$ compound, $(PPh_3)_2Pd(CH_2SMe)(Cl)$ with NH_4PF_6 or $AgClO_4$ yields the cationic complexes $[(PPh_3)_2Pd(\eta^2\text{-}CH_2SMe)]X$ ($X = PF_6$, ClO_4) according to eq 6.[6] X-ray structure investigations of

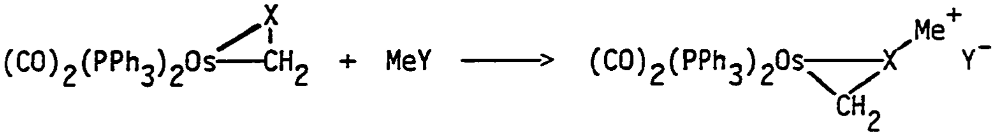
$$\text{L}_2\text{Pd(CH}_2\text{SMe)(Cl)} + X^+Y^- \longrightarrow [L_2Pd(CH_2SMe)]Y + XCl \qquad (6)$$

$X^+Y^- = NH_4PF_6,\ AgClO_4$

both compounds show that the PF_6^- salt has a stronger ion-pair interaction than the ClO_4^- salt;[6] despite the larger size of PF_6^- (P-F = 1.54 Å) than ClO_4^- (Cl-O = 1.42 Å), the Pd•••P distance, 4.759 Å, in the PF_6^- salt is significantly shorter than Pd-Cl distance (5.317 Å) in the ClO_4^- salt. In the PF_6^- salt, the CH_2SMe group is bonded to the Pd through both the C and S atoms, forming a Pd-C-S three-membered ring [$Pd\text{-}CH_2$ = 2.06(4), Pd-S = 2.367(8), $CH_2\text{-}S$ = 1.77(4), and $S\text{-}CH_3$ = 1.78(4) Å].[6] On the other hand, the $\eta^2\text{-}CH_2SMe$ group in the ClO_4^- salt is coordinated to Pd in a type (c) manner with essentially a C=S double bond ($CH_2\text{-}S$ = 1.68(1) Å) as compared with the $S\text{-}CH_3$ bond (1.86(4) Å).[6] The contribution from (c) seems greater in the ClO_4^- salt than in the PF_6^- salt. This difference may be due to the counter anions.

A similar oxidative addition of $ClCH_2SMe$ to $Ni(PPh_3)_2(C_2H_4)$ produces $(PPh_3)(Cl)Ni(\eta^2\text{-}CH_2SMe)$.[12]

Methylation of $L_nM(\eta^2\text{-}CH_2X)$, X = S, Se, Te The methylation of η^2-chalcogenoformaldehyde ligands is a useful method for the preparation of complexes containing $\eta^2\text{-}CH_2XMe$, X = S, Se, and Te.[13] For example, methylation of $(CO)_2(PPh_3)_2Os(\eta^2\text{-}CH_2X)$ yields $(CO)_2(PPh_3)_2Os(\eta^2\text{-}CH_2XMe)^+$ according to eq 7.[13] A similar methylation is observed in the reaction of $Cp(PMe_3)Rh(\eta^2\text{-}CH_2X)$, X = S, Se, with CF_3SO_3Me to give $Cp(PMe_3)Rh(\eta^2\text{-}CH_2XMe)^+$.[14]

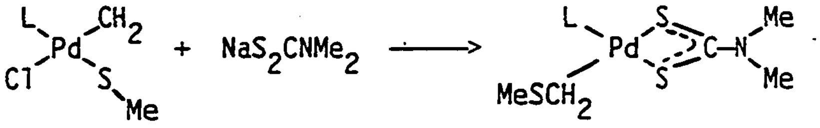


(7)

X = S ; Y = CF_3SO_3

X = Se, Te; Y = I

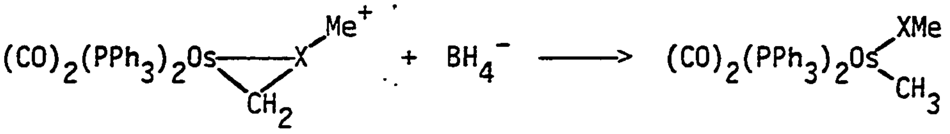
Reaction of $\eta^2\text{-}CH_2SMe$ ligands The reaction of $(PPh_3)(Cl)Pd(\eta^2\text{-}CH_2SMe)$ with NaS_2CNMe_2 converts the $\eta^2\text{-}CH_2SMe$ to $\eta^1\text{-}CH_2SMe$ according to eq 8.[10a] A similar conversion of η^2-to $\eta^1\text{-}CH_2SMe$ is observed in the reaction of $(CO)_2(PPh_3)_2Os(\eta^2\text{-}CH_2SMe)^+$ with Cl^-, affording $(CO)_2(PPh_3)_2Os(Cl)(\eta^1\text{-}CH_2SMe)$.[13a]



(8)

L = PPh_3

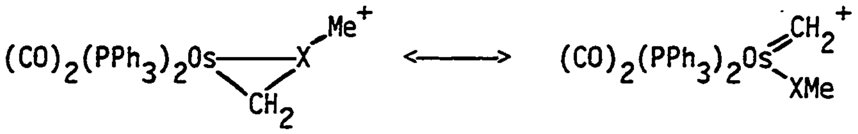
Reaction of $(CO)_2(PPh_3)_2Os(\eta^2\text{-}CH_2XMe)^+$, X = Se, Te, with BH_4^- leads to cleavage of the C-X bond, yielding $(CO)_2(PPh_3)_2Os(CH_3)(XMe)$ (eq 9).[13c] This surprising reaction perhaps suggests that the CH_2XMe



(9)

X = Se, Te

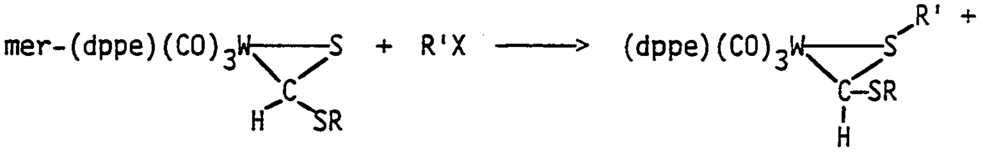
moiety might have some carbene character as in the form $L_nOs(=CH_2)(XMe)$ (eq 10).[13c] The CH_2 carbene ligand should be very



(10)

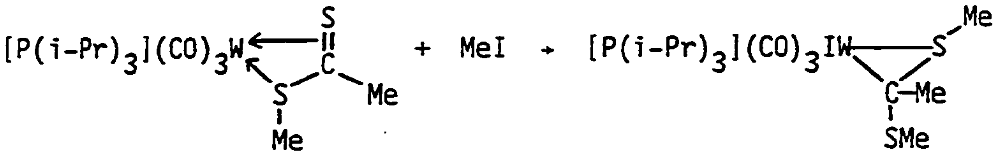
susceptible to BH_4^- attack which would be expected to give the observed CH_3 product (eq 9).

Preparation of $L_nM[\eta^2\text{-}C(SR)(R')(SR'')]$ complexes In a reaction similar to that (eq 7) of η^2-chalcogenoformaldehyde complexes, the η^2-dithioester complexes mer-(dppe)$(CO)_3W[\eta^2\text{-}C(=S)H(SR)]$ react with alkylating agents to produce three-membered ring compounds according to eq 11.[15] The similar conversion of an η^3-dithioester compound to a three-membered ring compound is also observed (eq 12).[16]



(11)

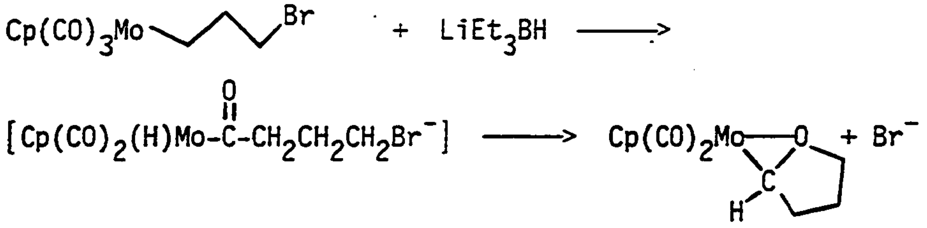
R, R' = Me, CH_2Ph



(12)

η^2-CHROR' LIGAND

Saturated three-membered ring complexes with oxygen, η^2-CHROR', are rare as compared with those with N, S, or P. Such a compound is prepared by reaction of $Cp(CO)_3Mo[CH_2(CH_2)_2Br]$ with $LiEt_3BH$ (eq 13).[17] The reaction was proposed to initially generate an acyl

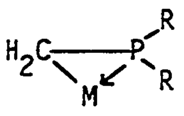


(13)

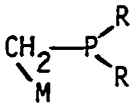
intermediate which would undergo ring closure followed by hydride migration from Mo to the carbene center to give the final product.[17] Alternatively, hydride migration from Mo to the acyl carbon followed by ring closure would result in the observed product. This three-membered ring compound can also be prepared by reaction of $Cp(CO)_2(I)Mo(=\overline{CCH_2CH_2CH_2O})$ with $LiBEt_3H$.[17]

η^2-CH_2PR_2 LIGANDS

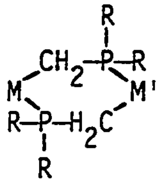
Three coordination modes are known for the CH_2PR_2 group, as shown below; they are the η^2-(d),[18] η^1-(e),[19] or bridging-(f) modes.[20]



(d)



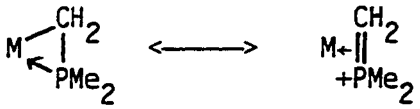
(e)



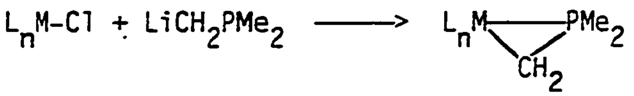
(f)

R = Me, Ph

Crystal structures of compounds with the η^2-CH_2PMe_2 ligand, $Re(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)$,[21] $Ta(PMe_3)_3(\eta^2\text{-}CH_2PMe_2)(\eta^2\text{-}CHPMe_2)$[22], and $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$,[23] reveal a common feature; the metallacycle P-C bond is shorter than that in terminal PMe_3 ligands by 0.08 Å. It would appear that the bonding in η^2-CH_2PMe_2 compounds is best understood in terms of the following resonance forms:



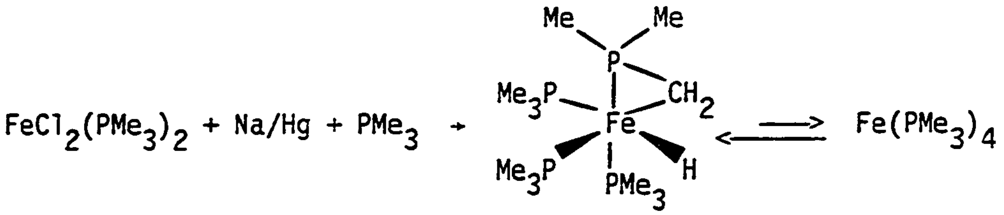
Reactions of metal chlorides with $LiCH_2PMe_2$ afford η^2-CH_2PMe_2 compounds according to eq 14.[24]



(14)

M= L_3Co, $L_2(CO)Co$, L_3Ni^+, $L_3(H)Fe$, $L_3(Me)Fe$, $L_2(Me)_2Co$; L = PMe_3

Intramolecular oxidative addition of a PMe_3 C-H bond to a metal also leads to three-membered ring compounds. For example, sodium amalgam reduction of $FeCl_2(PMe_3)_2$ in the presence of excess PMe_3 at 0°C produces a product having the empirical formula $Fe(PMe_3)_4$. As a result of intramolecular C-H fission, this product exists in solution almost completely as $Fe(H)(\eta^2\text{-}CH_2PMe_2)(PMe_3)_4$ (eq 15).[24b,25] However,

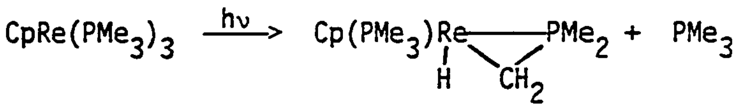


(15)

2

NMR spectral evidence suggests a slow equilibrium between the two isomers.[25,26] Supporting this equilibrium is the reaction of 2 with H_2 which gives $H_2Fe(PMe_3)_4$ in 70% yield.[25,27] Also, ligands favoring a low oxidation state for Fe shift this equilbrium to give complexes $Fe(PMe_3)_3L_2$ (L = PF_3, CO, $P(OMe)_3$).[27] Recently, analogous Os and Ru compounds $MH(\eta^2\text{-}CH_2PMe_2)(PMe_3)_4$ have also been prepared by reduction of $MCl_2(PMe_3)_4$ in the presence of PMe_3.[23,28]

Similarly, reduction of $Re(NPh)(Cl)_3(PMe_3)_2$ in the presence of PMe_3 yields $Re(\eta^2\text{-}CH_2PMe_2)(PMe_3)_4$.[21] Irradiation of $CpRe(PMe_3)_3$ in cylcohexane leads to cyclometalation, producing $CpRe(H)(\eta^2\text{-}CH_2PMe_2)(PMe_3)$ according to eq 16.[29]



(16)

The Mo compound $Mo(PMe_3)_6$ undergoes spontaneous dissociation of a PMe_3 ligand in benzene solution, forming $Mo(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ (eq 17).[30] The analogous $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ can be prepared by

$$M(PMe_3)_6 \rightleftharpoons M(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H + PMe_3 \qquad (17)$$

reduction of WCl_6 by sodium-potassium alloy in pure PMe_3.[23,31] There is no evidence for the presence of $W(PMe_3)_6$ in a benzene solution of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ containing an excess of free PMe_3. The shift of the equilibrium in eq 17 to the right-hand side for tungsten reflects the greater stability of the higher oxidation state for tungsten compared to molybdenum.[31]

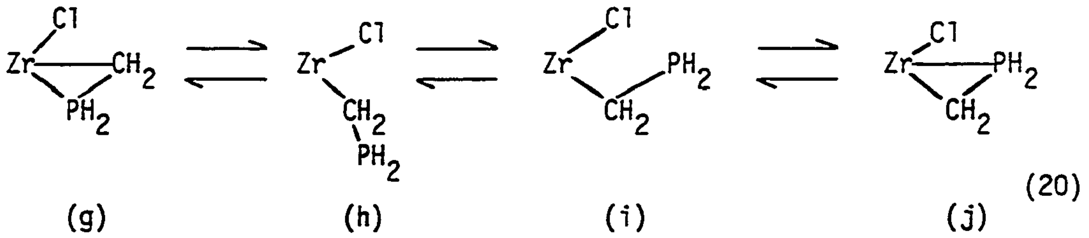
In contrast, the phosphinomethyl group frequently binds to early transition metals in an η^1-manner (eqs 18, 19).[24a,32]

$$Cp_2MCl_2 + LiCH_2PR_2 \longrightarrow Cp_2(Cl)M(CH_2PR_2) \qquad (18)$$

$$Cp_2MCl_2 + 2LiCH_2PR_2 \longrightarrow Cp_2M(CH_2PR_2)_2 \qquad (19)$$

M = Ti, Zr; R = Me, Ph

In spite of the presence of a lone pair on phosphorus and coordinative unsaturation at the metal, no bonding interaction between M-P, M = Ti, Zr, exists. Theoretical studies of the model system $Cp_2Zr(Cl)(\eta^1\text{-}CH_2PH_2)$ suggest three structural minima g, h, and j (eq 20).[33] The



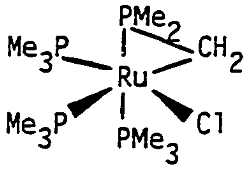
(20)

large P••••Zr non-bonding distance and the 130° Zr-C-P angle in $Cp_2Zr(Cl)(\eta^1-CH_2PPh_2)$[32a] are reproduced well in structure h and are explained by a strong P-Zr repulsive electronic interaction that exists in this geometry. The three-membered ring species (g and j) are actually calculated to be more stable than the η^1-form, although g and j are not observed. An electronic barrier separates h from g, while conversion to j requires rotation to i, which is not a local energy minimum, and should collapse directly to the Zr-P bonded structure. Assuming the validity of the calculations, the lack of Zr-P bonding in $Cp_2Zr(Cl)(\eta^1-CH_2PPh_2)$ is probably due both to these barriers to structural interconversion and to steric destabilization of the three-membered ring species by the substituents on phosphorus. The electronic barrier is found to vanish upon reduction of the metal and loss of chloride ion. Thus reducing $Cp_2M(Cl)(\eta^1-CH_2PPh_2)$ and $Cp_2M(\eta^1-CH_2PPh_2)_2$, M = Ti, Zr, gives $Cp_2M(\eta^2-CH_2PPh_2)$ and $Cp_2M(\eta^2-CH_2PPh_2)_2$, respectively;[20b,32a,34] EPR spectra show a strong coupling of the unpaired electron to phosphorus, demonstrating the presence of the $\eta^2-CH_2PPh_2$ ligand in these reduced compounds. Similarly, one-electron reduction of $Cp_2Zr(Cl)(\eta^1-CH_2PMe_2)$ produces a persistent P-bound Zr(III) species.[35] In contrast, reduction of $(C_5Me_2)_2Zr(Cl)(\eta^2-CH_2PPh_2)$ gives a Zr(III) species lacking appreciable Zr-P interaction; permethyl substitution on the Cp rings sterically prohibits Zr-P bonding, even when it might be strongly favored electronically.[35]

Reduction of $TaCl_5$ in excess PMe_3 with sodium sand under argon gives $Ta(PMe_3)_3(\eta^2\text{-}CH_2PMe_2)(\eta^2\text{-}CHPMe_2)$. An X-ray structural determination of the product shows that the $\eta^1\text{-}CHPMe_2$ is best represented as a carbene-like interaction;[22,23] the Ta-Ccarbene distance is 2.015 Å, whereas the Ta-CH_2 distance is 2.324 Å.

Deprotonation of PMe_3 can also lead to formation of the three-membered ring; reaction of <u>cis</u>-$Ru(O_2CMe)(Cl)(PMe_3)_4$ with 1 or 2 molar equivalents of $N(SiMe_3)_2^-$ gives $Ru(\eta^2\text{-}CH_2PMe_2)(Cl)(PMe_3)_3$ (eq 21).[20c] Similarly, the reaction of cis-$Ru(O_2CMe)_2(PMe_3)_4$ with 2 equivalents of $N(SiMe_3)_2^-$ yields $Ru(\eta^2\text{-}CH_2PMe_2)_2(PMe_3)_2$.

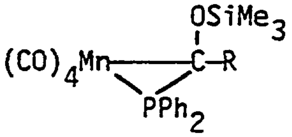
$$\text{cis-}Ru(O_2CMe)(Cl)(PMe_3)_4 + N(SiMe_3)_2^- \longrightarrow$$



(21)

Interestingly, the reaction of Ph_2PSiMe_3 with $(CO)_5MnR$ also leads to the formation of a three-membered ring (eq 22);[36] in this transformation, CO insertion and silicon-oxygen bond formation seem to be driving forces for the reaction.

$$Ph_2PSiMe_3 + (CO)_5MnR \longrightarrow$$



(22)

R = Me, CH_2SiMe_3, Ph

<u>Reactions of the $\eta^2\text{-}CH_2PR_2$ ligand</u> The reaction of $(PMe_3)_3Co(\eta^2\text{-}CH_2PMe_2)$ with $[Me_3PH]Cl$ results in the replacement of the

η^2-CH_2PMe_2 group to give $(PMe_3)_3CoCl$ (eq 23).[24b]

$$(PMe_3)_3Co(\eta^2\text{-}CH_2PMe_2) + [Me_3PH]Cl \longrightarrow (PMe_3)_3CoCl + 2PMe_3 \qquad (23)$$

The spirocycle $Ru(PMe_3)_2(\eta^2\text{-}CH_2PMe_2)_2$ reacts with H_2 to give cis-$RuH_2(PMe_3)_4$.[20c] Reaction of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ with H_2, SiH_4, and HF gives $X_2W(PMe_3)_5$, X = H, SiH_3, and F, respectively.[31] The compound $Os(PMe_3)_3(\eta^2\text{-}CH_2PMe_2)(H)$ reacts with Brønsted acids, HX (X = Cl, CF_3CO_2), to give $Os(PMe_3)_4X_2$.[28b]

Methyl iodide reacts with $M(PMe_3)_3(\eta^2\text{-}CH_2PMe_2)H$, M = Os, Ru, to give a product which retains the three-membered ring, as well as $MI_2(PMe_3)_4$ (eq 24).[28]

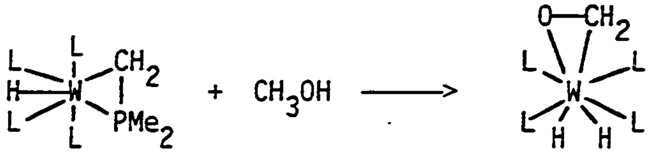
$$\begin{aligned} &M(PMe_3)_3(\eta^2\text{-}CH_2PMe_2)H + CH_3I \longrightarrow \\ &M(PMe_3)_3(\eta^2\text{-}CH_2PMe_2)I + cis\text{-}MI_2(PMe_3)_4 \end{aligned} \qquad (24)$$

M = Ru, Os

However, the reaction of $Re(\eta^2\text{-}CH_2PMe_2)(PMe_3)_4$ with MeI differs from eq 24 in producing a cation (eq 25); the η^2-CH_2PMe_2 group is lost, presumably as PMe_2Et.[21]

$$\begin{aligned} &Re(\eta^2\text{-}CH_2PMe_2)(PMe_3)_4 + CH_3I \longrightarrow \\ &[PMe_4]I + [ReI(Me)(PMe_3)_4]I\cdot[PMe_4]I \end{aligned} \qquad (25)$$

The compound $Os(PMe_3)_3(\eta^2\text{-}CH_2PMe_2)H$ reacts with methyl alcohol to give $(PMe_3)_4OsH_2$.[28b] Addition of methanol to $W((PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ gives the η^2-formaldehyde derivative $W(PMe_3)_4(\eta^2\text{-}CH_2O)H_2$ by dehydrogenation of methanol (eq 26).[37] It is proposed that the



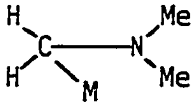
(26)

$L = PMe_3$

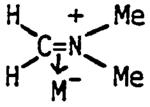
reaction proceeds via initial oxidative addition of MeOH to the starting compound to give the intermediate $W(PMe_3)_5(MeO)H$ or $W(PMe_3)_5(CH_2OH)H$, followed by loss of PMe_3 and intramolecular oxidative addition of the C-H bond of the methoxy group, or O-H bond of the hydroxymethyl group.

η^2-CH_2NMe_2 LIGANDS

Theoretical studies of the iminium cation $H_2C{=}NMe_2^+$ indicate that there is nearly full double bond character between the C and N atoms.[38] Compared to olefins, which are generally considered 2e$^-$ π-donors, iminium ions can have three possible bonding modes.

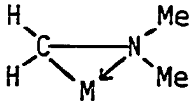


(k)



(l)

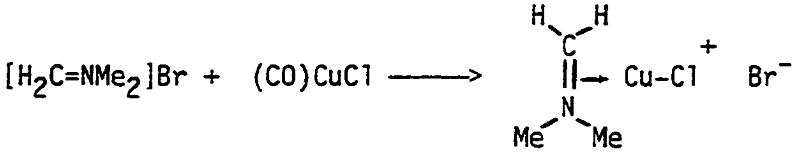
$\longleftrightarrow$



(m)

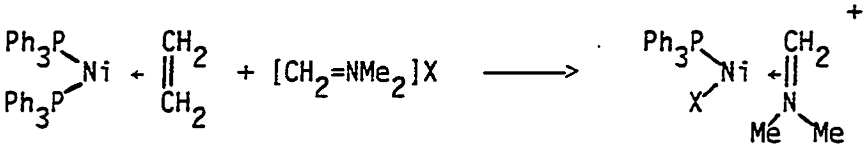
The iminium cation acts as a σ-bonded monodentate ligand in (k) or as a 2e$^-$ π-donor in (l). The (m) resonance structure can possibly contribute to the η^2-bonding of the CH_2NMe_2 ligand, as in the cases of η^2-CH_2SMe and CH_2PR_2 bonding. However, the contribution of (l) in η^2-CH_2NMe_2 probably plays a greater role than $CH_2{=}\overset{+}{S}Me$ and $CH_2{=}\overset{+}{P}R_2$ in η^2-CH_2SMe and η^2-CH_2PR_2 bonding, respectively.

Reaction of $[CH_2{=}NMe_2]Br$ with (CO)CuCl produces $[(Me_2N{=}CH_2)Cu(Cl)]Br$, in which the iminium cation is considered to act as a π-type ligand based on its $\nu(C{=}N)$ frequency of 1600 cm^{-1} (eq 27).[39]



$$[H_2C{=}NMe_2]Br + (CO)CuCl \longrightarrow [(Me_2N{=}CH_2)\rightarrow Cu{-}Cl]^+ \; Br^- \qquad (27)$$

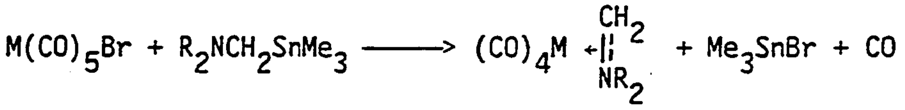
Similarly, reaction of $(CH_2{=}CH_2)Ni(PPh_3)_2$ with $[CH_2{=}NMe_2]X$ (X = Cl, Br, I) affords $(PPh_3)Ni(CH_2{=}NMe_2)(X)$, X = Cl, Br, and I, according to eq 28.[40] An X-ray structural determination of the Cl product shows the complex can be considered a trigonally coordinated molecule with the iminium cation bonded in a π-fashion to the Ni atom;[40] the


(28)

X = Cl, Br, I

geometry of the bound iminium cation is very similar to that of other π-complexes, e.g., $(PPh_3)_2Ni(C_2H_4)$ and $[(cyclohexyl)_3P]Ni(C_2H_4)_2$.[40] The C=N bond length in the compound (1.392(6) Å) increases over that of the uncomplexed ion by 0.09 Å; the decrease in C=N multiple bond character upon coordination to the metal atom is ascribed to π-backdonation from the metal.[40]

The organotin reagent $R_2NCH_2SnMe_3$ can be used as a precursor for the $CH_2{=}NR_2^+$ ligand; reaction of $M(CO)_5Br$, M = Mn, Re, with $R_2NCH_2SnMe_3$ produces $(CO)_4Mn(CH_2{=}NR_2)$ according to eq 29.[41] Reaction

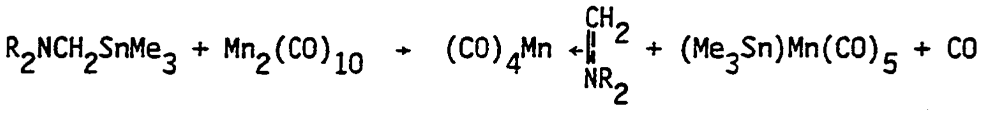


$$M(CO)_5Br + R_2NCH_2SnMe_3 \longrightarrow (CO)_4M \leftarrow \overset{CH_2}{\underset{NR_2}{\|}} + Me_3SnBr + CO \qquad (29)$$

M = Mn, Re

R = Me, Et, Pr

of $Mn_2(CO)_{10}$ with $R_2NCH_2SnMe_3$ leads to the same product $(CO)_4Mn(CH_2{=}NR_2)$ according to eq 30.[41b] An X-ray structural



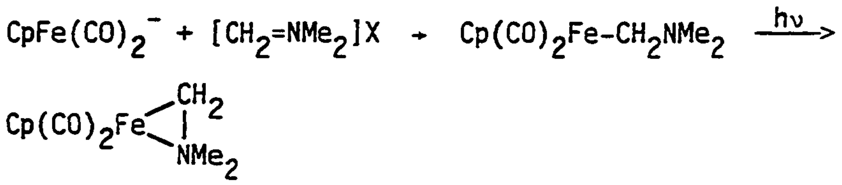
$$R_2NCH_2SnMe_3 + Mn_2(CO)_{10} \rightarrow (CO)_4Mn \leftarrow \begin{matrix} CH_2 \\ \| \\ NR_2 \end{matrix} + (Me_3Sn)Mn(CO)_5 + CO \qquad (30)$$

investigation of $(CO)_4Mn(CH_2{=}\overline{NCH_2CH_2})$ suggests that the $CH_2{=}\overline{NCH_2CH_2}$ ligand π-bonds to the Mn. The C-N bond length C=N (1.45 Å) in the compound is approaching that of a single C-N bond, suggesting high π-acidity of the ligand.[41]

The aforementioned $(PPh_3)Ni(CH_2{=}NMe_2)(Cl)$ reacts with Cp^- to give $CpNi(\eta^1\text{-}CH_2NMe_2)(PPh_3)$ according to eq 31.[40]

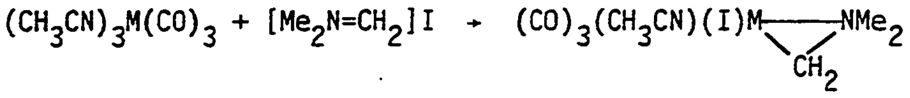
(31)

Reactions of metal carbonyl anions with $[CH_2NMe_2]X$ can give $LnM(\eta^1\text{-}CH_2NMe_2)$ complexes. $CpFe(CO)_2(\eta^1\text{-}CH_2NMe_2)$ is prepared by reaction of $CpFe(CO)_2^-$ with $[CH_2{=}NMe_2]X$, X = Cl, Br, I (eq 32).[42] Photolysis of $CpFe(CO)_2(\eta^1\text{-}CH_2NMe_2)$ results in evolution of CO with the formation of the $\eta^2\text{-}CH_2NMe_2$ compound according to eq 32.[42]



(32)

Similarly, the reactions of $CpM(CO)_3^-$, M = Mo, W, with $[CH_2{=}NMe_2]I$ afford $CpM(CO)_3(\eta^1\text{-}CH_2NMe_2)$.[43] Conversion of η^1-to-$\eta^2\text{-}CH_2NMe_2$ occurs by refluxing a light petroleum solution of $CpMo(CO)_3(\eta^1\text{-}CH_2NMe_2)$ to give $CpMo(CO)_2(\eta^2\text{-}CH_2NMe_2)$.[43] An $\eta^2\text{-}CH_2NMe_2$ compound can be obtained directly by treatment of $(CH_3CN)_3M(CO)_3$, M = Mo, W, with $[Me_2N{=}CH_2]I$ to yield $(CO)_3(CH_3CN)(I)M(\eta^2\text{-}CH_2NMe_2)$ according to eq 33.[43]



$$(CH_3CN)_3M(CO)_3 + [Me_2N{=}CH_2]I \rightarrow (CO)_3(CH_3CN)(I)\underset{CH_2}{M\text{——}NMe_2} \tag{33}$$

REFERENCES

1. (a) Treichel, P. M.; Dean, W. K. J. Chem. Soc., Chem. Commun. 1972, 804. (b) Dean, W. K.; Treichel, P. M. J. Organometal. Chem. 1974, 66, 87.
2. Dean, W. K.; Wetherington, J. B.; Moncrief, J. W. Inorg. Chem. 1976, 15, 1566.
3. Clark, G. R.; Collins, T. J.; Marsden, K.; Roper, W. R. J. Organometal. Chem. 1983, 259, 215.
4. (a) Fischer, E. O.; Reitmeier, R.; Ackermann, K. Angew. Chem., Int. Ed. Engl. 1983, 22, 411. (b) Fischer, E. O.; Reitmeier, R. Z. Naturforsch., B: Anorg. Chem., Org. Chem. 1983, 38B, 582.
5. Omae, I. Coord. Chem. Rev. 1979, 28, 97.
6. Miki, K.; Kai, Y.; Yasuoka, N.; Kasai, N. Bull. Chem. Soc. Jpn. 1981, 54, 3639.
7. (a) King, R. B.; Bisnette, M. B. J. Am. Chem. Soc. 1964, 86, 1267. (b) King, R. B.; Bisnette, M. B. Inorg. Chem. 1965, 4, 486.
8. de Gil, P. M.; Dahl, L. F. J. Am. Chem. Soc. 1969, 91, 3751.
9. Chong, K. S.; Retting, S. J.; Storr, A.; Trotter, J. Can. J. Chem. 1980, 58, 1080.
10. (a) Yoshida, G.; Matsumura, Y.; Okawara, R. J. Organomet. Chem. 1975, 92, C53. (b) Yoshida, G.; Kurosawa, H.; Okawara, R. J. Organomet. Chem. 1976, 113, 85.

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

12. Davidson, J. G.; Barefield, E. K.; Van Derveer, D. G. Organometallics **1985**, 4, 1178.

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

14. (a) Paul, W.; Werner, H. Angew. Chem., Int. Ed. Engl. **1983**, 22, 316. (b) Werner, H. Angew. Chem., Int. Ed. Engl. **1983**, 22, 927.

15. Schenk, W. A.; Schwietzke, T. Organometallics **1983**, 2, 1905.

16. Schenk, W. A.; Rüb, D.; Burschka, C. Angew. Chem., Int. Ed. Engl. **1985**, 24, 971.

17. Adams, H.; Bailey, N. A.; Cahill, P.; Rogers, D.; Winter, M. J. J. Chem. Soc., Chem. Commun. **1983**, 831.

18. (a) Bresciani, N.; Calligaris, M.; Delise, P.; Nardin, G.; Randaccio, L. J. Am. Chem. Soc. **1974**, 96, 5642. (b) Schmidbaur, H.; Blaschke, G. Z. Naturforsch., B: Anorg. Chem., Org. Chem. **1979**, 34B, 584.

19. Schmidbaur, H. Acc. Chem. Res. **1975**, 8, 62.

20. (a) Klein, H.-F.; Wenninger, J.; Schubert, U. Z. Naturforsch., B: Anorg. Chem., Org. Chem. **1979**, 34B, 1391. (b) Schore, N. E.; Young, S. J.; Olmstead, M. M.; Hofmann, P. Organometallics **1983**, 2, 1769. (c) Mains, V. V.; Anderson, R. A. Organometallics **1984**, 3, 675.

21. Chiu, K. W.; Howard, C. G.; Rzepa, H. S.; Sheppard, R. N.; Wilkinson, G. Polyhedron 1982, 1, 441.

22. Gibson, V. C.; Grebenik, P. D.; Green, M. L. H. J. Chem. Soc., Chem. Commun. 1983, 1101.

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

24. (a) Karsch, H. H.; Appelt, A. Phosphorus and Sulfur 1983, 18, 287. (b) Karsch, H. H.; Klein, H.-F.; Schmidbaur, H. Angew. Chem., Int. Ed. Engl. 1975, 14, 637. (c) Karsch, H. H.; Schmidbaur, H. Z. Naturforsch., B: Anorg. Chem., Org. Chem. 1977, 32B, 762.

25. Rathke, J. W.; Muetterties, E. L. J. Am. Chem. Soc. 1975, 97, 3272.

26. (a) Karsch, H. H. Chem. Ber. 1977, 110, 2213. (b) Karsch, H. H. Chem. Ber. 1977, 110, 2699. (c) Karsch, H. H. Chem. Ber. 1977, 110, 2222.

27. (a) Karsch, H. H.; Klein, H.-F.; Schmidbaur, H. Chem. Ber. 1977, 110, 2200. (b) Harris, T. V.; Rathke, J. W.; Muetterties, E. L. J. Am. Chem. Soc. 1978, 100, 6966.

28. (a) Werner, H.; Werner, R. J. Organomet. Chem. 1981, 209, C60. (b) Werner, H.; Gotzlg, J. Organometallics 1983, 2, 547.

29. Bergman, R. G.; Seidler, P. F.; Wenzel, T. T. J. Am. Chem. Soc. 1985, 107, 4358.

30. (a) Cloke, F. G. N.; Cox, K. P.; Green, M. L. H.; Bashkin, J.; Prout, K. J. Chem. Soc., Chem. Commun. 1982, 30. (b) Cox, K.

P.; Bashkin, J.; Brookhart, M.; Cloke, F. G. N.; Derome, A. E.; Grebenik, P. D.; Green, J. C.; Green, M. L. H.; Hare, P. M. J. Chem. Soc., Dalton Trans. **1985**, 423.

31. Green, M. L. H.; Parkin, G.; Mingqin, C.; Prout, K. J. Chem. Soc., Chem. Commun. **1984**, 1400.
32. (a) Schore, N. E.; Hope, H. J. Am. Chem. Soc. **1980**, 102, 4251. (b) Hofmann, P.; Stauffert, P.; Schore, N. E. Chem. Ber. 1982, 115, 2153. (c) Choukroun, R.; Gervais, D. J. Chem. Soc., Chem. Commun. **1982**, 1300.
33. Hofmann, P.; Stauffert, P.; Schore, N. E. Chem. Ber. **1982**, 115, 2153.
34. (a) Etienne, M.; Choukroun, R.; Basso-Bert, M.; Dahan, F.; Gervais, D. Nouv. J. Chim. **1984**, 8, 531. (b) Etienne, M.; Choukroun, R.; Gervais, D. J. Chem. Soc., Dalton Trans. **1984**, 915. (c) LeBlanc, J. E.; Moise, C.; Maisonnat, A.; Poilblanc, R.; Charrier, C.; Mathey, F. J. Organomet. Chem. **1982**, 231, C43.
35. Young, S. J.; Olmstead, M. M.; Knudsen, M. J.; Schore, N. E. Organometallics **1985**, 4, 1432.
36. Vaughn, G. D.; Krein, K. A.; Gladysz, J. A. Angew. Chem., Int. Ed. Engl. **1984**, 23, 245.
37. Green, M. L. H.; Parkin, G. Moynihan, K. J.; Prout, K. J. Chem. Soc., Chem. Commun. **1984**, 1540.
38. (a) Trefonas, L. M.; Flurry, R. L., Jr.; Majeste, R.; Meyers, E. A.; Copeland, R. F. J. Am. Chem. Soc. **1966**, 88, 2145. (b) Cook, A. G. "Enamines", Marcel Dekker, New York, N.Y., 1969; Chapter 5.

39. Mason, R.; Rucci, G. J. Chem. Soc., Chem. Commun. 1971, 1132.

40. Sepelak, D. J.; Pierpont, C. G.; Barefield, E. K.; Budz, J. T.; Poffenberger, C. A. J. Am. Chem. Soc. 1976, 98, 6178.

41. (a) Abel, E. W.; Rowley, R. J. Chem. Soc., Chem. Commun. 1974, 72. (b) Abel, E. W.; Rowley, R. J. J. Chem. Soc., Dalton Trans. 1975, 1096.

42. Barefield, E. K.; Sepelak, D. J. J. Am. Chem. Soc. 1979, 101, 6542.

43. Fong, C. W.; Wilkinson, G. J. Chem. Soc., Dalton Trans. 1975, 1100.

SECTION II. REACTIONS OF THE THIOCARBYNE $[HB(pz)_3](CO)_2W(\equiv CSMe)$ AND THIOCARBENE $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]^+$ COMPLEXES WITH PHOSPHINES

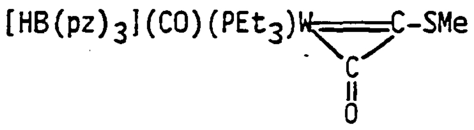
INTRODUCTION

In recent years, the preparations and reactions of thiocarbene[1] and thiocarbyne[2] complexes have been studied extensively in this laboratory. One of those studies led to the synthesis of the thiocarbyne complex $[HB(pz)_3](CO)_2W(\equiv CSMe)$, **1**,[3] where $HB(pz)_3^-$ is the hydrotris(1-pyrazolylborato) ligand. Aside from a communication[4] describing the reaction of **1** with strong acids to give the η^2-thiocarbene complex $\{[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]\}CF_3SO_3$, **6**, there are no other reports of reactions of 1. Only three other thiocarbyne compounds $[HB(3,5\text{-}Me_2\text{-}C_3HN_2)_3](CO)_2Mo(\equiv CSR)$, R = Me, Ph, $4\text{-}C_6H_4NO_2$,[5] and one other η^2-thiocarbene complex $\{(PPh_3)_2[CN(4\text{-}C_6H_4CH_3)](Cl)Os[\eta^2\text{-}C(SMe)(4\text{-}C_6H_4CH_3)]\}ClO_4$[6] have been reported, and very little is known about their reactivities. In this paper, we describe studies of **1** and **6** which demonstrate that they are highly reactive toward certain nucleophiles and electrophiles.

RESULTS AND DISCUSSION

Reaction of $[HB(pz)_3](CO)_2W(\equiv CSMe)$ with PEt_3 Terminal carbyne ligands in transition-metal complexes are frequently observed to undergo attack at the carbyne carbon by a variety of nucleophiles.[7] Phosphines are among the nucleophiles which react in this manner.[8] However, in electron-rich complexes, e.g., $(\eta^5\text{-}C_5H_5)(CO)_2W(\equiv CMe)$ and $(Ph_2PCH_2CH_2PPh_2)(CO)_2W(\equiv CCH_2Ph)^+$, where the carbyne ligand is not susceptible to nucleophilic attack, the PMe_3,[9a] CN^-,[9b] and $^-S_2CNMe_2$[9c] nucleophiles cause carbonylation of the carbyne to give the unusual η^1- or η^2- ketenyl compounds, whose bonding has been recently discussed.[9d] Similarly, we observe that the thiocarbyne complex, $[HB(pz)_3](CO)_2W(\equiv CSMe)$, 1, reacts with PEt_3 at 40°C to give the air-stable η^2-ketenyl complex $[HB(pz)_3](CO)(PEt_3)\overline{W(C(O)C}SMe)$, 2, in 61% yield according to eq 1. The reaction of $(\eta^5\text{-}C_5H_5)(CO)_2W(\equiv CS\text{-}DNP)$,

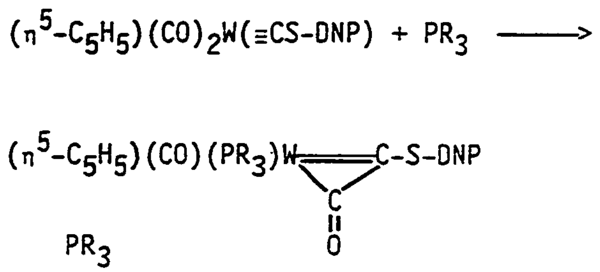
$$\underset{\textbf{1}}{[HB(pz)_3](CO)_2W(\equiv CSMe)} + PEt_3 \xrightarrow{\Delta}$$



(1)

2

where DNP is 2,4-dinitrophenyl, with PPh_3 and PPh_2Me at room temperature gives the corresponding η^2-ketenyl compounds (eq 2). The reaction of $[HB(pz)_3](CO)_2W(\equiv CSMe)$ with PEt_3 takes place under more forcing conditions than the $(\eta^5\text{-}C_5H_5)(CO)_2W(\equiv CS\text{-}DNP)$ reactions



(2)

PR_3

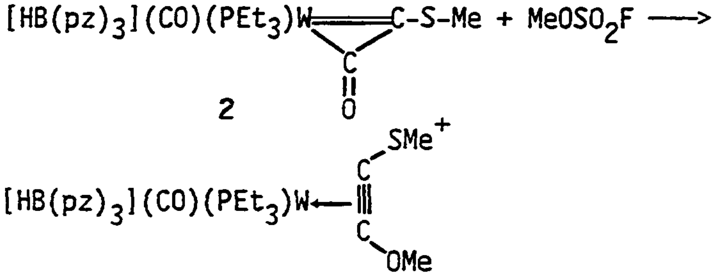
3, PPh_2Me

4, PPh_3

probably because of the great electron donor ability and steric hindrance of the $HB(pz)_3^-$ ligand. The characteristic ν(CO) of the ketenyl CO was observed (Table I) between 1660-1680 cm^{-1}.[9] The ^{13}C NMR spectrum of **2** was assigned (Table III) by comparison with assignments for the related complexes, $(\eta^5\text{-}C_5H_5)(CO)(PMe_3)\overline{W(C(O)C}\text{-}R)$, reported by Kreissl;[9a] in particular, the relationship, $J_{P\text{-}ketenylC} > J_{P\text{-}ketenylCO}$,[9a] was used to assign the two carbon atoms bonded to the W atom in the ketenyl ligand. No reaction was observed between **1** and the nitrogen donors: NH_2Me (25°C, 1 h, CH_2Cl_2), NH_2Et (40°C, 13 h, CH_2Cl_2), and $LiNEt_2$ (50°C, 19 h, THF). Sulfur atom sources (elemental sulfur and ethylene sulfide) did not react (25°C, 20 h, CH_2Cl_2), while $3\text{-}ClC_6H_4CO_3H$ only gave decomposition; there was no evidence for the formation of $W\text{-}C(=X)SMe$ or $W\equiv CS(=X)Me$, X = O or S, products in these reactions. The reaction of **1** with Cl_2 did not give CO-containing products, as detected by IR.

Reaction of $[HB(pz)_3](CO)(PEt_3)\overline{W(C(O)C}SMe)$ with $MeOSO_2F$

Kreissl et al.[10] reported the methylation and addition of XCl_3 (X = B, Al, or In) to the ketenyl CO in $(\eta^5-C_5H_5)(CO)(PMe_3)\overline{W(C(O)C}-R)$ (R = Me, $4-C_6H_4CH_3$) to give $(\eta^5-C_5H_5)(CO)(PMe_3)W(RC{\equiv}COMe)^+$ and $(\eta^5-C_5H_5)(CO)(PMe_3)W(RC{\equiv}COXCl_3)$. A related conversion of a carbyne to an alkyne complex was observed in the coupling reaction of $Cl(PMe_3)_4W({\equiv}CH)$ and CO in the presence of $AlCl_3$ to give $(CO)(PMe_3)_3(Cl)W(HC{\equiv}COAlCl_3)$.[11] We find that $[HB(pz)_3](CO)(PEt_3)\overline{W(C(O)C}SMe)$ reacts similarly with $MeOSO_2F$ at room temperature (eq 3), producing the air-stable violet complex $\{[HB(pz)_3](CO)(PEt_3)W(MeOC{\equiv}CSMe)\}FSO_3$ with the unusual $MeOC{\equiv}CSMe$ acetylene ligand. To our knowledge, this acetylene has not previously been prepared as either the free molecule or the ligand. IR, ^1H, and ^{13}C NMR data for 5


2

5

(3)

are similar to those for the related complex, $(\eta^5-C_5H_5)(CO)(PMe_3)W(MeOC{\equiv}CMe)^+$.[10] The low-field positions of the alkyne carbon atoms (δ 231.13, 198.02 ppm) in the ^{13}C NMR spectrum of complex 5 are similar to those in $(\eta^5-C_5H_5)(CO)(PMe_3)W(MeOC{\equiv}CMe)^+$ (δ 227.1,

Table I. IR Data for the Complexes in CH_2Cl_2 Solvent

Complex	IR ν(CO), cm^{-1}
$[HB(pz)_3](CO)_2W(\equiv CSMe)$, (1)	1980s, 1888s
$[HB(pz)_3](CO)(PEt_3)\overline{W(C(O)C}SMe)$, (2)	1881s, 1665m[a]
$(\eta^5\text{-}C_5H_5)(CO)(PPh_2Me)\overline{W(C(O)C}S\text{-}DNP)$, (3)	1917s, 1679m[a]
$(\eta^5\text{-}C_5H_5)(CO)(PPh_3)\overline{W(C(O)C}S\text{-}DNP)$, (4)	1925s, 1671m[a]
$\{[HB(pz)_3](CO)(PEt_3)W(\eta^2\text{-}MeOC\equiv CSMe)\}FSO_3$, (5)	1959s
$\{[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]\}CF_3SO_3$, (6)	2067m, 1996s
$[HB(pz)_3](CO)_3WCl$, (7)	2033 s, 1947 vs, 1904 s
$[HB(pz)_3](CO)_3WI$, (8)	2021 s, 1942 vs, 1904 s
$\{[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)(PPh_3)]\}CF_3SO_3$, (9)	1950s, 1837s
$\{[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)(PEt_3)]\}CF_3SO_3$, (10)	1943s, 1820s
$\{[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)(P(OMe)_3)]\}CF_3SO_3$, (11)	1955s, 1826s
$\{[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)(PPh_2H)]\}CF_3SO_3$, (12)	1946s, 1831s
$[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)(PPh_2)]$, (13)	1935s, 1809s

[a] ν(CO) of ketenyl CO.

Table II. ^{1}H NMR Data for the Complexes in CD_2Cl_2 solvent at Room Temperature [a]

Complex	H3 of pz	H4 of pz	H5 of pz	CH	SMe	other
1[b]	7.91 (br)	6.23 (br)	7.65 (br)		2.69	
2[b]	8.29(d,J=1.45)	6.41(t,J=2.02)[c]	7.72(d,J=2.01)		2.80	1.74 (m,PCH_2)
	8.06(d,J=1.66)	6.29(t,J=2.09)	7.51(d,J=1.42)			0.64
	7.77(d,J=2.14)	6.04(t,J=2.08)	7.20(d,J=1.48)			(quintet,CH_3)[d]
5[b]	8.00(d,J=2.15)	6.58(t,J=2.13)[c]	7.91(d,J=1.88)		1.94	4.45 (OMe)
	7.98(d,J=2.30)	6.45(t,J=2.18)	7.75(d,J=2.22)			1.82 (m,PCH_2)
	7.93(d,J=1.88)	6.21(t,J=2.21)	6.91(d,J=1.96)			0.66
						(quintet,CH_3)[e]
6	8.07(d,J=2.21)	6.50(t,J=2.37)[c]	7.91(d,J=2.36)	12.78	2.37	
	7.94(t,J=2.90)[c]	6.47(t,J=2.35)	7.83(d,J=2.14)	(s, J_{WH}=		
			7.81(d,J=2.07)	19.83)		
7[b]	8.23(d,J=1.22)	6.30(t,J=1.10)[c]	7.70(d,J=0.98)			
8[b]	8.42(d,J=1.21)	6.30(br)	7.68(d,J=1.38)			

9[b]	8.50(d,J=1.50) 8.04(d,J=1.52 7.93(d,J=1.73)	6.52(t,J=1.05)[c] 6.30(t,J=2.34) 6.19(t,J=1.92)		5.67	1.93	7.70 (m,H5 of pz and Ph)
10	8.11(br)	6.31 (br)	7.75 (br)	4.75	1.74	2.35 (m,PCH_2) 1.40 (quintet,CH_3)[f]

---

[a] Chemical shifts in δ and coupling constants in Hz. Signals are singlets unless indicated otherwise.

[b] $CDCl_3$ solvent.

[c] Due to overlapping d of d.

[d] J_{HH}=7.53, J_{PH} = 15.03.

[e] J_{HH} = 7.76, J_{PH} = 15.77.

[f] J_{HH} = 7.75, J_{PH} = 17.82.

Table II (Continued)

Complex	H3 of pz	H4 of pz	H5 of pz	CH	SMe	other
11	8.15 (br)	6.31 (br)	7.75 (br)	4.99 (d, J_{PH} = 3.2)	1.81 (d, J_{PH} = 1.57)	4.23(d, J_{PH}=10.98,OMe)
12		6.29 (br)		5.45	1.89	8.05(d,J_{PH}=510.25,PH) 8.08-7.30 (m,H3,H5 of pz and Ph)
13	8.09 (d,J=1.73)	6.26(t,J=2.20)^{c}	7.69(d,J=2.19)	4.65(d, J_{PH}= 1.45)	1.47	7.74-7.30 (m,Ph)

Table III. ^{13}C NMR Data for the Complexes in CD_2Cl_2 solvent at Room Temperature[a]

Complex	CO	C3 of pz	C4 of pz	C5 of pz	CH	SMe	Other
1[b]	224.7	144.9	105.7	135.2		17.4	264.4 (W-CS)
2	229.75	145.67, 144.72, 142.21	107.54, 106.67	135.96, 135.10 134.67		16.18	209.16 (d, J_{PC}=5.86 ketenyl C), 205.22 (ketenyl CO), 18.44 (d, J_{PC}=27.34, PCH_2), 6.04(CH_3)

5	221.20 (d, J_{PC}=9.97)	145.93, 144.98, 142.55	107.45, 106.67	137.96, 136.83 136.23		19.57	231.13 (W-C-O) 198.02 (W-C-S) 66.54 (OMe) 18.79 (d, J_{PC}=27.34, PCH_2) 6.22 (CH_3)
6	212.98, 212.55	147.21, 146.31 145.95	109.06, 108.48 108.33	138.76, 138.51, 138.27	227.95	28.40	121.53(quartet, J_{CF}=320.81, CF_3SO_3)
9	244.83, 216.31	147.15, 143.51	106.50	136.05, 134.23	38.72 (d, J_{PC}=54.69)	22.77	[133.06 (d, J_{PC}=5.86), 129.42 (d, J_{PC}=9.77), 122.27, 118.46, Ph]

---

[a] Chemical shifts in δ and coupling constants in Hz.

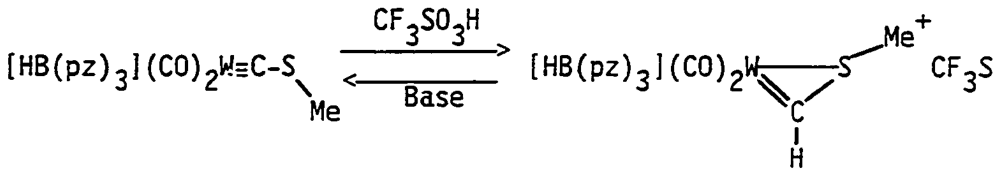
[b] $CDCl_3$ solvent.

Table III (Continued)

Complex	CO	C3 of pz	C4 of pz	C5 of pz	CH	SMe	Other
10	245.12 (d, J_{PC}=4.99) 218.26	147.94, 147.49 144.53	107.39, 106.99 106.41	136.56, 136.37	39.65 (d, J_{PC}=50.18)	22.08	15.04 (d, J_{PC}=49.07, PCH_2), 6.42 (d, J_{PC}=4.37, CH_3)
13	239.89 (d, J_{PC}=12.12), 220.55	146.06	106.28	135.81	58.21 (d, J_{PC}=45.32)	22.25	[143.56 (d, J_{PC}=19.91), 140.99 (d, J_{PC}=14.50), 133.39, 133.11, 132.91, 132.66, 128.76, 128.29, 128.22, 128.13, Ph]

197.7 ppm),[10] $(\eta^5\text{-}C_5H_5)(PMe_3)_2W(MeOC{\equiv}CMe)$ (δ 227.9, 200.5 ppm),[12] and $(CO)(\eta^2\text{-}S_2CNEt_2)_2W(HC{\equiv}CH)$ (δ 206.6, 207.1 ppm),[13] where the acetylene moiety is believed to be a 4 electron donor. The violet compound **5** exhibits a low-energy absorption in the visible spectrum, λ_{max} = 560 nm. This absorption is probably a d-d transition as was proposed for the cationic alkyne complexes, $(\eta^5\text{-}C_5H_5)(PMe_3)(CO)W[MeOC{\equiv}C(4\text{-}C_6H_4CH_3)]^+$ (λ_{max} = 465 nm)[12] and $(\eta^5\text{-}C_5H_5)(PMe_3)_2W[MeOC{\equiv}C(4\text{-}C_6H_4CH_3)]^+$ (λ_{max} = 562 nm).[12] Both electronic spectroscopy and electrochemical measurements have been used as convenient probes of the dπ interactions in the acetylene complexes.[14] Compound **5** exhibits a reversible reduction wave ($E_{\frac{1}{2}}$) at -1.16 V and a reversible oxidation wave ($E_{\frac{1}{2}}$) at 1.00 V (vs. Ag/AgCl in 0.10 M $(n\text{-}Bu)_4NPF_6$, 200 mV/sec scan rate, CH_3CN).

<u>Preparation of $\{[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]\}CF_3SO_3$</u> In a Communication,[4] we reported that protonation of $[HB(pz)_3](CO)_2W({\equiv}CSMe)$ with CF_3SO_3H gives the violet air-stable complex $\{[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]\}CF_3SO_3$, **6**, in which the carbene ligand is bonded to the metal through both the C and S atoms, as shown by an X-ray diffraction study (eq 4). Reaction 4 also occurs with $HBF_4{\cdot}Et_2O$ and CF_3CO_2H but not



(4)

1 **6**

with acetic acid. Carbyne **1** is regenerated in approximately 10% yield when **6** is treated with the bases K_2CO_3 or Et_3N in CH_2Cl_2 (30 min) or with NaH in THF (4 h).[4,15] There was no adduct formation between **1** and other electrophiles such as BF_3, $MeOSO_2F$, or diphenylketene.

Related to equation 4 are the reactions of $(Cl)(CO)(PPh_3)_2Os(\equiv CR)$, where R = p-tolyl, with HCl[16] to give $Os(=CHR)(Cl)_2(CO)(PPh_3)_2$ and $(\eta^5\text{-}C_5H_5)(CO)_2W(\equiv CNEt_2)$ with HCl[17] to give $(\eta^5\text{-}C_5H_5)(CO)_2(Cl)W[=C(H)(NEt_2)]$. The reaction of **1** with HCl appears to give initially η^2-carbene $\{[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]\}Cl$ or possibly the η^1-carbene $[HB(pz)_3](CO)_2W(Cl)[=CH(SMe)]$ as suggested by an IR spectrum ($\nu(CO)$: 2056, 1985 cm^{-1}, CH_2Cl_2) of the reaction mixture. However, the compound is not stable under the reaction conditions and could not be isolated. The only product that could be isolated was $[HB(pz)_3](CO)_3WCl$, **7**, although in low yield (16%), eq (5). Similarly, the reaction of **1** with HI gives a low yield (10%) of $[HB(pz)_3](CO)_3WI$, **8**. IR and ^1H NMR data for **7** and **8** are similar to those for the related complexes, $[HB(pz)_3](CO)_3MoX$, X = Br, I, prepared from the reaction of $[HB(pz)_3](CO)_3Mo^-$ and X_2.[18]

$$[HB(pz)_3](CO)_2W{\equiv}C{-}S{-}Me + HX \longrightarrow [HB(pz)_3](CO)_3WX \qquad (5)$$

7, Cl
8, I

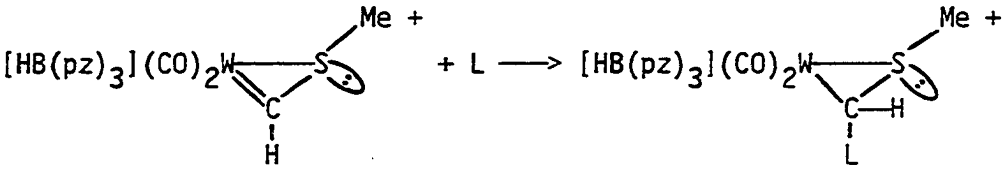
Expecting the sulfur group in **1** to be reactive toward Hg(II) compounds, **1** was treated with $HgCl_2$ and $HgPh_2$ at room temperature in CH_2Cl_2; however, there was no reaction. Thus, the sulfur is very nonnucleophilic, probably because of π-bonding into the carbyne carbon atom.

In the ^{1}H NMR spectrum of **6**, the carbene proton occurs at low field (δ 12.78, J_{WH} = 19.83, natural abundance of ^{183}W = 14.4%), as observed in η^1 cationic carbene complexes $(\eta^5\text{-}C_5H_5)(CO)_2Fe[CH(SMe)]^+$ (δ 14.86),[1d] $(\eta^5\text{-}C_5H_5)(NO)(PPh_3)Re[CH(SMe)]^+$ (δ 14.90),[19] and $(Cl)(CO)_2(PPh_3)_2Os[CH(SMe)]^+$ (δ 14.70).[20] One-bond ^{13}C-H coupling constants ($^1J_{CH}$) are indicators of the amount of carbon s character in the C-H bond.[21] In the proton-coupled ^{13}C NMR spectrum of **6**, the carbene carbon resonance (δ 227.95 ppm) has a $^1J_{CH}$ coupling constant of 211 Hz, which is in the range ($^1J_{CH}$ = 140~230 Hz)[21] of C(sp^2)-H coupling constants in organic molecules. However, the observed $^1J_{CH}$ coupling constant (211 Hz) in **6** is larger than those found in other carbene complexes, $(\eta^5\text{-}C_5H_5)(CO)_2Fe[CH(Ph)]^+$ (δ 324.4 ppm, $^1J_{CH}$ = 146 Hz),[22] $(Cl)(PMe_3)_4W(CH_2)^+$ (δ 220 ppm, $^1J_{CH}$ = 119 Hz),[23] and $(\eta^5\text{-}C_5H_5)(CO)_2(Cl)W[CH(NEt_2)]$ (δ 236.2 ppm, $^1J_{CH}$ = 138.5 Hz).[17] The difference may be due to the three-membered ring geometry and electronegativity of the substituents on the carbon atom in **6**.

In the ^{1}H and ^{13}C NMR spectra (Tables II and III) of **6** at room temperature, a sharp singlet corresponding to the SMe group is observed at δ 2.37 and δ 28.40, respectively. In ^{13}C (-20°C, CD_2Cl_2) and ^{1}H NMR (-8°C, -40°C, and -75°C, CD_2Cl_2) spectra of **6** at low temperatures, the SMe resonance remains a singlet. While inversion of the sulfur atom in other sulfide complexes is frequently observed,[24] there is no evidence for inversion at the sulfur atom in the η^2-CH(SMe) carbene ligand of **6** in this temperature range (-75°C-25°C).

Reactions of $[HB(pz)_3](CO)_2W[CH(SMe)]^+$ with Phosphorus Donors

The C(carbene) atom in transition-metal carbene complexes is frequently the site of attack by a variety of nucleophiles.[25] Phosphines are among the nucleophiles which react in this manner.[26] Recent examples are the reactions of $(\eta^5\text{-}C_5H_5)(CO)_2Fe[CH(SMe)]^+$ [1d] and $(CO)_5W[CH(Ph)]$[27] with phosphines and phosphites to give the adducts $(\eta^5\text{-}C_5H_5)(CO)_2Fe[CH(SMe)(L)]^+$ (L = PPh_2Me, PPh_3, PPh_2Cl, PPh_2H, $P(OPh)_3$, $P(OCH_2)_3CMe$) and $(CO)_5W[CH(Ph)(PPh_3)]$. Similarly, $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]^+$ reacts at room temperature with phosphorus donors to give the adducts $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)L]^+$ (eq **6**) in <u>ca</u>. 90% yield.



6 **9-12** (6)

L = PPh_3 (**9**), PEt_3 (**10**), $P(OMe)_3$ (**11**), PPh_2H (**12**)

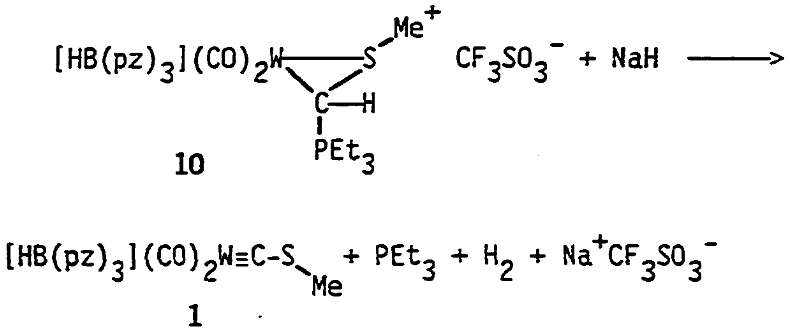
Based on the structure of deprotonated **12** discussed in the next section, the phosphine adducts (**9-12**) probably have the structure (eq 6) in which the phosphorus donor adds to the carbene carbon on the side opposite the Me on the S atom, which is also the side opposite the bulky $[HB(pz)_3]$ group. Despite the strained 3-membered ring in **6**, there is no evidence for phosphine displacement of the sulfur from the

W to give products $[HB(pz)_3](CO)_2(L)W{=}CH(SMe)^+$ with an η^1-carbene ligand.

The ^1H NMR resonance of the methine hydrogen in **9**, **10**, and **12** occurs as a singlet. The absence of coupling to the P atom may be due to a Karplus-like dependence of $^2J_{PH}$ on the angle between the H and P atoms;[28] $^2J_{PH}$ ranges from 0 to 26 Hz depending on the angle between them. In contrast to the phosphine adduct situation, the methine hydrogen in the $P(OMe)_3$ adduct, **11**, does occur as a doublet (J_{PH} = 3.2 Hz) due to coupling with the P atom. A correlation between the chemical shifts of the methine hydrogen (**9** (PPh_3) δ 5.67, **12** (PPh_2H) δ 5.45, **11** ($P(OMe)_3$) δ 4.99, **10** (PEt_3) δ 4.75) and the methyl hydrogens of the SMe group (**9** δ 1.93, **12** δ 1.89, **11** δ 1.81, **10** δ 1.74) is noticeable. Since this order is not in accord with the order of either the donor ability or the steric bulkiness of L,[29] it is not clear what factors determine this trend. The large J_{PH} coupling constant (510.25 Hz) observed in the ^1H NMR spectrum of the PPh_2H adduct **12** is characteristic of H atoms bound directly to a phosphorus atom.[30]

In the ^{13}C NMR spectrum of **9** and **10**, the methine carbon occurs as a doublet due to coupling with the phosphorus P atom. The chemical shifts of the two CO groups differ (Table III) by as much as 28 ppm.

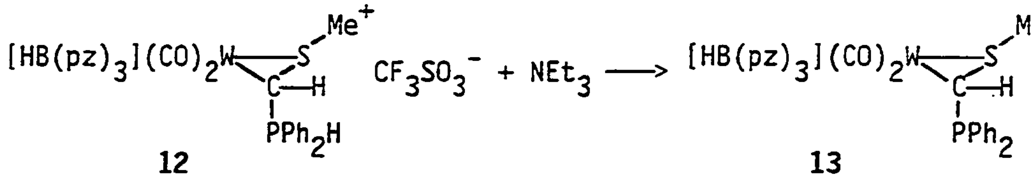
Deprotonation of the methine hydrogen in **10** with NaH (25°C, 24 h, CH_2Cl_2) gives the thiocarbyne compound **1** in 90% yield (eq 7). However, deprotonation of **6** with NaH (eq 4), as mentioned earlier,



(7)

produces the thiocarbyne compound **1** in low yield (10%), as well as a side product $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)_2]$ in 40% yield.[4,15] Although the mechanisms of these two reactions are not clear, PEt_3 seems to play an important role in blocking the formation of the side product, yielding mainly the thiocarbyne compound **1**.

Reaction of $\{[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)(PPh_2H)]\}CF_3SO_3$ with NEt_3 The P-H proton in **12** is readily removed with NEt_3 in CH_2Cl_2 at room temperature to give $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)(PPh_2)]$, **13** (eq 8). The ^1H NMR resonances of the methine hydrogen (δ 4.65) and methyl



(8)

hydrogens δ 1.47) in **13** are upfield from those of the parent PPh_2H adduct, **12** (δ 5.45, 1.89), as expected for the removal of a proton. In the ^{31}P NMR spectrum of **13**, a singlet (δ 10.52), without W satellite peaks, is observed, which establishes that the P atom is not bound to the W; when phosphines are bound to a W atom, $^1J_{WP}$ is usually about 200~300 Hz.[31] These NMR results, together with the lower $\nu(CO)$

values, suggest that complex **13** contains a $[CH(SMe)(PPh_2)]$ ligand which is bonded to the metal through both the C and S atoms, as is the η^2-CH(SMe) ligand in the starting complex **6**. ^1H NMR spectra (50°C, 80°C) of **13** in CD_3NO_2 at elevated temperatures are the same as at room temperature; thus, no rearrangement to the form in which the $[CH(SMe)(PPh_2)]$ ligand coordinates through the C and P atoms occurs. Several complexes with 3-membered metal-C-P rings are known,[32] and rearrangement of primary and secondary phosphine carbene adducts to give complexes with metal-P bonds have been reported. Thus, the reaction of $(CO)_5Cr[C(OMe)Ph]$ with PMe_2H gives the adduct $(CO)_5Cr[C(OMe)Ph(PMe_2H)]$ which upon stirring in acetone rearranges to give the phosphine complex $(CO)_5Cr[PMe_2[CH(Ph)(OMe)]]$.[33] Also, the reaction of $(CO)_5W[C(SMe)_2]$ with PPh_2H is believed to give initially the adduct, which rapidly rearranges to yield the final phosphine product $(CO)_5W[PPh_2[CH(SMe)_2]]$.[1a,34] $(\eta^5\text{-}C_5H_5)(CO)_2Fe[CH(SMe)\text{-}(PPh_2H)]^+$ also rearranges to give $(\eta^5\text{-}C_5H_5)(CO)_2Fe[PPh_2(CH_2SMe)]^+$ at 168°C in the solid state.[1d]

To ensure that the ligand $[CH(SMe)(PPh_2)]$ is bonded to the tungsten through both the C and S atoms, and to establish the stereochemistry within the ligand, an X-ray structural determination of **13** was undertaken. The $[HB(pz)_3](CO)_2W[CH(SMe)]$ portion of the molecule **13** retains the atomic connectivity of the carbene cation **6** as shown in Fig. 1. Some structural changes, however, are noticeable. The W-S bond distance, 2.440(9)Å is somewhat shorter than the 2.481(6)Å found in **6**. The W-C(3) distance (2.22(3)Å) is substantially

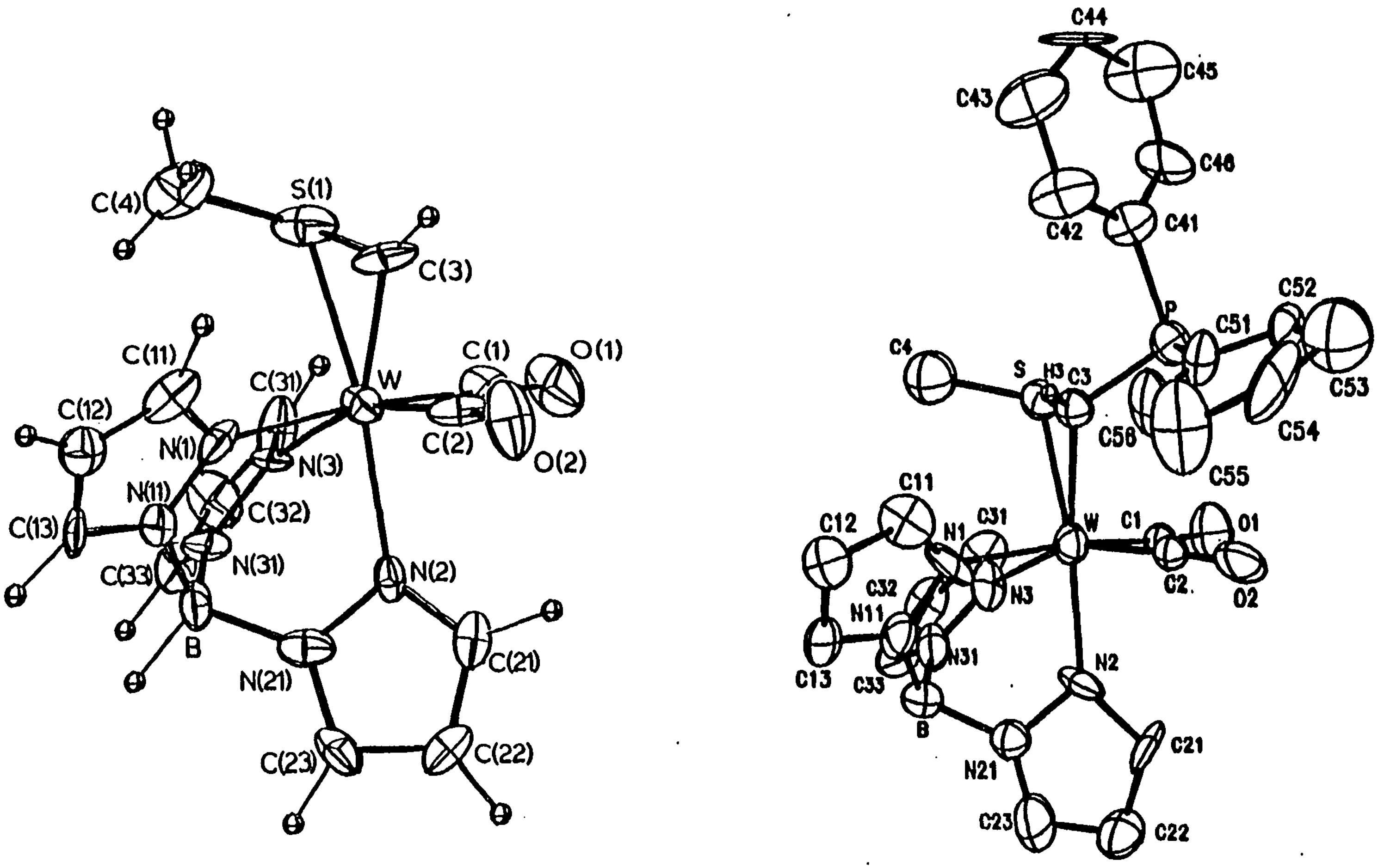


Figure 1. ORTEP plots of [HB(pz)$_3$](CO)$_2$W[η^2-CH(SMe)]$^+$, 6,[4] (left) and [HB(pz)$_3$](CO)$_2$W[η^2-CH(SMe)(PPh$_2$)], 13, (right)

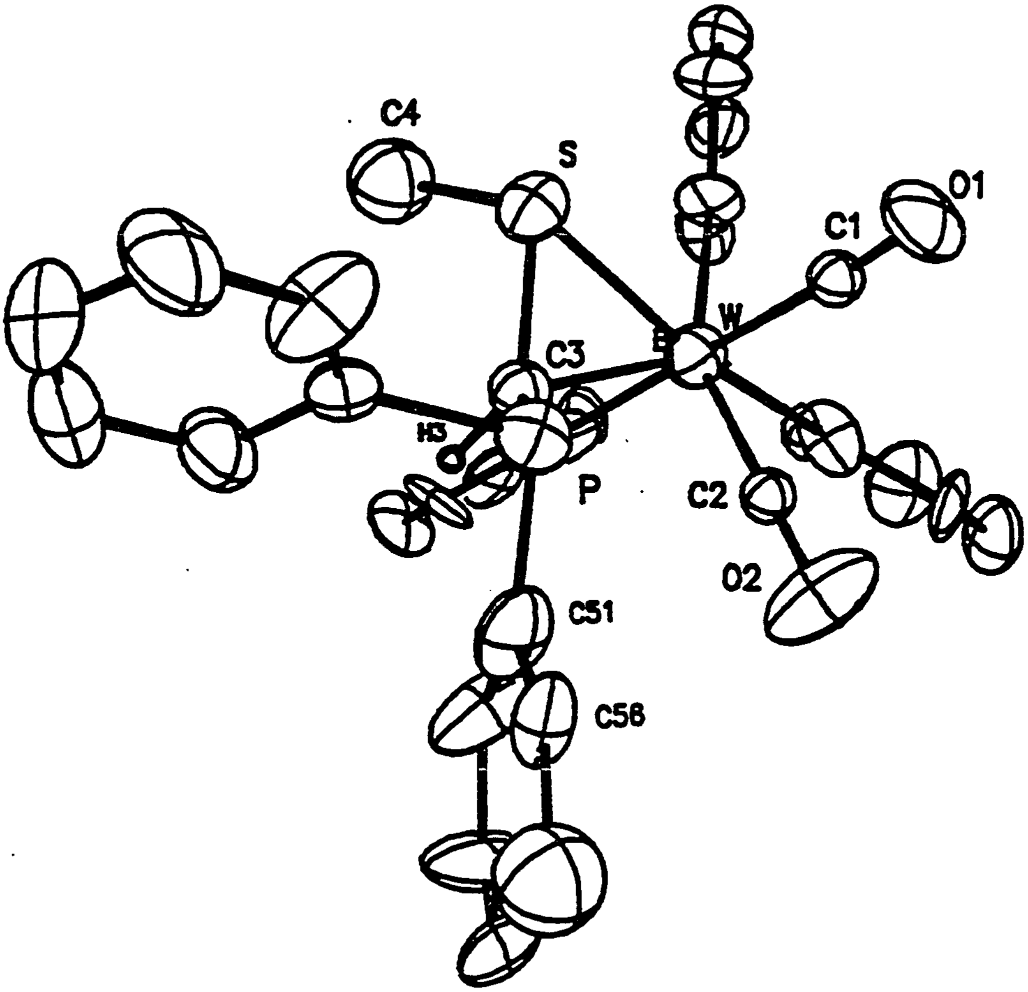


Figure 2. Perspective of $[HB(pz)_3](CO)_2W[\eta^2-CH(SMe)(PPh_2)]$, 13

Table IV. Final Atomic Parameters[a] for $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)(PPh_2)]$, 13

	x	y	z	Ueq[b]
W	913(1)	2732(1)	3737(2)	39(0)
S	-884(7)	3828(5)	5056(11)	43(3)
P	-2184(8)	3256(5)	1617(11)	43(3)
B	3329(30)	1611(25)	6351(48)	42(14)
C(1)	931(25)	3644(19)	2538(36)	30(7)
O(1)	876(24)	4258(16)	1854(33)	64(11)
C(2)	624(24)	2355(17)	1291(36)	29(6)
O(2)	475(22)	2075(18)	-325(32)	77(11)
C(3)	-1081(26)	2882(19)	3476(37)	35(7)
C(4)	-1017(36)	3530(27)	7162(54)	70(11)
N(1)	1129(23)	1592(18)	5257(33)	51(11)
N(11)	2214(23)	1280(16)	6264(32)	42(10)
C(11)	415(29)	1125(20)	5511(46)	47(14)
C(12)	983(31)	510(19)	6575(48)	50(14)
C(13)	2177(28)	555(22)	7028(36)	45(13)

---

[a] Estimated standard deviations are given in parentheses. Positional parameters x 10^4.

[b] $U_{eq} = (1/3)\ \Sigma\Sigma \vec{a}_i \cdot \vec{a}_j U_{ij} a_i^* a_j^* \times 10^3$.

Table IV (Continued)

	x	y	z	Ueq^b
N(2)	2718(20)	1905(17)	3104(36)	42(10)
N(21)	3614(22)	1444(16)	4349(33)	41(6)
C(21)	3377(31)	1636(24)	1591(38)	50(15)
C(22)	4569(31)	1065(27)	1850(46)	59(17)
C(23)	4641(37)	996(30)	3607(47)	70(19)
N(3)	2022(23)	3180(17)	6156(29)	40(10)
N(31)	2947(23)	2592(19)	7043(33)	46(11)
C(31)	1854(35)	4006(21)	7025(49)	56(15)
C(32)	2833(36)	3878(25)	8468(45)	55(17)
C(33)	3469(29)	3034(25)	8420(42)	49(15)
C(41)	-3701(29)	3620(19)	2528(44)	46(13)
C(42)	-4029(33)	3031(23)	3315(59)	67(17)
C(43)	-5178(41)	3324(32)	3992(66)	88(24)
C(44)	-6020(27)	4204(32)	3709(64)	81(20)
C(45)	-5715(41)	4732(26)	2875(75)	91(24)
C(46)	-4542(33)	4396(26)	2294(56)	74(17)
C(51)	-2266(33)	2219(27)	251(41)	58(16)
C(52)	-2855(29)	2238(29)	-1403(38)	55(17)
C(53)	-2971(47)	1549(36)	-2753(70)	95(14)
C(54)	-2433(44)	654(34)	-2158(46)	86(24)

Table IV (Continued)

	x	y	z	Ueq^b
C(55)	-1703(48)	570(23)	-532(53)	83(21)
C(56)	-1731(39)	1381(23)	633(45)	70(16)

Table V. Selected Bond Distances (A°)[a] in $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)(PPh_2)]$, **13**, and $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]^+$, **6**[4]

	13	6		13	6
W-S	2.440(9)	2.481(6)	W-N(1)	2.30(3)	2.21(2)
W-C(1)	1.90(3)	2.04(2)	W-N(2)	2.14(3)	2.20(1)
W-C(2)	1.87(3)	2.09(2)	W-N(3)	2.22(3)	2.20(1)
W-C(3)	2.22(3)	1.93(2)	S-C(4)	1.82(4)	1.85(2)
S-C(3)	1.80(3)	1.72(2)	B-N(11)	1.54(5)	1.57(3)
P-C(3)	1.81(3)		B-N(21)	1.58(5)	1.58(3)
P-C(41)	1.85(3)		B-N(31)	1.50(5)	1.54(3)
P-C(51)	1.81(4)		C(2)-O(2)	1.24(4)	1.09(3)
C(1)-O(1)	1.19(4)	1.13(3)			

[a] Estimated standard deviations are given in parentheses.

Table VI. Selected Bond Angles(°)[a] for $[HB(pz)_3](CO)_2W[\eta^2$-$CH(SMe)(PPh_2)]$, **13**, and $[HB(pz)_3](CO)_2W[\eta^2$-$CH(SMe)]^+$, **6**[4]

	13	6		13	6
S-W-C(1)	85.7(9)	89.4(6)	C(1)-W-C(2)	73(1)	89.3(8)
S-W-C(2)	113.6(9)	116.2(6)	C(1)-W-C(3)	102(1)	88.0(8)
S-W-C(3)	45.3(8)	43.8(6)	C(1)-W-N(1)	174(1)	171.4(7)
S-W-N(1)	98.9(7)	95.8(4)	C(1)-W-N(2)	94(1)	90.2(7)
S-W-N(2)	166.7(7)	164.8(4)	C(1)-W-N(3)	93(1)	90.3(7)
S-W-N(3)	86.3(7)	84.2(4)	C(2)-W-C(3)	79(1)	72.4(8)
C(3)-W-N(1)	85(1)	100.5(7)	C(2)-W-N(1)	109(1)	94.5(7)
C(3)-W-N(2)	147(1)	151.3(7)	C(2)-W-N(2)	79(1)	78.9(7)
C(3)-W-N(3)	127(1)	127.9(7)	C(2)-W-N(3)	154(1)	159.6(7)
N(1)-W-N(2)	81(1)	83.0(6)	C(3)-P-C(41)	104(1)	
N(1)-W-N(3)	82.8(9)	83.5(5)	C(3)-P-C(51)	103(2)	
N(2)-W-N(3)	80(1)	80.6(5)	C(41)-P-C(51)	99(2)	
W-S-C(3)	61(1)	51.0(7)	N(11)-B-N(21)	104(3)	107(2)
W-S-C(4)	109(1)	110.5(7)	N(11)-B-N(31)	109(3)	109(2)
C(3)-S-C(4)	102(2)	106(1)	N(21)-B-N(31)	110(3)	109(2)
W-C(3)-S	74(1)	85.3(8)	W-C(1)-O-(1)	176(3)	177(2)
W-C(3)-P	126(2)		W-C(2)-O(2)	177(3)	176(2)
S-C(3)-P	110(2)				

[a] Estimated standard deviations are given in parentheses.

Table VII. Selected Torsion Angles (°) for $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)(PPh_2)]$, 13

W-C(3)-P-C(41)	-160.4	W-C(3)-P-C(51)	97.2
S-C(3)-P-C(41)	-76.3	S-C(3)-P-C(51)	-178.7
P-C(3)-S-W	-122.6	P-C(3)-S-C(4)	132.4
W-C(3)-S-C(4)	-105.0		

longer than the W=C(carbene) distance (1.93(2)Å) in **6** and is comparable to W-C(sp^3) bond distances found in W(≡$CCMe_3$)(=$CHCMe_3$)(-CH_2CMe_3)(dmpe) (2.258(9)Å)[35] and in [$Cp_2W(CH_3)(CH_2CH_2$-$PMe_2Ph)]PF_6$ (avg. 2.26(3)Å).[36] The S-C(3) distance (1.80(3)Å) is similar to single bond S-C(sp^3) distances obtained in microwave studies of MeSH (1.819Å)[37] and Me_2S (1.802Å).[38] Also, S-C(3) is comparable to S-C(4)(1.82(4)Å), but is longer than the S-C(3) distance (1.72(2)Å) in **6**. Unfortunately, the large estimated standard deviations make more precise comparisons impossible. The single bond C(3)-P distance (1.81(3)Å) is similar to P-C(sp^3) distances (avg. 1.829(3)Å) found in $PPh_2CH_2CH_2PPh_2$ (DPPE).[39] These changes in bond distances from molecules **6** to **13** involving C(3) can be easily rationalized by recognizing that the C(3) atom is approximately sp^2 hybridized in **6** and sp^3 in **13**. All of the bonds around C(3) in **13** are those expected for single bond distances to an sp^3 C atom.

P and C(4) are trans to each other with respect to the WSC(3) plane[40] minimizing possible steric hindrance of the PPh_2 group with the methyl or pyrazolyl group. The groups around the C(3)-P bond have a staggered conformation, C(41) being trans to W and C(51) trans to S (Table VII). One may view the remaining lone pair on P as being trans to H(3). Thus, the orientation of the PPh_2 group minimizes steric repulsion with the remainder of the molecule.

W-CO distances (avg. 1.89(3)Å) are significantly shorter than those of **6** (avg. 2.07(2)Å), suggesting enhanced π-backbonding to the carbonyls, which is supported by the substantially lower ν(CO) values for **13** than for **6** (Table I). The bond angle C(1)-W-C(2), 73(1)°, is substantially smaller than that of **6** (89.3(8)°); this change in the orientation of the C(2)O(2) group might be ascribed to the close proximity of one of the phenyl rings (O(2)•••C(51) = 3.19(5)Å, O(2)•••C(56) = 3.34(5)Å) and the phosphorus atom (P•••C(2) = 3.11(3)Å, P•••O(2) = 3.42(3)Å) (Fig. 2).

EXPERIMENTAL SECTION

General Procedures All reactions were carried out under an N_2 atmosphere. CH_2Cl_2 and hexane were dried over CaH_2 and distilled under N_2. Diethyl ether was distilled from Na-benzophenone under N_2. Reagent grade methanol was stored over type 4A molecular sieves. Reactions were carried out at room temperature unless stated otherwise. Products were crystallized using a layering technique, whereby the compound dissolved in CH_2Cl_2 (1 - 10 mL) was layered with hexane or ether (5 - 50 mL) and allowed to stand at -20°C.

Infrared spectra were recorded on a Perkin-Elmer 281 spectrometer, and band positions were calibrated against gaseous CO. The UV-visible spectrum was obtained on a Varian DMS 90 spectrometer. ^1H NMR spectra were obtained with a JEOL FX-90Q (89.55 MHz), Nicolet NT-300 (300 MHz), or Bruker WM-300 (300 MHz) spectrometer. Proton-decoupled ^{13}C NMR spectra were measured on a JEOL FX-90Q (22.5 MHz), Nicolet NT-300 (75.46 MHz), or WM-300 (75.43 MHz) spectrometer. Broad band decoupled ^{31}P NMR spectra were run on a Bruker WM-300 (121.44 MHz) spectrometer. Variable temperature NMR studies were done on the Bruker WM-300 spectrometer. To reduce ^{13}C NMR data collection times, $Cr(acac)_3$ (ca. 0.1 M) was added to the solutions.[41] Tetramethylsilane (Me_4Si) was the standard of reference for all ^1H NMR spectra; chemical shifts are reported in δ downfield from Me_4Si. Chemical shifts of ^{13}C nuclei are reported in δ units using CD_2Cl_2 ($\delta = 53.80$) as the internal standard. ^{31}P resonances, downfield from the H_3PO_4 external reference (in a capillary insert), are given in positive values (ppm). Electron impact mass spectra (EIMS) were obtained on a Finnigan 4000 spectrometer. Fast atom bombardment (FAB, glycerol matrix) mass spectra were recorded on a Kratos MS-50, Finnigan MAT 8230, or Hitachi M-80A spectrometer. Conductivity measurements were made by using a Markson 4402 conductivity meter and dip cell. Elemental microanalyses were performed by Galbraith Laboratories Inc., Knoxville, Tennessee.

The complexes $[HB(pz)_3](CO)_2W(\equiv CSMe)$ (**1**) and $(\eta^5\text{-}C_5H_5)(CO)_2W(\equiv CS\text{-}DNP)$, where DNP is the 2,4-dintrophenyl group, were prepared using previously described procedures.[3] PPh_3 was recrystallized from hexane, and Et_3N was distilled from KOH in an N_2 atmosphere. All other chemicals were used as received from commercial sources. $MeOSO_2F$ was acquired from Tridom Chemical (Fluka).

$\underline{[HB(pz)_3](CO)(PEt_3)\overline{W(C(O)C}SMe), 2}$ A solution of 40 mL of CH_2Cl_2 containing PEt_3(0.22 mL, 1.5 mmol) and the thiocarbyne compound, **1**, (0.39 g, 0.76 mmol) was refluxed for 22h, yielding a dark-red solution. The solution was evaporated to dryness under reduced pressure, and the residue was redissolved in a minimum amount of CH_2Cl_2. This CH_2Cl_2 solution was chromatographed on a 1 x 30 cm Florisil column. Unreacted starting material was eluted first with CH_2Cl_2. Then, a dark red band on the top of the column was eluted with methanol. The methanol eluate was evaporated to give a solid, which was recrystallized from CH_2Cl_2/hexane at -20°C yielding air-stable maroon needles of $[HB(pz)_3](CO)_2\overline{W(C(O)C}SMe)$, 2 (0.29 g, 61%). Anal. Calcd for $C_{19}H_{28}BN_6O_2PSW$: C, 36.21; H, 4.48; N, 13.34. Found: C, 36.26; H, 4.66; N, 13.15. EIMS (18 eV): m/e 602 (M^+-CO), 512 (M^+-PEt_3), 484 (M^+-PEt_3-CO).

$(\eta^5$-$C_5H_5)(CO)(PPh_2Me)\overline{W(C(O)C}S$-DNP), 3 Upon addition of $PMePh_2$ (27 μL,0.15 mmol) to a 10 mL CH_2Cl_2 solution of $(\eta^5$-$C_5H_5)(CO)_2W(\equiv CS$-DNP)(60 mg, 0.12 mmol), the color of the solution changed to yellow. After 15 min, the solvent was removed under vacuum. The resulting yellow solid was washed with heptane. Air-stable yellow crystals of $(\eta^5$-$C_5H_5)(CO)(PPh_2Me)\overline{W(C(O)C}S$-DNP), 3, were obtained by recrystallizing the solid from CH_2Cl_2/hexane at -20°C (77 mg, 90%). ^1H NMR ($CDCl_3$): 7.44 (m, Ph), 5.48 (d, J_{PH} = 1.2 Hz, Cp), 2.30 (d, J_{PH} = 9.77 Hz, CH_3).

$(\eta^5$-$C_5H_5)(CO)(PPh_3)\overline{W(C(O)C}S$-DNP), 4 In a procedure similar to the one directly above, PPh_3 (18 mg, 0.069 mmol) was allowed to react with $(\eta^5$-$C_5H_5)(CO)_2W(\equiv CS$-DNP) (32 mg, 0.062 mmol) in 5 mL CH_2Cl_2 for 2 h. The product $(\eta^5$-$C_5H_5)(CO)(PPh_3)\overline{W(C(O)C}S$-DNP), 4, was characterized only by its IR spectrum.

$\{[HB(pz)_3](CO)(PEt_3)W(MeOC\equiv CSMe)\}FSO_3$, 5 Into a 30 mL CH_2Cl_2 solution of 2 (0.20 g, 0.31 mmol) was added $MeOSO_2F$ (25 μL, 0.31 mmol). After the reaction mixture was stirred for 30 min, the solvent was removed under vacuum. The residue was washed with hexane (30 mL) three times. Air-stable violet crystals of 5 were obtained by recrystallizing the solid from CH_2Cl_2/Et_2O at -20°C (0.21 g, 93%).

Anal. Calcd for $C_{20}H_{31}BFN_6O_5PS_2W$: C, 32.28; H, 4.20; N, 11.29. Found: C, 31.91; H, 4.13; N, 11.08. ^{31}P NMR ($CDCl_3$): δ 10.07 (J_{WP} = 305.17 Hz). MS(FAB): m/e 645 (parent cation), 602 (parent cation-CO-Me). Molar conductivity (CH_2Cl_2): Λ_M = 56.40 Ω^{-1} cm^2 mol^{-1} at 10^{-3} M (1:1 electrolyte).[42] UV-vis: λ_{max} = 560 nm.

$\{[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]\}CF_3SO_3$, **6** Addition of CF_3SO_3H (53 μL, 0.60 mmol) to a solution of 1 (0.31 g, 0.60 mmol) in 40 mL of CH_2Cl_2 at 0°C produced an immediate color change from orange to the violet color of product **6**. After the solvent was removed under vacuum, the resulting solid was washed several times with hexane. Air-stable violet crystals of **6** were obtained by recrystallizing the solid from CH_2Cl_2/Et_2O at -20°C in essentially quantitative yield. Anal. Calcd for $C_{14}H_{14}BF_3N_6O_5S_2W$: C, 25.40; H, 2.13; N, 12.69. Found: C, 25.31; H, 2.47; N, 12.71. MS(FAB): m/e 513 (parent cation), 485 (parent cation-CO), 457 (parent cation - 2CO). Molar conductivity (CH_2Cl_2): Λ_M = 33.93 Ω^{-1} m^2 mol^{-1} at 10^{-3} (1:1 electrolyte).[42]

$[HB(pz)_3](CO)_3WCl$, 7 Hydrogen chloride was bubbled slowly through a 10 mL CH_2Cl_2 solution of the thiocarbyne complex, 1, (56 mg, 0.11 mmol) for 30 min. The solvent was removed under vacuum, and the resulting solid was redissolved in a minimum amount of CH_2Cl_2. This solution was chromatographed on a 1 x 30 cm Florisil column. The starting thiocarbyne complex, 1, was eluted first with a 1:2 mixture of CH_2Cl_2 and hexane. Then, a yellow band was eluted with the same solvent mixture. The yellow eluate was evaporated to dryness. The resulting solid was recrystallized from CH_2Cl_2/hexane at -20°C to give brown crystals of 7 (9 mg, 16%). EIMS (22 eV): m/e 488(M^+-CO), 481(M^+-Cl).

[HB(pz)$_3$](CO)$_3$WI, 8 Hydrogen iodide was bubbled through a 20 mL CH_2Cl_2 solution of the thiocarbyne complex, **1**, (0.19 g, 0.37 mmol) until the IR spectrum showed no CO bands corresponding to the starting thiocarbyne complex, 1 (ca. 1 min). The solution was evaporated to dryness under reduced pressure, and the residue was redissolved in a minimum amount of CH_2Cl_2. This solution was chromatographed on a 1 x 30 cm column of Florisil. The yellow band was eluted with a 1:2 mixture of CH_2Cl_2/hexane, concentrated under vacuum, and diluted with hexane. Upon cooling to -20°C, air-stable, rusty-brown crystals of [HB(pz)$_3$](CO)$_3$WI, 8, resulted (0.22 mg, 10%). Anal. Calcd for $C_{12}H_{10}BIN_6O_3W$: C, 23.71; H, 1.66; N, 13.83. Found: C, 23.51; H, 1.78; N, 13.73. EIMS (20 eV): m/e 580(M^+-CO), 552(M^+-2CO), 524(M^+-3CO).

{[HB(pz)$_3$](CO)$_2$W[η^2-CH(SMe)(PPh$_3$)]}CF$_3$SO$_3$, 9 A CH_2Cl_2 (30 mL) solution containing {HB(pz)$_3$(CO)$_2$W[η^2-CH(SMe)]}CF$_3$SO$_3$, **6**, (0.19 g, 0.29 mmol) and PPh_3 (76 mg, 0.29 mmol) was allowed to stir for 15 min. The brownish solution was then evaporated to dryness, and the resulting residue was washed with hexane. Crystallization of this residue from CH_2Cl_2/Et_2O at -20°C afforded air-stable brown crystals of 9 (0.24 g, 90%). Anal. Calcd for $C_{32}H_{29}BF_3N_6O_5PS_2W\cdot(CH_2Cl_2)_{0.3}$:

C, 40.85; H, 3.14; N, 8.85. Found: C, 40.80; H, 3.52; N, 8.93. ^{31}P NMR ($CDCl_3$): δ 38.68 (J_{WP} = 10.49 Hz). MS(FAB): m/e 775 (parent cation), 719 (parent cation - 2CO). Molar conductivity (CH_2Cl_2): $\Lambda_M = 41.08\ \Omega^{-1}\ cm^2\ mol^{-1}$ at 10^{-3} (1:1 electrolyte).[42]

{[HB(pz)$_3$](CO)$_2$W[η^2-CH(SMe)(PEt$_3$)]}CF$_3$SO$_3$, **10** This complex was prepared by a route analogous to that used for **9**. After the reaction mixture of 6 (0.19 g, 0.29 mmol) and PEt_3 (64 μL, 0.44 mmol) in 30 mL of CH_2Cl_2 was stirred for 1h, the solvent was removed under vacuum. The resulting solid was washed with hexane and ether and then recrystallized from CH_2Cl_2/Et_2O at -20°C to give air-stable brown crystals of **10** (0.21 g, 92%). Anal. Calcd for $C_{20}H_{29}BF_3N_6O_5PS_2W\cdot(CH_2Cl_2)_{0.3}$: C, 30.26; H, 3.70; N, 10.43. Found: C, 29.99; H, 3.91; N, 10.39. MS(FAB): m/e 631 (parent cation), 575 (parent cation - 2CO), 560 (parent cation - 2CO - Me). The presence of CH_2Cl_2 in crystals of 7 and 8 was also established by their ^1H NMR spectra.

Reaction of {HB(pz)$_3$(CO)$_2$W[η^2-CH(SMe)(PEt$_3$)]}CF$_3$SO$_3$, **10**, with NaH

A 5 mL CH_2Cl_2 solution containing **10** (16 mg, 0.02 mmol) and dry NaH (1 mg, 0.04 mmol) was allowed to stir for 24 h. [HB(pz)$_3$](CO)$_2$W(≡CSMe), 1 , in about 90% yield, was identified by the IR spectrum of the reaction mixture. A small amount of [HB(pz)$_3$](CO)(PEt$_3$)$\overline{\text{W(C(O)C}}$SMe), 2, was also obtained from the further reaction of **1** and the liberated PEt_3.

$\{[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)(P(OMe)_3)]\}CF_3SO_3$, **11** In a procedure similar to the one used for **9**, $P(OMe)_3$ (14 μL, 0.12 mmol) was allowed to react with $\{[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]\}CF_3SO_3$, **6**, (52 mg, 0.079 mmol) in CH_2Cl_2 (7 mL) for 10 min. Purification as for **10** afforded **11** (55 mg, 90%). However, the product was not sufficiently stable to be obtained pure for elemental analysis. MS(FAB): m/e 637 (parent cation), 622 (parent cation - Me), 566 (parent cation - Me - 2CO).

$\{[HB(pz)_3](CO)_2W(\eta^2\text{-}CH(SMe)(PPh_2H)]\}CF_3SO_3$, **12** The method used to prepare **9** was also used for this complex. PPh_2H (20 μL, 0.12 mmol) was injected into a 5 mL CH_2Cl_2 solution of **6** (56 mg, 0.085 mmol). After the reaction had proceeded for 20 min, the same workup as in the synthesis of **9** was employed. The product was recrystallized from CH_2Cl_2/Et_2O, giving **12** (66 mg, 92%) as an air-stable brown solid. It was characterized by its IR and ^1H NMR spectra (Table 1 and II). MS(FAB): m/e 699 (parent cation), 643 (parent cation - 2CO), 513 (parent cation - PPh_2H).

$[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)(PPh_2)]$, **13** A CH_2Cl_2 solution (10 mL) of **12** (0.11 g, 0.13 mmol) was treated with NEt_3 (18 μL, 0.13 mmol). After the solution was allowed to stir for 30 min, a reddish-yellow solution was obtained. It was diluted with 30 mL of hexane; slow evaporation under reduced pressure furnished a white precipitate ($Et_3NH^+CF_3SO_3^-$). After the salt was removed by filtration through Celite, the solution was evaporated to dryness. The resulting solid was recrystallized from CH_2Cl_2/hexane at -20°C to give air-stable orange crystals of 13 (82 mg, 90%). Microscopic crystals were found which were suitable for X-ray analysis. Anal. Calcd for $C_{25}H_{24}BN_6O_2$-PSW: C, 43.00; H, 3.46; N, 12.04. Found: C, 42.92; H, 3.66; N, 11.79. $^{31}P(CDCl_3)$: δ10.52. EIMS (20 ev): m/e 698 (M^+), 642 (M^+-2CO), 513 (M^+-PPh_2), 457 (M^+-2CO-PPh_2).

Crystal Data and Data Collection [HB(pz)$_3$](CO)$_2$W[η^2-CH(SMe)(PPh_2)], 13: mol wt. 698.20 g/mol, triclinic $P\bar{1}$, a = 11.548(14), b = 16.148(7), c = 7.682(5)Å, α = 101.67(6), β = 99.06(7), γ = 70.49(5)°, V = 1316.1(18) Å^3, Z = 2, ρ_{calc} = 1.761 g/cm^3, μ = 48.09 cm^{-1} (MoKα, λ = 0.71069Å, monochromated by a graphite crystal).

An orange crystal of the title compound of approximate dimensions 0.2 x 0.2 x 0.15 mm, was wedged into a Lindeman glass capillary and aligned on an automated four-circle diffractometer (DATEX) designed and built at the Ames Laboratory. Four preliminary ω-oscillation photographs were taken at various ϕ positions, and the coordinates of 12 independent reflections were input to the automatic indexing procedure ALICE.[43] The resulting triclinic reduced cell and reduced cell scalars indicated no transformation to a higher symmetry group. Inspection of the axial ω-oscillation photographs confirmed the triclinic cell noted above and also indicated that the crystal was an aggregate of at least three slightly misoriented grains of various sizes. Other crystals tried earlier showed a similar tendency even to a greater extent. The orientation matrix for the data collection was determined by centering the strongest in each cluster of reflections, *i.e.*, focusing only the largest grain. Unit cell parameters were obtained by a least-squares fit to 2θ values of 12 independent high angle reflections on the diffractometer mentioned above.

All data within a sphere of $2\theta \leq 45°$ (4125 reflections) were measured using an ω-stepscan procedure. The intensity data were corrected for Lorentz and polarization effects. Empirical absorption corrections were made using ϕ-scan data for a reflection at $\chi \cong 90°$. Equivalent data were averaged ($R_{ave} = 4.9\%$), yielding 2015 independent observed reflections ($F \geq 3\sigma_F$).

Structural Solution and Refinement[44] The position of the tungsten atom was obtained from analysis of a Patterson function assuming the centrosymmetric space group. The remaining atoms were found by successive structure factor and electron density map calculations. The positions of the hydrogen atoms were calculated assuming ideal geometries with C-H and B-H bond distances set at 1.00Å and 1.26Å, respectively. The positional and anisotropic thermal parameters for most of the nonhydrogen atoms were refined by block/full-matrix least-squares procedures, minimizing the function $\Sigma\omega(|F_o|-|F_c|)^2$, where $\omega = 1/\sigma_F{}^2$, to $R = \Sigma||F_o|-|F_c||/\Sigma|F_o| = 0.088$ and $Rw = [\Sigma\omega(|F_o|-|F_c|)^2/\Sigma\omega|F_o|^2]^{1/2} = 0.108$. Six nonhydrogen atoms, C(1), C(2), C(3), C(4), C(53), and N(21), were refined isotropically because of difficulties in assigning physically meaningful anisotropic temperature factors. In the last stage of the refinement, 15 reflections were noticed to have large discrepancies in $||F_o| - |F_c||$ and excluded due apparently to the poor crystal quality.

The final atomic parameters are listed in Table IV, while selected bond lengths and bond angles are listed in Tables V and VI, respectively.

REFERENCES

1. (a) Pickering, R. A.; Jacobson, R. A.; Angelici, R. J. J. Am. Chem. Soc. 1981, 103, 817. (b) McCormick, F. B.; Angelici, R. J. Inorg. Chem. 1981, 20, 1118. (c) McCormick, F. B.; Angelici, R. J. Inorg. Chem. 1981, 20, 111. (d) Yu, Y. S.; Angelici, R. J. Organometallics 1983, 2, 1018. (e) Yu, Y. S.; Angelici, R. J. Organometallics 1983, 2, 1583. (f) Steinmetz, A. L.; Hershberger, S. A.; Angelici, R. J. Organometallics 1984, 3, 461. (g) Singh, M. M.; Angelici, R. J. Inorg. Chem. 1984, 23, 2691. (h) Matachek, J. R.; Angelici, R. J.; Schugart, K. A.; Haller, K. J.; Fenske, R. F. Organometallics 1984, 3, 1038.
2. (a) Dombek, B. D.; Angelici, R. J. Inorg. Chem. 1976, 15, 2397. (b) Greaves, W. W.; Angelici, R. J.; Helland, B. J.; Klima, R.; Jacobson, R. A. J. Am. Chem. Soc. 1979, 101, 7618. (c) Quick, M. H.; Angelici, R. J. Inorg. Chem. 1981, 20, 1123. (d) Schroeder, N.; Richardson, J. W., Jr.; Wang, S. L.; Jacobson, R. J.; Angelici, R. J. Organometallics 1985, 4, 1226.
3. Greaves, W. W.; Angelici, R. J. Inorg. Chem. 1981, 20, 2983.
4. Kim, H. P.; Kim, S.; Jacobson, R. A.; Angelici, R. J. Organometallics 1984, 3, 1124.
5. Desmond, T.; Lalor, F. J.; Ferguson, G.; Parvez, M. J. Chem. Soc., Chem. Commun. 1984, 75.
6. Clark, G. R.; Collins, T. J.; Marsden, K.; Roper, W. R. J. Organomet. Chem. 1983, 259, 215.

7. For example, see the following: (a) Fischer, E. O.; Clough, R. L.; Besl, G.; Kreissl, F. R. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 543. (b) Fischer, E. O.; Stückler, P.; Kreissl, F. R. *J. Organomet. Chem.* **1977**, *129*, 197. (c) Fischer, E. O.; Meineke, E. W.; Kreissl, F. R. *Chem. Ber.* **1977**, *110*, 1140. (d) Fischer, E. O.; Frank, A. *Chem. Ber.* **1978**, *111*, 3740. (e) Fischer, E. O.; Schambeck, W. *J. Organomet. Chem.* **1980**, *201*, 311. (f) Kostić, N. M.; Fenske, R. F. *J. Am. Chem. Soc.* **1981**, *103*, 4677. (g) Kostić, N. M.; Fenske, R. F. *Organometallics* **1982**, *1*, 489. (h) Fischer, E. O.; Wittman, D.; Himmelreich, D.; Schubert, U.; Ackermann, K. *Chem. Ber.* **1982**, *115*, 3141. (i) Fischer, H. In "Transition metal Carbene Complexes"; Dötz, K. H.; Fischer, H.; Hoffman, P.; Kreissl, F. R.; Schubert, U.; Weiss, K., Eds.; Verlag Chemie: Weinheim, 1983; pp 18-23. (j) Fischer, H.; Motsch, A.; Markl, R.; Ackermann, K. *Organometallics* **1985**, *4*, 726.

8. (a) Fischer, E. O.; Ruhs, A.; Kreissl, F. R. *Chem. Ber.* **1977**, *110*, 805. (b) Kreissl, F. R.; Stückler, P.; Meineke, E. W. *Chem Ber.* **1977**, *110*, 3040. (c) Kreissl, F. R.; Uedelhoren, W.; Kreis, G. *Chem. Ber.* **1978**, *111*, 3283.

9. (a) Uedelhoven, W.; Eberl, K.; Kreissl, F. R. *Chem. Ber.* **1979**, *112*, 3376. (b) Kreissl, F. R.; Sieber, W. J.; Alt, H. G. *Chem. Ber.* **1984**, *117*, 2527. (c) Birdwhistell, K. R.; Tonker, T. L.; Templeton, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 4474. (d) Brower,

D. C.; Birdwhistell, K. R.; Templeton, J. L. Organometallics 1986, 5, 94.

10. Kreissl, F. R.; Sieber, W. J.; Wolfgruber, M. Z. Naturforsch., B: Anorg. Chem., Org. Chem. 1983, 38B, 1419.
11. Churchill, M. R.; Wasserman, H. J.; Holmes, S. J.; Schrock, R. R. Organometallics 1982, 1, 766.
12. Kreissl, F. R.; Sieber, W. J.; Hoffman, P.; Riede, J.; Wolfgurber, M. Organometallics 1985, 4, 788.
13. Templeton, J. L.; Ward, B. C. J. Am. Chem. Soc. 1980, 102, 3288.
14. Winston, P. B.; Nieter, S. J. N.; Templeton, J. L. Organometallics 1983, 2, 167.
15. Kim, H. P.; Angelici, R. J. the following paper.
16. Clark, G. R.; Marsden, K.; Roper, W. R.; Wright, L. J. J. Am. Chem. Soc. 1980, 102, 6570.
17. Kreissl, F. R.; Sieber, W. J.; Wolfgruber, M. J. Organomet. Chem. 1984, 270, C45.
18. Curtis, M. D.; Shiu, K.-B. Inorg. Chem. 1985, 24, 1213.
19. McCormick, F. B.; Gladysz, J. A. J. Organomet. Chem. 1981, 218, C57.
20. Collins, T. J.; Roper, W. R. J. Organomet. Chem. 1978, 159, 73.
21. Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. "Spectrometric Identification of Organic Compounds", 4th ed.; Wiley: New York, 1981; pp 272-3.
22. Nelson, G. O.; Brookhart, M. J. Am. Chem. Soc. 1977, 99, 6099.

23. Holmes, S. J.; Clark, D. N.; Turner, H. W.; Schrock, R. R. J. Am. Chem. Soc. **1982**, 104, 6322.

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

25. (a) Brown, F. J. Prog. Inorg. Chem. **1980**, 27, 1. (b) Casey, C. P. Reactive Intermediates **1981**, 2, 135; Reactive Intermediates **1985**, 3, 109.

26. (a) Bodnar, T.; Cutler, A. R. 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.

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

28. (a) In "Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis"; J. G. Verkade; L. D. Quin, eds.; Verlag Chemie: 1986, in press, Chapter 11. (b) Albrand, J. P.; Gagnaire, D.; Robert, J. B. J. Chem. Soc., Chem. Commun. **1968**, 1469.

29. Tolman, C. A. Chem. Rev. **1977**, 77, 313.

30. Reference 21, p 199.

31. (a) Grim, S. O.; Wheatland, D. A.; McFarlane, W. J. Am. Chem. Soc. **1967**, 89, 5573. (b) Grim, S. O.; Wheatland, D. A. Inorg. Chem. **1969**, 8, 1716.

32. (a) Mainz, V. V.; Anderson, R. A. Organometallics **1984**, 3, 675 and references therein. (b) Gibson, V. C.; Grebenik, P. D.; Green, M. L. H. J. Chem. Soc., Chem. Commun. **1983**, 1101. (c) Etienne, M.; Choukroun, R.; Basso-Bert, M.; Dahan, F.; Gervais,

D. Nouv. J. Chim. 1984, 8, 531. (d) Schore, N. E.; Young, S. J.; Olmstead, M. M. Organometallics 1983, 2, 1769. (e) Fischer, E. O.; Reitmeier, R. Z. Naturforsch., B: Anorg. Chem., Org. Chem. 1983, 38B, 582.

33. Kreissl, H.; Fischer, E. O.; Kreiter, C. G.; Fischer, H. Chem. Ber. 1973, 106, 1262.

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

35. Churchill, M. R.; Youngs, W. J. Inorg. Chem. 1979, 18, 2454.

36. Forder, R. A.; Gale, G. D.; Prout, K. Acta Cryst. 1975, B31, 307.

37. Kojima, T.; Nachikawa, T. J. J. Phys. Soc. Jpn. 1957, 12, 680.

38. (a) Pierce, L.; Hayashi, M. J. J. Chem. Phys. 1961, 35, 479. (b) Sijima, T.; Tsuchiya, S.; Kimura, M. Bull. Chem. Soc. Jpn. 1977, 50, 2564.

39. Pelizzi, C.; Pelizzi, G. Acta Cryst. 1979, B35, 1785.

40. Least squares plane of W-S-C(3): -1.659x - 10.624y + 6.570z + 0.599 = 0; W .000; S .000; C(3) .000; P-1.436; C(4) 1.722.

41. Gansow, O. A.; Burke, A. R.; LaMar, G. N. J. Chem. Soc., Chem. Commun. 1972, 456.

42. (a) (n-Bu)$_4$NBF$_4$, Molar Conductivity (CH$_2$Cl$_2$): Λ_M = 28.69 Ω^{-1} cm^2 mol^{-1} at 10^{-3} M. (b) Muetterties, E. L.; Alegrant, C. W. J. Am. Chem. Soc. 1972, 94, 6386.

43. Jacobson, R. A. J. Appl. Cryst. 1976, 9, 115.

44. Calculations were carried out on a VAX 11/780 computer. Structure factor calculations and least squares refinements were

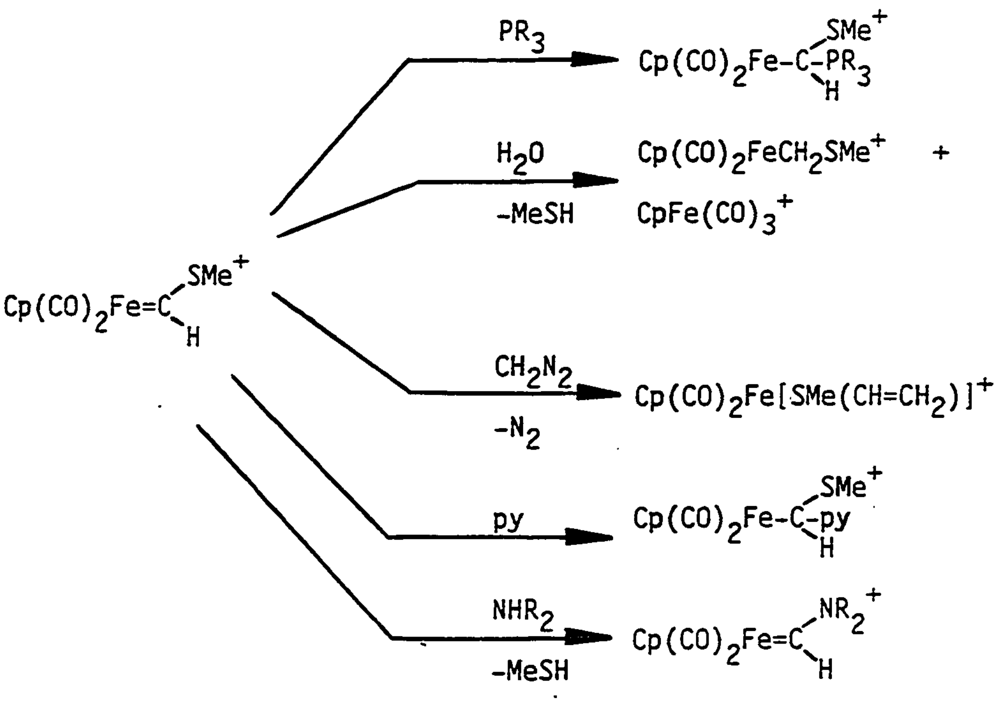
done using the block matrix/full matrix program ALLS (R. L. Lapp and R. A. Jacobson, U.S. Department of Energy Report IS-4708, Iowa State University, Ames, Iowa, 1979), Fourier series calculations were done using the program FOUR (D. R. Powell and R. A. Jacobson, U.S. Department of Energy Report IS-4737, Iowa State University, Ames, Iowa, 1980), and for molecular drawings the program ORTEP (C. K. Johnson, U.S. Atomic Energy Commission Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn, 1970) was used. An empirical absorption correction was carried out using diffractometer ϕ-scan data and the program ABSN (B. A. Karcher, Ph.D. Dissertation, Iowa State University, 1981).

SECTION III. REACTIONS OF THE THIOCARBENE COMPLEX $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]^+$ WITH SULFUR, CARBON, AND NITROGEN NUCLEOPHILES

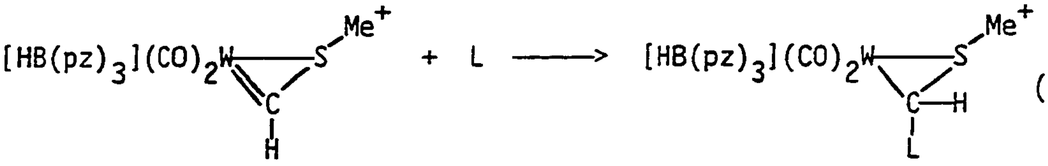
INTRODUCTION

The thiocarbene complex $Cp(CO)_2Fe[=CH(SMe)]^+$, Cp = η^5-C_5H_5, reacts with a variety of nucleophiles to give a range of products (Scheme I).[1,2] All of the reactions are presumed to proceed by

Scheme I



initial attack at the carbene carbon atom. In recent papers,[3,4] we reported the preparation of the thiocarbene complex $[HB(pz)_3](CO)_2W$-$[\eta^2$-$CH(SMe)]^+$, 2, in which the [CH(SMe)] carbene ligand is coordinated to the W via both the carbene C and S atoms. Only one other η^2-thiocarbene complex $\{(PPh_3)_2[CN(4$-$C_6H_4CH_3)](Cl)Os[\eta^2$-$C(SMe)(4$-$C_6H_4CH_3)]\}ClO_4$[5] has been reported. Very little is known about the reactivities of either of these complexes. Like the simple η^1 carbene complex $Cp(CO)_2Fe[CH(SMe)]^+$,[1,2] 2 reacts with phosphorus donors, L (PPh_3, PEt_3, PPh_2H, $P(OMe)_3$), to give carbene adducts $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)L]^+$, in which both the C and S atoms remain coordinated to the W (eq 1).[4] The phosphonium proton


(1)

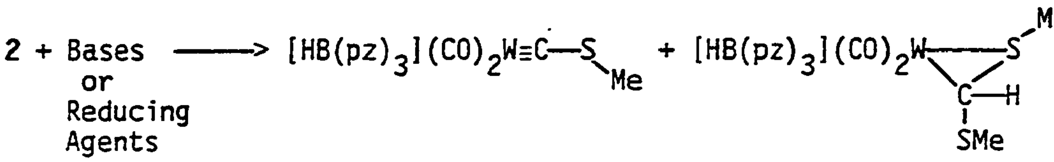
2

L = PPh_3, PEt_3, PPh_2H, $P(OMe)_3$

in $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)(PPh_2H)]^+$ is removed by NEt_3 to give $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)(PPh_2)]$, whose structure was established by an X-ray diffraction study.[4] In the present report, we describe reactions of **2** with compounds having nucleophilic S, C, and N atoms.

RESULTS AND DISCUSSION

Reactions of {[HB(pz)$_3$](CO)$_2$W[η^2-CH(SMe)]}CF$_3$SO$_3$, 2, with Bases or Reducing Agents Most of the reactions of 2 described in the preceding paper involve nucleophilic addition to the carbene carbon atom. Nucleophiles are also bases. In fact, there are some Lewis bases that give no product resulting from nucleophilic addition. Thus, the bases, dry NaH, NaBH$_4$, NaOMe, NaOPh, PPNSH, NaSCH$_2$Ph, NaSePh, LiCH$_3$, NEt$_3$, K$_2$CO$_3$, NH$_2$NH$_2$, NHMeNH$_2$, and NHMeNHMe, react with 2 to give [HB(pz)$_3$](CO)$_2$W(≡CSMe), 1 (10-20%), and [HB(pz)$_3$](CO)$_2$W[η^2-CH(SMe)$_2$], 3 (5-40%), according to eq 2. The highest yield of 1 (90%) is found when 2 is reacted with NaSCH$_2$Ph. As



(2)

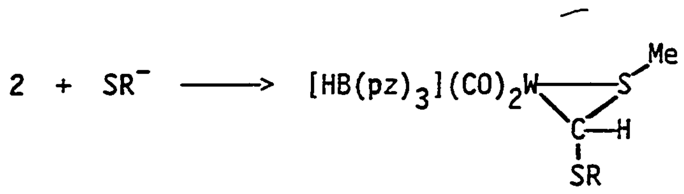
1 3

discussed in the following sections, 1 and 3 are side products of reactions with other nucleophiles; presumably they are formed according to eq 2.

The reducing agent, sodium naphthalenide, also produces 1 (10%) and 3 (40%). Thus, it is possible that some or all of the nucleophiles noted above behave as reducing agents, although no attempt was made to identify oxidation products. There is no evidence for CO-containing products other than **1** and **3**. While the mechanism of reaction 2 is unclear, transfer of MeS$^-$ from **2** to form **3** must be involved and is presumably related to the demonstrated good leaving group ability of MeS$^-$ in thiocarbene complexes.[2,6]

Reactions of $\{[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]\}CF_3SO_3$, with SR$^-$

Complex **2** reacts readily with mercaptides to give the corresponding air-stable bis(organothio)methyl complexes **3-5** in about 90% yield (eq 3). The reaction appears to be a simple nucleophilic addition of the



(3)

R

3, Me

4, Et

5, i-propyl

mercaptide to the carbene carbon.[7] Similar reactions of $Cp(CO)_2Fe[CH(SMe)]^{+2}$ and $Cp(CO)_2Fe[C(SMe)_2]^{+6a}$ have also been reported. The thiocarbyne compound **1** is also obtained from reaction 3 in 5% yield. With SCH_2Ph^- and SH$^-$, only the base reaction (eq 2) occurs yielding **1** and **3**.

IR, ^1H, and ^{13}C NMR spectra of **3** (Tables I-III) show two sets of peaks, suggesting the presence of two isomers. The isomers could not

Table I. IR Data for the Complexes in CH_2Cl_2 Solvent

Complex	IR ν(CO), cm^{-1}
$[HB(pz)_3](CO)_2W(\equiv CSMe)$, (1)	1980 s, 1888 s
$\{[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]\}CF_3SO_3$, (2)	2067 m, 1996 s
$[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)_2]$, [3(A)]	1937 s, 1832 s[a]
[3(B)]	1957 w, 1821 w[a]
$[HB(pz)_3](CO)_2\overline{W[CH(S}Me)(SEt)]$, [4(A)]	1936 s, 1833 s[a]
[4(B)]	1958 w, 1820 w[a]
$[HB(pz)_3](CO)_2\overline{W\{CH(S}Me)[SCH(Me)_2]\}$, [5(A)]	1935 s, 1832 s[a]
[5(B)]	1958 w, 1820 w[a]
$\{[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SEt)]\}CF_3SO_3$, (6)	2065 m, 1990 s
$[HB(pz)_3](CO)_2W\{\eta^2\text{-}CH(SMe)[CH(CO_2Me)_2]\}$, (7)	1932 s, 1805 s, 1747 m, 1730 m
$\{[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)(NC_5H_5)]\}CF_3SO_3$, (8)	1957 s, 1823 s
$\{[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)(4\text{-}NC_5H_4Me)]\}CF_3SO_3$, (9)	1955 s, 1819 s
$\{[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)[4\text{-}NC_5H_4N(Me)_2]]\}CF_3SO_3$, (10)	1953 s, 1813 s
$[HB(pz)_3](CO)_2W(\equiv CNMe_2)$, (11)	1941 s, 1837 s
$[HB(pz)_3](CO)_2W(\equiv CNEt_2)$, (12)	1938 s, 1831 s
$[HB(pz)_3](CO)_2W(\equiv CNHMe)$, (13)[b,c]	1943 s, 1837 s

---

[a] Hexane solvent.

[b] ν(CN):2125 cm^{-1}.

[c] $[HB(pz)_3](CO)_2(H)W(CNR)$ tautomer present; see text.

Table I (Continued)

Complex	IR $\nu(CO)$, cm^{-1}
$[HB(pz)_3](CO)_2W(\equiv CNHEt)$, (14)[d,c]	1943 s, 1841 s
$[HB(pz)_3](CO)_2W(\equiv CNHCH_2CH_2OH)$, (15)[e,c]	1942 s, 1844 s
$[HB(pz)_3](CO)_2W[\equiv CNHCH(Me)_2]$, (16)[f,c]	1943 s, 1843 s
$[HB(pz)_3](CO)_2W[\equiv CNHC(Me)_3]$, (17)[g,c]	1945 s, 1840 s
$[HB(pz)_3](CO)_2W[\equiv CNH(4\text{-}C_6H_4Me)]$, (18)	1956 s, 1860 s
$[HB(pz)_3](CO)_2W(\equiv CNH_2)$, (19)	1950 s, 1855 s

[d] $\nu(CN)$:2118 cm^{-1}.

[e] $\nu(CN)$:2090 cm^{-1}.

[f] $\nu(CN)$:2100 cm^{-1}.

[g] $\nu(CN)$:2100 cm^{-1}.

Table II. ^1H NMR Data for the Complexes in CD_2Cl_2 solvent at Room Temperature [a]

Complex	H3 of pz	H4 of pz	H5 of pz	other
1[b]	7.91(br)	6.23(br)	7.65(br)	2.69(SMe)
2	8.07 (d,J=2.21) 7.94 (t,J=2.90)[c]	6.50 (t,J=2.37)[c] 6.47 (t,J=2.35)[c]	7.91 (d,J=2.36) 7.83 (d,J=2.14) 7.81 (d,J=2.07)	12.78 (s, J_{WH}=19.83, CH), 2.37(SMe)
3(A)	8.10 (d,J=1.58)	6.24 (t,J=2.20)[c]	7.65 (d,J=2.37)	4.89 (s,J_{WH}=3.46, CH), 2.47(CSMe), 2.35(WSMe)
3(B)	not resolved	6.26(br)	7.69 (d,J=2.17)	5.39(CH), 2.59(CSMe), 1.57(WSMe)
4(A)	8.13(br)	6.23 (t,J=2.23)[c]	7.65 (d,J=1.98)	4.82(s,J_{WH}=3.91, CH), 2.71 (q,J=7.42, SCH_2), 2.44(SMe), 1.38(t,J=7.44, Me)

4(B)	not resolved	6.25 (t,J=2.02)[c]	7.68 (d,J=2.15)	5.43(CH), 2.97(q,J=7.36, SCH_2), 1.57(SMe), 1.15 (t,J=7.57, Me)
5(A)	8.16(br)	6.23 (t,J=2.19)[c]	7.65 (d,J=2.08)	4.71(s,J_{WH}=4.39, WCH), 2.97(h,J=6.76, CH), 2.40(SMe), 1.41 (d,J=6.56, Me), 1.36 (d,J=6.81, Me)
5(B)	not resolved	6.25 (t,J=2.36)[c]	7.69 (d,J=2.14)	5.40(WCH), 3.23 (h,J=6.84, CH), 1.57(SMe), 1.49(d,J=6.65, Me), 1.43(d,J=6.50, Me)
6	8.07 (d,J=2.22) 7.94 (t,J=2.29)[c]	6.49 (t,J=2.39)[c] 6.47 (t,J=2.19)[c]	7.91 (d,J=2.30), 7.81 (d,J=2.11), 7.78 (d,J=2.06)	12.81(s,J_{WH}=19.77, CH), (2.68(m, SCH_2), 1.21 (t,J=7.54, Me)

---

[a] Chemical shifts in δ and coupling constants in Hz.

[b] $CDCl_3$ solvent.

[c] Due to overlapping d of d.

Table II (Continued)

Complex	H3 of pz	H4 of pz	H5 of pz	other
7	8.22(br)	6.26(br)	7.69(br)	4.87(d,J=10.36, WCH), [3.80, 3.79, OMe], 3.74(d,J=10.35, CH), 1.52(SMe)
9[d]	8.22(br)	6.43(br)	7.93(br)	8.62(d,J=6.74,H2 and H6 of pic), 7.92(d,J=6.62, H3 and H5 of pic), 7.58(CH), 2.67(Me), 1.96(SMe)
10[d]	8.25(br)	6.41(br)	7.91(br)	8.11(d,J=7.76, H2 and H6 of py), 7.01(d,J=7.75, H3 and H5 of py), 7.34(CH), 3.31(NMe_2), 1.84 (SMe)
11	7.79 (d,J=1.74)	6.20 (t,J=1.99)[c]	7.67 (d,J=2.03)	3.21(NMe_2)
12	7.80 (d,J=1.57)	6.20 (t,J=2.08)[c]	7.67 (d,J=1.97)	3.42(q,J=7.23, NCH_2), 1.37(t,J=7.28, Me)
13[b]	7.80 (d,J=1.79)	6.16 (t,J=2.20)[c]	7.64 (d,J=1.85)	3.15(d,J=4.27 NMe), [3.60(NMe), -2.36(WH)][e]

14	7.79 (d,J=0.94)	6.19 (t,J=1.81)^c	7.69 (d,J=1.59)	3.44(q,J=7.35,NCH$_2$), 1.88(t,J=7.36,Me), [3.15(q,J=7.11, NCH$_2$), 1.84(t,J=7.36, Me), -2.36(WH)]^e
15	7.81(br)	6.20 (t,J=1.63)^c	7.71 (d,J=2.04)	3.80(t,J=5.08,OCH$_2$), 3.50(t,J=5.22, NCH$_2$), [4.07(t,J=5.08, OCH$_2$), 3.46(t,J=5.00, NCH$_2$), -2.28(WH)]^e
16	7.80 (d,J=1.15)	6.20 (t,J=1.99)^c	7.67 (d,J=2.22)	4.18(h,J=6.43,CH), 1.30(d,J=6.53,Me), [4.55(h,J=6.43,CH), 1.40(d,J=6.86,Me), -2.36(WH)]^e
17	7.81 (d,J=1.49)	6.19 (t,J=2.21)^c	7.67 (d,J=2.11)	1.37(Me), [1.47(Me), -2.34(WH)]^e

---

[d] CD_3NO_2 solvent.

[e] Values in square brackets correspond to the $[HB(pz)_3](CO)_2(H)W(CNR)$ tautomer; other values are for $[HB(pz)_3](CO)_2W(\equiv CNHR)$ tautomer.

Table II (Continued)

Complex	H3 of pz	H4 of pz	H5 of pz	other
18	7.86 (d,J=2.23)	6.21 (t,J=2.16)[c]	7.69 (d,J=2.14)	7.23(d,J=8.34,Ph), 7.14(d,J=8.35, Ph), 2.32(Me)
19	7.98 (d,J=0.94)	6.27 (t,J=2.08)[c]	7.67 (d,J=2.39)	

Table III. ^{13}C NMR Data for the Complexes in CD_2Cl_2 Solvent at Room Temperature[a]

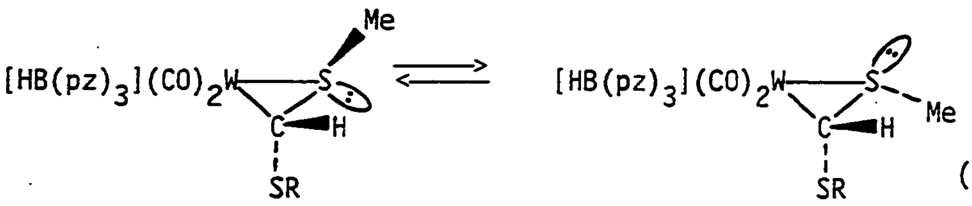
Complex	CO	C3 of pz	C4 of pz	C5 of pz	Other
1[b]	224.7	144.9	105.7	135.2	264.4 (W-CS), 17.4(SMe)
2	212.98 212.55	147.21 146.31 145.95	106.06 108.48 108.33	138.76 138.51 138.27	227.95 (CH), 28.40 (SMe)
3(A)	232.58 (J_{WC}=151.67) 230.66 (J_{WC}=151.67)	144.81	105.89	135.38	61.79 (J_{W-C}=32.17, CH) 22.44 (SMe), 20.44 (WSMe)
3(B)	236.04, 220.02	not resolved	106.05	135.59	71.69 (CH), 26.20 (SMe), 21.35 (WSMe)
12[b]	225.83	144.46	105.03	134.39	254.61 (WC), 44.66 (NCH_2), 14.46 (Me)

[a] Chemical shifts in ppm and coupling constants in Hz.

[b] $CDCl_3$ solvent.

be separated by column chromatography or recrystallization. The relative ratio of the major isomer (A) to minor isomer (B) was obtained by integration of the methine protons (CH). The ratio of these two isomers of 3 depends on the solvent and temperature; the ratio is 14:1 at 25°C in C_6D_6, 7:1 at 25°C in $CDCl_3$, 6:1 at 25°C in CD_2Cl_2, 5:1 at 25°C in $(CD_3)_2CO$, 4:1 at 25°C in CD_3NO_2, and 3:1 at 50°, 70°, 85° in CD_3NO_2 solution.

The isomers presumably result from inversion at the coordinated sulfur atom (eq 4). The major isomer (A) of 3 probably has the structure in which the sulfur donor (SR, R = Me) adds to the carbene carbon on the side opposite the Me on the sulfur atom, which is also on the side opposite the bulky $[HB(pz)_3]$ group; this structure would be essentially the same as that of $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)(PPh_2)]$ (Figure 1),[4] except SMe replaces PPh_2. Inversion of the sulfur atom has been observed in numerous sulfide (e.g., R_2S and $RSCH_2CH_2SR$) complexes;[8a] the coalescence temperatures for pyramidal inversion in the complexes $W(CO)_5(PhCH(Me)SCH_3)$[8b] and $(CO)_4W(PhCH_2SCH_2CH_2SCH_2Ph)$[8c] are -76.5°C ($\Delta G^{\ddagger}$ = 28.0 kJ/mol) and 27°C ($\Delta G^{\ddagger}$ = 51.5 kJ/mole), respec-



(4)

A B

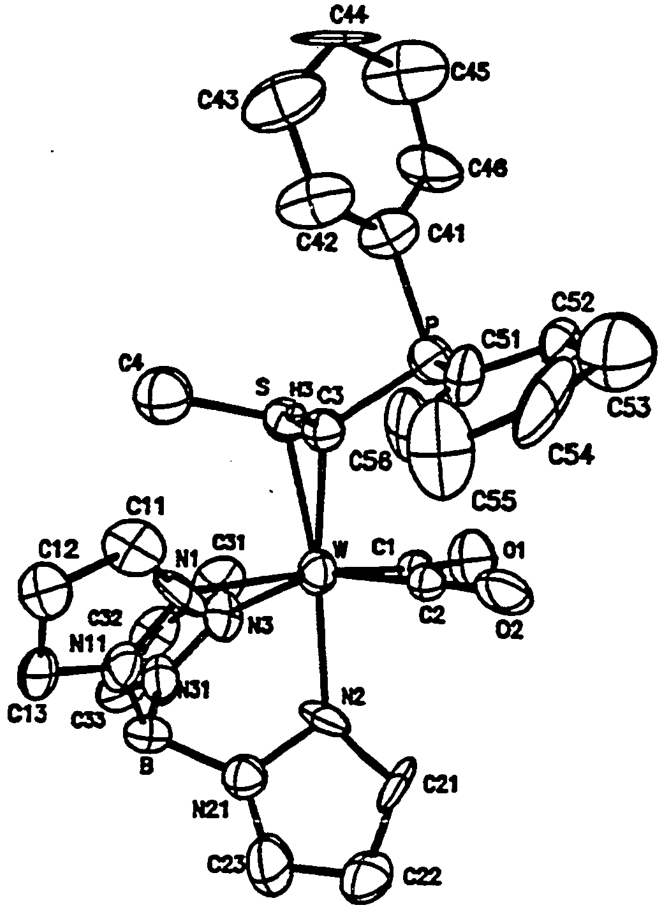


Figure 1. ORTEP plot of $[HB(pz)_3](CO)_2W(\eta^2\text{-}CH(SMe)(PPh_2)]$

tively. The SMe peaks of the two isomers of **3** do not coalesce up to 85°C in CD_3NO_2. The high coalescence temperature for **3** may be caused by the three-membered ring which has been found to increase the inversion barrier in trans-$PdCl_2(\overline{SCMe_2C}Me_2)_2$.[8d] Two non-interconverting isomers were also observed for the 3-membered ring complex, $(dppe)(CO)_3\overline{W[CH(SR)(S}R)]^+$;[8e] these were likewise ascribed to E and Z isomers resulting from inversion at the coordinated sulfur atom. IR and ^1H NMR spectra (Tables I and II) reveal the presence of two isomers for **4** and **5** also. The relative ratios of the two isomers of **4** and **5** at 25°C in CD_2Cl_2 are 8:1 and 3:1, respectively.

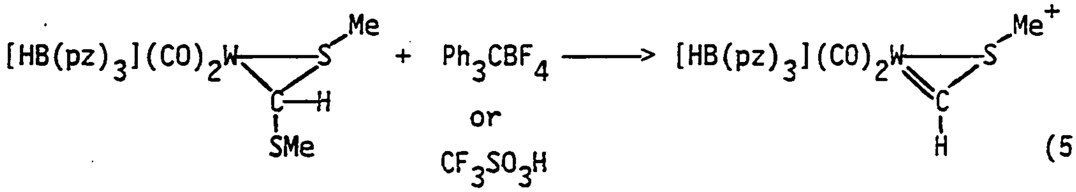
Although the isomers of **3-5** may result from inversion at the sulfur, it is not possible to discount the possibility that they arise from rotation of the whole η^2-CH(SMe)(SR) unit around an axis from the W to the center of the η^2-C-S bond. A similar three-membered ring (η^2-CH_2PMe_2) rotation was proposed in $(PMe_3)_4WH(\eta^2\text{-}CH_2PMe_2)$.[9]

A third isomerization process to be considered is that involving cleavage of the C-S bond in the η^2-CH(SMe)(SR) ligand to give the carbene-mercaptide complex W[=CH(SR)](SMe), which could interchange the positions of the H and SR groups by rotation around the W[=CH(SR)] carbene bond. In another context, Headford and Roper[10] has proposed such a C-X (X = O, Se, Te) cleavage. Although this type of isomerization cannot be dismissed, it seems less likely than the other two possibilities.

The SMe carbene compound **2**, $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]^+$, reacts with SEt^- to give $[HB(pz)_3](CO)_2\overline{W[CH(S}Me)(SEt)]$, **4**; no $[HB(pz)_3](CO)_2$-

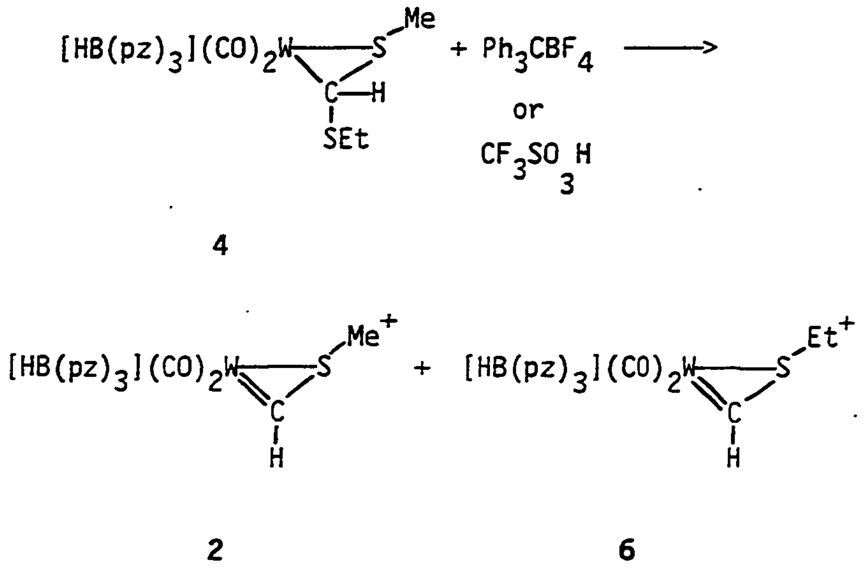
$\overline{\text{W[CH(SMe)(S}}\text{Et)]}$ is detected in this reaction. Likewise, the SEt carbene compound **6**, $[HB(pz)_3](CO)_2W[\eta^2\text{-CH(SEt)}]^+$, reacts with SMe^- to give $[HB(pz)_3](CO)_2\overline{\text{W[CH(SMe)(S}}\text{Et)]}$;[11] no **4** is detected in this reaction. No interconversion of **4** to $[HB(pz)_3](CO)_2\overline{\text{W[CH(SMe)(S}}\text{Et)]}$ or vice versa occurs at room temperature. Therefore, scrambling of the bound (SMe) and dangling sulfide (SEt) groups does not occur in **4** and probably also not in **3** and **5**. Other results also suggest the W-S bond is inert; **3** does not react with CO (1 atm, 30°C, 30 min, CH_2Cl_2) nor PEt_3 (25°, 1 h, CH_2Cl_2). An attempt to cleave the W-S bond in **2** with CO (80 psig, 40°C, 22 h) was also not successful. Thus, the W-S bond is robust in **3** and **2**.

One of the MeS^- groups is removed quantitatively from $[HB(pz)_3](CO)_2W[\eta^2\text{-CH(SMe)}_2]$ upon treatment with Ph_3CBF_4 (eq 5). The reaction of **3** with CF_3SO_3H also yields **2** (eq 5), but in only 20% yield; decomposition is also observed. Compound **4** reacts with Ph_3CBF_4 to form both the thiomethyl **2** (30%) and thioethyl **6** carbene (70%)



3 **2** (5)

products (eq 6). The reaction of **4** with CF_3SO_3H also gives **2** (10%) and **6** (10%) (eq 6). The identity of **6** was established by comparing its ^1H NMR spectrum with an authentic sample of this compound

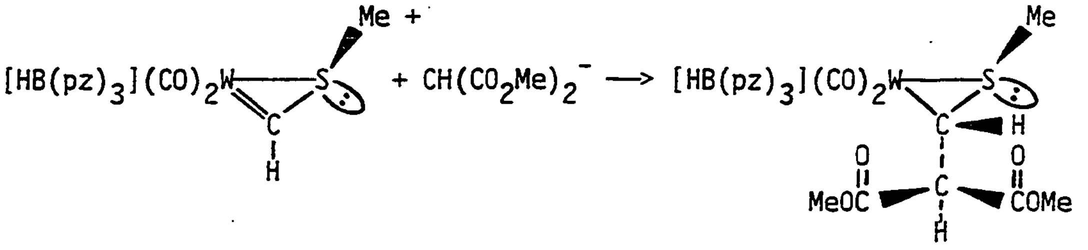


(6)

prepared by the reaction of $[HB(pz)_3](CO)_2W(\equiv CSEt)$ with CF_3SO_3H. Although it might seem that the uncoordinated SEt would be abstracted by Ph_3CBF_4 or CF_3SO_3H more readily than the bound sulfide (SMe), the product distribution establishes that the SMe group is removed preferentially. As noted above, **4** does not isomerize to $[HB(pz)_3](CO)_2\overline{W[CH(SMe)(S}Et)]$ at these temperatures: thus, this isomerization of **4** cannot account for the formation of both *2* and **6**. It is possible that both the coordinated (SMe) and uncoordinated (SEt) groups are abstracted at about the same rates or Ph_3C^+ and H^+ oxidize **4** to give a radical intermediate which interconverts the SMe and SEt groups. There is, however, no direct evidence for either of these mechanistic possibilities.

Reaction of $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]^+$, 2, with $CH(CO_2Me)_2^-$

Carbanions are known to add to carbene carbon centers.[12] Similarly, the η^2-carbene of 2 reacts with the carbanion, $CH(CO_2Me)_2^-$, to produce the air-stable malonate adduct 7 in 92% yield (eq 7). The more



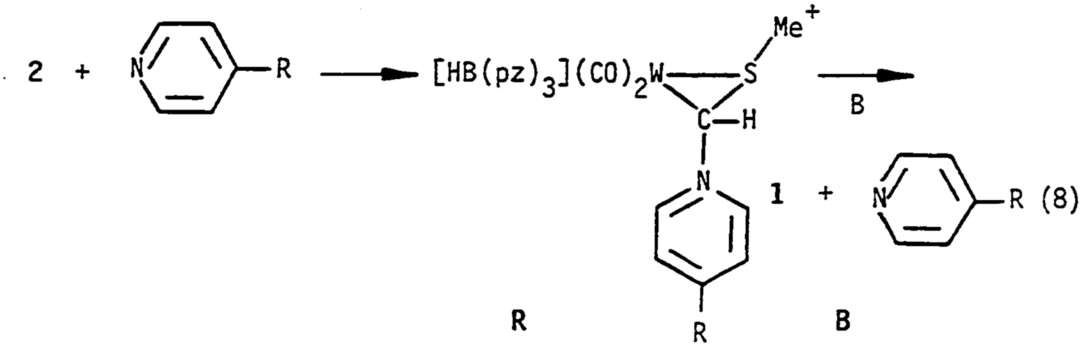
2 7 (7)

nucleophilic MeLi, however, does not form an adduct but, gives the typical base reaction (eq 2) products 1 and 3. In the ^1H NMR spectrum of 7, the two Me groups of the malonate are nonequivalent (δ 3.80, 3.79) due to the chiral center at the methine carbon.[13]
The large coupling constant ($^3J_{HH}$ = 10.35 Hz) of the two methine hydrogens suggests that the H atoms are anti to each other;[14] this configuration minimizes repulsion between the two CO_2Me groups and the CO ligands.

Reactions of $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]^+$, 2, with Pyridines

Pyridine (py) is known to form carbene adducts such as $Cp(CO)_2Fe[CH(SMe)(py)]^{+2}$ and $Cp(NO)(PPh_3)Re[CH_2(py)]^+$.[15] In contrast to these adduct-forming reactions, 2 reacts at room temperature with tertiary amines such as Et_3N to give 1 (10%) and 3 (30%) according to eq 2. Even though there is no spectroscopic evidence for it, 3 probably results from initial formation of the adduct $[HB(pz)_3]$-$(CO)_2W[\eta^2$-$CH(SMe)(NEt_3)]^+$ followed by transfer of a MeS^- group to another carbene ligand, as suggested for related reactions of iron thiocarbene complexes with tertiary amines.[2,6]

The η^2-carbene compound, **2**, combines with pyridine ($pK_a = 5.2$) at room temperature (eq 8) to form an unstable adduct, **8**, which was only characterized by its IR spectrum (Table I). Even with excess pyridine (4.2 equivalents), the reaction is not complete after 2 h of stirring. The pyridine adduct **8** decomposes (eq 8) to the thiocarbyne compound **1** within 2 h at room temperature in solution in the presence of pyridine (4.2 equivalents).



	R	B
8	H	py
9	Me	4-picoline
10	NMe_2	NaOMe

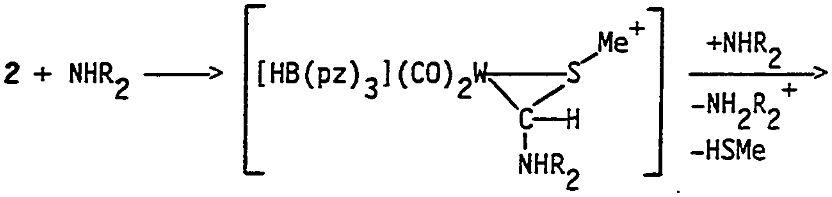
Compound 2 also forms an adduct **9** with 4-picoline ($pK_a = 6.1$) according to eq 8. The 4-picoline complex **9** undergoes transformation to the thiocarbyne compound **1** in the presence of 4-picoline (1 equivalent) in CD_2Cl_2 solution within 5 h. The reaction of 2 with 4-

dimethylaminopyridine (pK_a = 9.7) gives an air-stable isolable adduct **10** (eq 8) in 90% yield. No conversion of **10** to **1** in the presence of excess 4-dimethylaminopyridine (10 equivalents) is observed. However, the reaction of **10** with 4 equivalents of NaOMe (pK_a = 16) gives **1** within 5 min. Thus, the conversion of **8**, **9**, and **10** to **1** (eq 8) requires a base, presumably to remove the methine proton. The strength of the base required appears to depend on the donor ability of the pyridine in the adduct. For pyridine and 4-picoline which are relatively weak donors, excess pyridine or 4-picoline are sufficiently strong bases to cause the conversion of **8** and **9** to **1**. For the adduct, **10**, of the much more basic 4-dimethylaminopyridine, the much stronger base NaOMe is required. Related to the conversion of **8**, **9**, and **10** to **1** is the similar deprotonation of the methine hydrogen in $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)(PEt_3)]^+$ with NaH to give **1** in 90% yield.[4] In all of these reactions, it appears that deprotonation of the adduct gives an unstable intermediate which loses the pyridine or phosphine and rearranges to carbyne **1**. In contrast to these deprotonations, base reactions of **2** with NaH or NaOMe (eq 2) produce both **1** (10%) and **3** (40% and 30%, respectively). The formation of **3** in the latter reaction is apparently blocked in the deprotonation reactions of the adducts of **2**.

The IR spectra of **8** - **10** show two strong ν(CO) absorptions (**8**; 1957, 1823 cm^{-1}) close to those observed for the adducts $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)L]^+$ (e.g., L = $P(OMe)_3$; 1955, 1826 cm^{-1}).[4] However, the methine proton resonance of **10** at δ 7.34 is considerably more deshielded than the corresponding signal in the adducts $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)L]$ (e.g., L = $P(OMe)_3$; δ 5.45).[4]

Reaction of $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]^+$, 2, with NHR_2

Secondary amines (HNR_2) replace[6b,16] a thioalkoxy group in $Cp(CO)_2Fe[C(SMe)_2]^+$ to give aminothiocarbenes $Cp(CO)_2Fe[C(SMe)(NR_2)]^+$ and MeSH. Similar reactions of other η^1-thiocarbene complexes have also been reported.[2,17] In contrast, 2 reacts with NHR_2 (R = Me, Et) to produce air-stable aminocarbyne compounds in about 30% yield (eq 9). Compound 3 is also obtained as a side product in this reaction.



(9)

$[HB(pz)_3](CO)_2W\equiv C\text{-}NR_2$

	R
11,	Me
12,	Et

The amine, NHR_2, presumably initially gives the adduct (eq 9), then deprotonation of NHR_2 takes place with another mole of NHR_2. Finally, ring-opening with elimination of HSMe yields the aminocarbyne product. The average $\nu(CO)$ frequency of $[HB(pz)_3](CO)_2W(\equiv CNEt_2)$ (1956, 1864 cm^{-1}/hexane) is 9 cm^{-1} lower than that of the corresponding Cp complex $Cp(CO)_2W(\equiv CNEt_2)$ (1958, 1880 cm^{-1}/hexane),[18] suggesting that $HB(pz)_3$ is a better electron donor than Cp, as observed previously.[19] The chemical shift of the carbyne carbon atom (δ 254.61 ppm) in the ^{13}C NMR spectrum of **12** is similar to those in $[HB(pz)_3](CO)_2W(\equiv CSMe)$ (δ 264.4)[20] and $Br(CO)_4W(\equiv CNEt_2)$ (δ 235.62).[21] The structures of **11** and **12** (Figure 2) suggest that two of the pyrazolyl groups are different than the other. Indeed, ^1H NMR spectra of **11** and **12** at -63°C show two identical and one different pyrazolyl group (Figure 3). As the temperature is increased, the pyrazolyl signals broaden and coalesce and are equivalent at room temperature (Table II). These spectral changes suggest the $HB(pz)_3$ ligand is rotating or the two CO and the carbyne groups are rapidly exchanging positions at room temperature. Rapid rotation of the $HB(pz)_3$ group has been proposed in $[HB(pz)_3](CO)_2Mo(\eta^3\text{-}CH_2CRCH_2)$, R = Me or Ph;[22] the limiting high- and low-temperature spectra (R=Me) were obtained at +50 and -40°C, respectively.

Varying degrees of $HB(pz)_3$ ligand fluxionality have been observed in other compounds in our studies. The energy barrier for rotation of the $HB(pz)_3$ ligand around the B-H axis is found to be sensitive to the electronic environment at the metal center. Most cationic complexes such as $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]^+$, $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)(PPh_3)]^+$,[4] and $[HB(pz)_3](CO)(PEt_3)W(MeOC\equiv CSMe)^{+}$[4] show inequivalence of all three pyrazolyl rings in ^1H NMR spectra taken at room temperature, suggesting that rotation is slow on the NMR time scale. Whereas, electron-richer neutral complexes such as **3**, **11**, **12**, $[HB(pz)_3](CO)_3WX$, (X = Cl, I),[4] and $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)(PPh_2)]$[4]

show equivalence of all three pyrazolyl rings in ^1H NMR spectra taken at room temperature. The intermediate stage, broadening of the pyrazolyl ring peaks is observed in the room temperature ^1H NMR spectra of $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)(PEt_3)]^+$,[4] **9**, and **10**.

The above variations of $HB(pz)_3$ fluxionality may, in general, reflect the Lewis acidity of the metal center. In cases where the metal has the highest acidity, the N donors of the $HB(pz)_3$ ligand are bound more strongly, and fluxionality is not observed at room temperature. In more electron-rich complexes, which generally have a zero charge and the metal is not as acidic, the pyrazolyl groups are not bound to the metal as strongly and fluxionality is observed. These trends are illustrated by **2** and its adducts: (1) $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]^+$ and $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)(PPh_3)]^+$ are not fluxional at room temperature; (2) $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)(PEt_3)]^+$ and $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)(4\text{-}NC_5H_4R)]^+$, R = Me, NMe_2, have broadened pyrazolyl protons indicating some fluxionality; (3) $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)_2]$ and $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)(PPh_2)]$ are completely fluxional at room temperature (25°C). The importance of the electron-richness of the metal is supported by a correlation of the average $\nu(CO)$ values of **2** and its adducts with the fluxionality of the $HB(pz)_3$ ligand. Carbene compound **2** and the PPh_3 adduct show relatively high average $\nu(CO)$ values at 2032 cm^{-1} and 1894 cm^{-1}, respectively. The intermediate complexes have lower average $\nu(CO)$ values at 1887 cm^{-1} (4-picoline complex, **9**), and 1883 cm^{-1} (4-

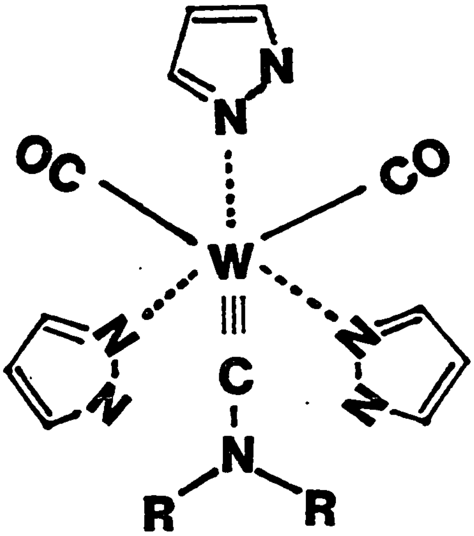


Figure 2. Proposed structure of $[HB(pz)_3](CO)_2W(\equiv CNR_2)$, R = Me (**11**) or Et (**12**). H and B atoms are omitted

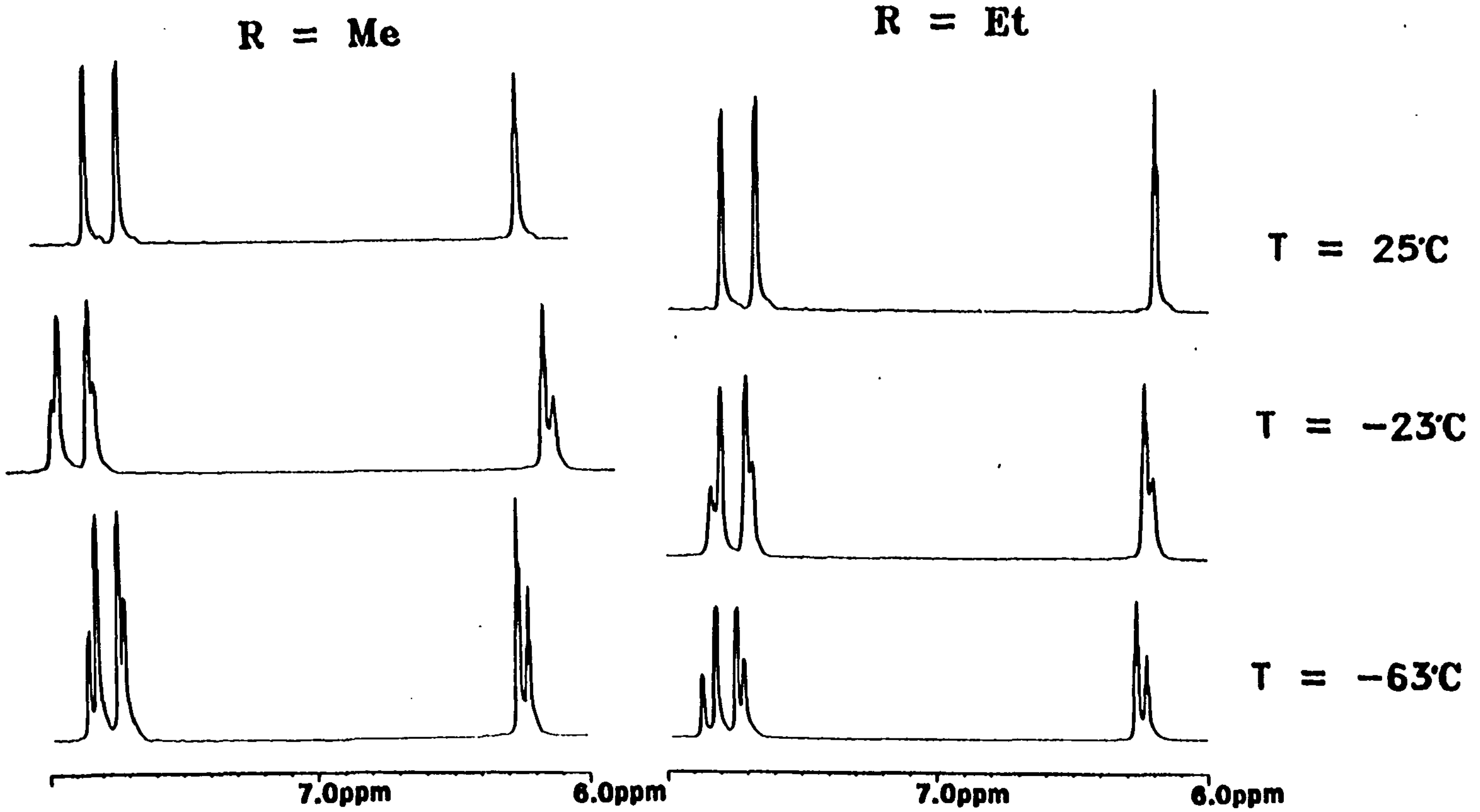
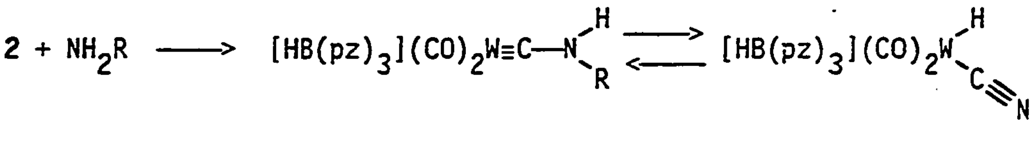


Figure 3. Temperature dependent ^{1}H NMR spectra of $[HB(pz)_3](CO)_2W(\equiv CNR_2)$, R = Me (**11**) or Et (**12**), in CD_2Cl_2 solvent

$NC_5H_4NMe_2$ compound, **10**), 1882 cm^{-1} (PEt_3 complex). The neutral SMe, **3**, and PPh_2 compounds show the lowest average ν(CO) values at 1872 cm^{-1} and 1864 cm^{-1}, respectively.

Reactions of $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]^+$, **2**, with Primary Amines and NH_3 Like secondary amines, a variety of primary amines react with **2** at room temperature to produce the corresponding aminocarbyne compounds in 25-35% yield (eq 10). The usual side products, **1** (0-5%)[23] and **3** (30-50%), are also formed. The aminocarbyne compounds **13-19** are so air-sensitive, that they


(10)

13-17

	R
13,	Me
14,	Et
15,	CH_2CH_2OH
16,	$CH(Me)_2$
17,	$C(Me)_3$
18,	$4\text{-}C_6H_4Me$
19,	H

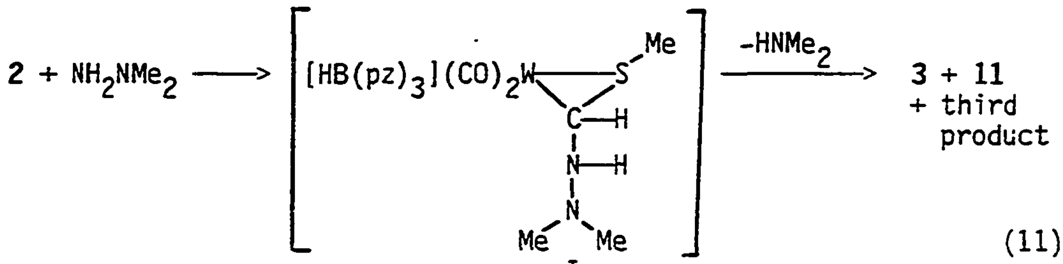
were not isolated; however, they were characterized by the similarity of their IR and ^1H NMR spectra (Tables I and II) to those of **11** and **12**. The $\nu(CO)$ frequencies of **13-19** are very close to those of **11** and **12**. However, IR spectra of **13-17** show an extra weak band in the $\nu(CN)$ region (2090-2125 cm^{-1}) suggesting the presence of a CNR ligand. In the ^1H NMR spectra of **13-17**, there are peaks for the aminocarbyne compound along with additional peaks for another type of R group and a metal hydride (<u>ca</u>. δ -2.3 ppm). The additional peaks in the IR and ^1H NMR spectra of **13-17** indicate the carbyne complexes, $[HB(pz)_3](CO)_2W(\equiv CNHR)$, are in equilibrium with the isocyanide-hydride tautomer, $[HB(pz)_3](CO)_2(H)W(CNR)$. In contrast, the absence of $\nu(CN)$ and a hydride resonance in the spectra of compounds **18** and **19** shows that these compounds exist only in the aminocarbyne structure. It thus appears that the electron-rich alkyl R groups in **13-17** promote formation of the isocyanide-hydride tautomer. The relative ratio of the aminocarbyne to isocyanide-hydride tautomer is obtained by integration of the peaks for the R groups. The ratio of the amount of the aminocarbyne to the hydride compound is dependent on the solvent but not on the bulkiness of R; the ratio is 4:1 in $CDCl_3$ for **13**, 5:1 in CD_2Cl_2 for **14**, 4:1 in CD_2Cl_2 for **15**, 4:1 in CD_2Cl_2 for **16**, 4:1 in CD_2Cl_2 for **17**, and 9:1 in CD_3NO_2 for **17**. It is interesting that the related Cp complex, $Cp(CO)_2Mo(H)(C\equiv NMe)$ shows no evidence for the carbyne tautomer $Cp(CO)_2Mo\equiv C\text{-}NHMe$.[24] Perhaps, it is the preference of $HB(pz)_3$ complexes for 6, rather than 7 coordination,[19] or the greater electron-donor ability of $HB(pz)_3$ which favors the aminocarbyne structure in compounds **13-19**, as contrasted with the Cp system.

Compounds **13-19** slowly decompose in solution even under an N_2 atmosphere. During the decomposition of **17**, the relative amounts of the aminocarbyne and hydride tautomers remain constant at 4:1 during a 52 h period, during which time 50% of **17** had decomposed. Thus, the equilibrium process between the tautomers is faster than the rate of decomposition.

To our knowledge, the tautomerism described here is the only example of an equilibrium between aminocarbyne and isocyanide-hydride isomers, although Pombeiro and Richards[25] has suggested $Mo(dppe)_2(CNR)(\equiv CNHR)^+$ as an intermediate in the protonation of $Mo(dppe)_2(CNR)_2$ to give $Mo(dppe)_2(CNR)_2(H)^+$.

The secondary aminocarbyne $[HB(pz)_3](CO)_2W(\equiv CNMe_2)$, **11**, does not undergo methyl transfer analogous to the above tautomerism to give $[HB(pz)_3](CO)_2(Me)W(CNMe)$ even at 70°C for 5 h; there is no reaction.

Reaction of 2 with the hydrazine NH_2NMe_2 (eq 11) produces 3 (28%), **11** (28%), and a third product which is not sufficiently stable



I

(11)

to be isolated. This reaction possibly involves NH_2NMe_2 addition to the carbene carbon and deprotonation with another mole of NH_2NMe_2 to form intermediate I. Migration of the proton from N-H to NMe_2 and fission of the N-N bond liberates free $NHMe_2$. The $NHMe_2$ could react with **2** to form the observed **3** and **11**. According to eq 11, the third product would then have the chemical formula $[HB(pz)_3](CO)_2$-W[CH(SMe)N], which is consistent with the IR and ^1H NMR spectra reported in the Experimental section. This same compound (10%) is also formed in the reaction of **2** and NaN_3 which also gives **1** (10%) and **3** (10%). It is not unreasonable that N_3^- addition to the carbene carbon of **2** followed by loss of N_2 would also lead to the composition $[HB(pz)_3](CO)_2W[CH(SMe)N]$ for the third product; unfortunately, this compound could not be characterized further.

With other hydrazines, NH_2NH_2, $NHMeNH_2$, NHMeNHMe, only the base reaction (eq 2) occurs, yielding **1** (2-20%) and **3** (40%). A reaction related to (11) is that of asy-dimethylhydrazine with $(CO)_5Cr$-[C(OMe)(Me)] to give the likely intermediate $(CO)_5Cr[C(NHNMe_2)(Me)]$, which rearranges to $(CO)_5Cr(NCMe)$ with loss of $HNMe_2$.[26] Similarly, $CpFe(CO)_3^+$ reacts with NH_2NMe_2 or N_3^- to give an intermediate adduct, which rearranges to $CpFe(CO)_2(NCO)$.[27]

EXPERIMENTAL SECTION

General Procedures Methods and instrumentation were the same as described in the previous paper.[4] THF was distilled from Na-benzophenone under N_2. All amines, except Me_2NH, $MeNH_2$, $EtNH_2$, $H_2NCH_2CH_2OH$, and NH_3, were stored over KOH overnight and distilled from KOH. Ethanolamine ($H_2NCH_2CH_2OH$) was purified by vacuum distillation (5 mm, 40°C) before use. The complexes $NaCpFe(CO)_2$,[28] $PPNCo(CO)_4$,[29] $[HB(pz)_3](CO)_2W(\equiv CSMe)$,[20] and $[HB(pz)_3](CO)_2W(\equiv CSEt)$,[20] were prepared using the previously described procedures. Synthesis of the complex $\{[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]\}CF_3SO_3$, 2, was described previously.[3,4] $NaC_{10}H_8$,[30] NaSePh,[31] $NaCH(CO_2Me)_2$,[32] PPNSH,[33] and NHMeNHMe[27] were synthesized according to the literature references given. 4-Dimethylaminopyridine was recrystallized from CH_2Cl_2/hexane. All other chemicals were commerical products of the highest purity available and were used as received.

Reaction of $\{[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]\}CF_3SO_3$, 2, with Bases

The thiocarbene compound, 2, (47 mg, 0.071 mmol) in 10 mL of CH_2Cl_2 was treated with $KOCMe_3$ (49 mg, 0.44 mmol). The reaction mixture was allowed to stir for 3 h. The solution was diluted with 30 mL of hexane; slow evaporation under reduced pressure furnished a white precipitate (KO_3SCF_3). After the salt was removed by filtration through Celite, the solution was evaporated to dryness.
The resulting residue was redissolved in a minimum amount of CH_2Cl_2.

This solution was chromatographed on a 1 x 30 cm silica gel column. $[HB(pz)_3](CO)_2W(\equiv CSMe)$, 1, was eluted first with a 1:2 mixture of CH_2Cl_2/hexane, yield 40%. Then, a yellow band was eluted with a 2:1 mixture of CH_2Cl_2/hexane. The yellow eluate was evaporated to dryness, and the resulting solid was recrystallized from CH_2Cl_2/hexane at -20°C to give air-stable, orange crystals of 3 (8 mg, 20%), whose spectra were identical to those of an authentic sample (see below).

In a procedure similar to the one above, the reactions of 2 (*ca.* 30 mg, 0.045 mmol) in 5-10 mL of solvent with 1-2 equivalents of various bases gave the following yields of 1 and 3, respectively, in parentheses: dry NaH (10, 40%), $NaBH_4$ (10, 40%), NaOMe (10, 30%), NaOPh (15, 30%), PPNSH (10, 5%), NaSePh (5, 40%), $LiCH_3$ (10, 10%)/THF, NEt_3 (10, 30%), K_2CO_3 (10, 30%), NH_2NH_2 (2, 40%), $NHMeNH_2$ (20, 40%), and NHMeNHMe (20, 40%)/CH_2Cl_2.

Reaction of $\{[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]\}CF_3SO_3$, 2, with Reducing Agents A THF solution of 2 (38 mg, 0.057 mmol) with $NaC_{10}H_8$ (1.5 mL, 0.039 M) was stirred at 0°C for 10 min. According to the IR spectrum of the reaction mixture, the products included 1 (10%) and 3 (40%).

In a procedure similar to the one above, 2 (*ca.* 30 mg, 0.045 mmol) was reacted in 5-10 mL of THF with 1-1.6 equivalents of various reducing agents to give 1 and 3 in yields noted in parentheses: $NaCpFe(CO)_2$ (10, 40%), $PPNCo(CO)_4$ (10, 30%).

$[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)_2]$, 3 Dry NaH (42 mg, 1.8 mmol) was dissolved in 30 mL of THF, and CH_3SH was slowly bubbled through the solution for 1 h. The solution was stirred for another 6 h, until H_2 production ceased. Then, THF was decanted from the white NaSMe precipitate, which was washed with THF and dried under vacuum. A THF solution (15 mL) containing $\{[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]\}CF_3SO_3$, 2, (60 mg, 0.091 mmol) and NaSMe (8 mg, 0.11 mmol) was allowed to stir for 15 min. Purification as for the $KOCMe_3$ reaction mixture described earlier afforded 1 (5%) and air-stable, orange crystals of 3 (46 mg, 90%). Anal. Calcd for $C_{14}H_{17}BN_6O_2S_2W$: C, 30.02; H, 3.06; N, 15.00; S, 11.45. Found: C, 29.81; H, 3.13; N, 14.83; S, 11.45. EIMS (18 eV): m/e 560(M^+), 512(M^+-HSMe), 504(M^+-2CO), 473(M^+-2CO-2Me-H). IR (CH_2Cl_2): 1925 s, 1802 s cm^{-1}.

$[HB(pz)_3](CO)_2\overline{W[CH(S}Me)(SEt)]$, 4 A 40 mL solution of THF containing dry NaH (1.24 g, 0.052 mol) and ethanethiol (8.1 mL, 0.11 mol) was stirred for 8 h, yielding a white precipitate (NaSEt). The THF was decanted from the precipitate, and the resulting solid was washed with THF and dried under vacuum. In a procedure similar to the one used for the synthesis of 3, a mixture of $\{[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]\}CF_3SO_3$, 2, (66 mg, 0.10 mmol) and NaSEt (9 mg, 0.11 mmol) in 40 mL of THF was stirred for 30 min. Then, hexane (20 mL) was added to the reaction mixture, and the solution volume was reduced giving a white precipitate (NaO_3SCF_3). After the salt was removed by filtration through Celite, the solution was evaporated to dryness. The residue was redissolved in a minimum amount of CH_2Cl_2. This solution was chromatographed on a 1 x 30 cm silica gel column. $[HB(pz)_3](CO)_2W(\equiv CSMe)$, **1**, eluted first with a 1:2 mixture of CH_2Cl_2/hexane; yield 5%. Then, a yellow band which eluted with a 2:1 mixture of CH_2Cl_2/hexane was evaporated to give a solid. Air-stable, orange crystals of $[HB(pz)_3](CO)_2\overline{W[CH(S}Me)(SEt)]$, **4**, were obtained by recrystallizing the solid from CH_2Cl_2/hexane at -20°C (54 mg, 94%). The thioethyl compound, **4**, was always contaminated with some $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)_2]$, **3** (5%); neither recrystallization nor repeated chromatography separated the two completely. EIMS (18 ev): m/e 574(M^+), 518(M^+-2CO), 489(M^+-2CO-Et).

$[HB(pz)_3](CO)_2\overline{W\{CH(S}Me)[SCH(Me)_2]\}$, **5** A mixture of dry NaH (0.42 g, 0.018 mol) and $(CH_3)_2CHSH$ (4.7 mL, 0.050 mol) in 20 mL of THF was stirred for 8 h, yielding a white precipitate ($NaSCH(Me)_2$). The THF was decanted from the white solid, which was washed with THF and dried under vacuum. Analogous to the preparation of **3**, a THF solution (5 mL) containing **2** (21 mg, 0.032 mmol) and $NaSCH(CH_3)_2$ (4 mg, 0.041 mmol) was stirred for 15 min. Purification as for **4** afforded **1** (5%) and air-stable, orange crystals of **5** (17 mg, 90%). The product, **5**, was always contaminated with **3** (5%). EIMS(18 ev): m/e 588 (M^+), 532 (M^+-2CO), 489 (M^+-2CO-$CH(Me)_2$).

Reaction of $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)_2]$, **3**, with CPh_3BF_4

Into a 4 mL CH_2Cl_2 solution of **3** (15 mg, 0.027 mmol) was added Ph_3CBF_4 (12 mg, 0.036 mmol) at 0°C. After the solution was warmed to room temperature, it was stirred for 30 min. The solvent was removed under vacuum, and the resulting residue was washed with diethyl ether and hexane. The thiomethylcarbene compound, **2**, was obtained in essentially quantitative yield.

Reaction of $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)_2]$, **3**, with CF_3SO_3H A 0.4 mL CD_2Cl_2 solution of 3 (20 mg, 0.036 mmol) was placed in an NMR tube. Upon addition of CF_3SO_3H (3.2 μL, 0.036 mmol) to the solution, the color changed to violet. The IR and ^1H NMR spectra of the reaction mixture showed that the thiomethylcarbene compound, **2**, was produced in 20% yield.

$\{[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SEt)]\}CF_3SO_3$, **6** In a procedure similar to the one used for the preparation of **2**, addition of CF_3SO_3H (10 μL, 0.11 mmol) to a solution of $[HB(pz)_3](CO)_2W(\equiv CSEt)$ (60 mg, 0.11 mmol) in 6 mL of CH_2Cl_2 at 0°C produced an immediate color change from orange to the violet color of product **6**. After the solvent was removed under vacuum, the resulting solid was washed several times with hexane and diethyl ether. Air-stable violet crystals of **6** were obtained by recrystallizing the solid from CH_2Cl_2/Et_2O at -20°C in essentially quantitative yield. Anal. Calcd. for $C_{15}H_{16}BF_3N_6O_5S_2W$: C, 26.64; H, 2.39; N, 12.43. Found: C, 26.39; H, 2.52; N, 12.15. MS(FAB): m/e 527 (M^+), 458 (M^+-2CO-CH), 429 (M^+-2CO-CH-Et).

$[HB(pz)_3](CO)_2W\{[\eta^2\text{-}CH(SMe)[CH(CO_2Me)_2]\}$, **7** A solution of 2 (88 mg, 0.13 mmol) and $NaCH(CO_2Me)_2$ (1.0 mL, 0.13 M) in 5 mL of THF was allowed to stir for 15 min. The solvent was removed under vacuum, and the residue was redissolved in a minimum amount of CH_2Cl_2. This solution was chromatographed on a 1 x 30 cm column of silica gel with a 1:5 mixture of hexane/CH_2Cl_2; a single yellow band was collected. The eluate was concentrated, diluted with hexane, and cooled to -20°C. Air-stable, yellow crystals of **7** resulted (77 mg, 92%). Anal. Calcd. for $C_{18}H_{21}BN_6O_6SW$: C, 33.56; H, 3.29; N, 13.05. Found: C, 33.64; H, 3.54; N, 12.98. EIMS (18 ev): m/e 644 (M^+), 616 (M^+-CO), 588 (M^+-2CO), 573 (M^+-2CO-Me).

{[HB(pz)$_3$](CO)$_2$W[η^2-CH(SMe)(4-NC$_5$H$_4$Me)]}CF$_3$SO$_3$, **9** A 0.4 mL CD_2Cl_2 solution of **2** (13 mg, 0.020 mmol) was placed in an NMR tube. The solution was degassed and purged with N_2. Upon addition of 4-picoline (3.7 μL, 0.038 mmol), the color of the solution changed to dark red to give complete conversion of **2** to **9**. After ^1H NMR spectra of the reaction mixture were taken, the solvent was removed under vacuum and the resulting residue was washed with ether. Air-stable maroon crystals of **9** were obtained by recrystallizing the solid from CH_2Cl_2/Et_2O at -20°C (12 mg, 80%). The product **9** decomposed in the presence of NC_5H_4Me (1 equivalent) in CD_2Cl_2 solution within 5 h to give **1** (10%). MS(FAB): m/e 606 (parent cation), 559 (parent cation-SMe), 513 (parent cation-4-picoline).

{[HB(pz)$_3$](CO)$_2$W[η^2-CH(SMe)(4-NC$_5$H$_4$NMe$_2$)]}CF$_3$SO$_3$, **10** Into a 10 mL CH_2Cl_2 solution of **2** (43 mg, 0.065 mmol) was added 4-dimethylaminopyridine (10 mg, 0.082 mmol). After the reaction mixture was stirred for 10 min, the solvent was removed under vacuum and the resulting residue was washed with ether. Air-stable orange crystals of **10** were obtained by recrystallizing the solid from CH_2Cl_2/Et_2O at -20°C (46 mg, 90%). Anal. Calcd. for $C_{21}H_{24}BF_3N_8O_5S_2W$: C, 32.16; H, 3.08; N, 14.29. Found: C, 31.71; H, 3.33; N, 13.75. MS(FAB): m/e 635 (parent cation), 513 (parent cation-4-dimethyaminopyridine).

Reaction of $\{[HB(pz)_3](CO)_2W[\eta^2-CH(SMe)(4-NC_5H_4NMe_2)]\}CF_3SO_3$, **10**, with NaOMe A 2 mL THF solution containing **10** (15 mg, 0.019 mmol) and NaOMe (4 mg, 0.074 mmol) was allowed to stir for 5 min. Complete conversion of **10** to **1** occurred as indicated by the IR spectrum of the reaction mixture.

$[HB(pz)_3](CO)_2W(\equiv CNMe_2)$, **11** Into a 20 mL CH_2Cl_2 solution of **2** (94 mg, 0.14 mmol) was injected $NHMe_2$ vapor (7 mL, *ca.* 0.28 mmol) using a syringe. After the reaction mixture was stirred for 10 min, it was diluted with 20 mL of hexane; slow evaporation under reduced pressure furnished a white precipitate, $(NMe_2H_2)O_3SCF_3$. After the salt was removed by filtration through Celite, the solution was evaporated to dryness. The residue was redissolved in a minimum amount of CH_2Cl_2 and chromatographed on a 3 x 30 cm silica gel column. $[HB(pz)_3](CO)_2W(\equiv CNMe_2)$, **11**, eluted first with a 5:2 mixture of hexane and CH_2Cl_2. This fraction was evaporated to dryness, and the resulting residue was recrystallized from CH_2Cl_2/hexane, giving **11** (21 mg, 29%) as an air-stable, yellow solid. Anal. Calcd. for $C_{14}H_{16}BN_7O_2W$: C, 33.04; H, 3.17; N, 19.26. Found: C, 32.84; H, 3.20; N, 18.99. EIMS (21 ev): m/e 509 (M^+), 481 (M^+-CO), 453 (M^+-2CO), 438

(M^+-2CO-Me), 397 (M^+-2CO-$CNMe_2$). A second band (orange) was eluted with a 2:1 mixture of CH_2Cl_2/hexane. Evaporation of this fraction and recrystallization of the residue from CH_2Cl_2/hexane gave orange crystals of **3** (24 mg, 31%).

<u>$[HB(pz)_3](CO)_2W(\equiv CNEt_2)$, **12**</u> The method used to prepare **11** was also used for this complex. A 20 mL CH_2Cl_2 solution containing **2** (91 mg, 0.14 mmol) and $NHEt_2$ (22 μL, 0.21 mmol) was stirred for 10 min. The same workup as in the synthesis of **11** was employed to give air-stable yellow crystals of **3** (24 mg, 31%) and **12** (23 mg, 31%). Anal. Calcd. for $C_{16}H_{20}BN_7O_2W$: C, 35.78; H, 3.75; N, 18.26. Found: C, 35.69; H, 3.79; N, 18.07. EIMS (21 ev): m/e 537 (M^+), 509 (M^+-CO), 481 (M^+-2CO), 452 (M^+-2CO-Et), 397 (M^+-2CO-$CNEt_2$).

<u>$[HB(pz)_3](CO)_2W(\equiv CNHMe)$, **13**</u> Into a 5 mL CH_2Cl_2 solution of **2** (35 mg, 0.053 mmol) was injected NH_2Me vapor (12 mL, <u>ca.</u> 0.48 mmol). After the reaction had proceeded for 15 min, hexane (10 mL) was added. The solution volume was reduced giving a white precipitate, $(NH_3Me)CF_3SO_3$. The salt was removed by filtration through Celite, and the solution was evaporated to dryness to give a yellow solid. Compounds **1** (5%), **3** (30%), and $[HB(pz)_3](CO)_2W(\equiv CNHMe)$, **13** (25%), were identified from IR and ^1H NMR spectra of the reaction mixture. The aminocarbyne compound, **13**, was not sufficiently stable to be isolated.

<u>$[HB(pz)_3](CO)_2W[\equiv CNHC(Me)_3]$, **17**</u> A 0.4 mL CD_2Cl_2 solution of **2** (16 mg, 0.024 mmol) was placed in an NMR tube. The solution was degassed and purged with N_2, and $NH_2C(Me)_3$ (2.6 μL, 0.025 mmol) was

injected into the solution yielding a yellow solution. IR and ^{1}H NMR spectra of the reaction mixture showed the presence of **3** (40%) and **17** (35%). The aminocarbyne compound, **17**, was not sufficiently stable to be isolated.

Reaction of $\{[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]\}CF_3SO_3$, **2**, with NH_2NMe_2 A 5 mL CH_2Cl_2 solution containing **2** (46 mg, 0.070 mmol) and NH_2NMe_2 (6.9 μL, 0.091 mmol) was stirred for 5 min, yielding a greenish-yellow solution. It was diluted with 30 mL of hexane; slow evaporation under reduced pressure furnished a white precipitate $NH_2NMe_2 \cdot nCF_3SO_3H$, n = 1 or 2, which was removed by filtration through Celite. The solution was evaporated to dryness, and the resulting residue was redissolved in a minimum amount of CH_2Cl_2. This CH_2Cl_2 solution was chromatographed on a 1 x 30 cm silica gel column. $[HB(pz)_3](CO)_2W(\equiv CNMe_2)$, **11**, (10 mg, 28%) was eluted first with a 5:2 mixture of hexane/CH_2Cl_2. Then an orange band, **3**, (11 mg, 28%) was eluted with a 2:1 mixture of CH_2Cl_2/hexane. A third product (30%) decomposed on the column and could not be isolated. In the reaction mixture, this product had bands in its IR spectrum at 1951 and 1852 cm^{-1} (hexane) and in the ^{1}H NMR (CD_2Cl_2) spectrum at δ 7.78 (d, J=2.61), 7.72 (d, J=1.88), 6.27 (t, J=2.18), 4.72 (s, J_{WH}=4.60), and 2.27 (s).

REFERENCES

1. Yu, Y. S.; Angelici, R. J. Organometallics 1983, 2, 1018.
2. Yu, Y. S.; Angelici, R. J. Organometallics 1983, 2, 1583.
3. Kim, H. P.; Kim, S.; Jacobson, R. A.; Angelici, R. J. Organometallics 1984, 3, 1124.
4. Kim, H. P.; Kim, S.; Jacobson, R. A.; Angelici, R. J. preceding paper.
5. Clark, G. R.; Collins, T. J.; Marsden, K.; Roper, W. R. J. Organomet. Chem. 1983, 259, 215.
6. (a) McCormick, F. B.; Angelici, R. J.; Pickering, R. A.; Wagner, R. E.; Jacobson, R. A. Inorg. Chem. 1981, 20, 4108.
   (b) McCormick, F. B.; Angelici, R. J. Inorg. Chem. 1981, 20, 1118.
7. Brown, F. J. Prog. Inorg. Chem. 1980, 27, 1.
8. (a) Abel, E. W.; Orrell, K. J; Bhargava, S. K. Prog. Inorg. Chem. 1984, 32, 1.
   (b) Eekhof, J. H.; Hogeveen, H.; Kellogg, R. M.; Klei, E. J. Organometal. Chem. 1978, 161, 183.
   (c) Cross, R.; Hunter, G.; Massey, R. C. J. Chem. Soc., Dalton Trans. 1976, 2015.
   (d) Abel, E. W.; Booth, M; Orrell, K. J. Chem. Soc., Dalton Trans. 1979, 1994.
   (e) Schenk, W. A.; Schwietzke, T. Organometallics 1983, 2, 1905.

9. Gibson, V. C.; Graimann, C. E.; Hare, P. M.; Green, M. L. H.; Bandy, J. A.; Grebenik, P. D.; Prout, K. J. Chem. Soc., Dalton Trans. 1985, 2025.

10. Headford, C. E. L.; Roper, W. R. J. Organometal. Chem. 1983, 244, C53.

11. The $[HB(pz)_3](CO)_2\overline{W[CH(SMe)(S}Et)]$ complex is prepared by a procedure similar to the one used (see Experimental) for **3**. The ^1H NMR spectrum of the major isomer of $[HB(pz)_3](CO)_2\overline{W[CH(SMe)(S}Et)]$ taken in CD_2Cl_2 solution shows peaks at δ 8.14 (H3 of pz), 7.65 (d, J=1.85 Hz, H5 of pz), 6.24 (t, J=2.22 Hz, H4 of pz), 4.79 (s, J_{WH}=4.91, CH), 2.66 (m, SCH_2), 2.42 (s, SMe), and 1.16 (t, J=7.57 Hz, Me).

12. (a) Casey, C. P.; Burkhardt, T. J. J. Am. Chem. Soc. 1973, 95, 5833.
    (b) Fischer, E. O.; Reidmüller, S. Chem. Ber. 1976, 109, 3358.
    (c) Fischer, E. O.; Held, W.; Kreissl, F. R. Chem. Ber. 1977, 110, 3842.

13. Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. "Spectrometric Identification of Organic Compounds", 4th ed.; Wiley:New York, 1981; p 207.

14. Ibid. pp. 208-10.

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

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

17. (a) Collins, T. J.; Roper, W. R. J. Organomet. Chem. **1978**, 159, 73.

(b) Pickering R. A.; Angelici, R. J. Inorg. Chem. **1981**, 20, 2977.

18. Fischer, E. O.; Lindner, T. L; Huttner, G.; Friedrich, P.; Kreissl, R. F.; Besenhard, J. O. Chem. Ber. **1977**, 110, 3397.

19. Curtis, M. D.; Shiu, K. B. Inorg. Chem. **1985**, 24, 1213.

20. Greaves, W. W.; Angelici, R. J. Inorg. Chem. **1981**, 20, 2983.

21. Fischer, E. O.; Kreis, G.; Kreissl, F. R.; Kalbfus, W.; Winkler, E. J. Organomet. Chem. **1974**, 65, C53.

22. Trofimenko, S. J. Am. Chem. Soc. **1969**, 91, 3183.

23. The $NH_2CH_2CH_2OH$ and NH_2-t-Bu reactions do not produce the thiocarbyne compound, **1**.

24. Adams, R. A. Inorg. Chem. **1976**, 15, 169.

25. Pombeiro, A. J. L.; Richards, R. L. Transition Met. Chem. **1980**, 5, 55.

26. Fischer, E. O.; Aumann, R. Chem. Ber. **1968**, 101, 963.

27. Angelici, R. J.; Busetto, L. J. Am. Chem. Soc. **1969**, 91, 3197.

28. Dombek, B. D.; Angelici, R. J. Inorg. Synth. **1977**, 17, 100.

29. Ruff, J. K.; Schlientz, W. J. Inorg. Synth. **1974**, 15, 84.

30. Closson, W. D.; Wriede, P.; Bank, S. J. Am. Chem. Soc. **1966**, 88, 1581.

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

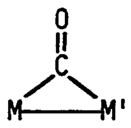
32. Hegedus, L. S.; Inoue, Y. J. Am. Chem. Soc. 1982, 104, 4917.

33. Gingerich, R. G. W.; Angelici, R. J. *J. Am. Chem. Soc.* **1979**, *101*, 5604.

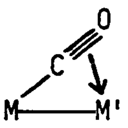
SECTION IV. SYNTHESES AND STRUCTURES OF $[HB(pz)_3](CO)_2(CS)W\text{-}Au(PR_3)$. FIRST EXAMPLES OF A SEMIBRIDGING CS LIGAND

INTRODUCTION

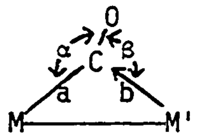
The similarity of carbon monosulfide (CS) to CO has stimulated much interest in the synthesis and reactivity of CS complexes.[1] The CS group is found as a terminal ligand (e.g., $(CO)_5W(CS)$,[2] $CpFe(CO)_2(CS)^+$,[3] $CpMn(CO)_2(CS)$[4]), as a carbon-bridging ligand (e.g., $Cp_2Fe_2(CO)_3(CS)$,[5] $MnPt(\mu\text{-}CS)(CO)_2(PMePPh_2)_2Cp$[6]), and as an end-to-end bridging ligand (e.g., $(dppe)_2(CO)WC{\equiv}SW(CO)_5$[7]). In its complexes, CS is a better σ-donor and π-acceptor than CO[1b] and generally binds more strongly to metals than does CO. The CO ligand participates in 3 types of metal-metal bridging in polynuclear systems:[8] carbon bridging (I), side-on bonding (II), and semibridging (III). Bonding features of these bridging ligands were reviewed recently by Horwitz and Shriver.[9] The side-on bonding CO (II) acts as a four-electron donor, providing two σ electrons to M and two π electrons to M'; both M'-O and M'-C interactions are relatively strong. The semibridging CO group (III) is characterized by different M-C distances (a < b) and unequal MCO angles (α > β); the M'-C interaction is relatively weak. Extended Hückel molecular orbital calculations on $Cp_2M_2(CO)_4$ (M = Cr, Mo)[10] suggest that the primary interaction between the more distant



I



II



III

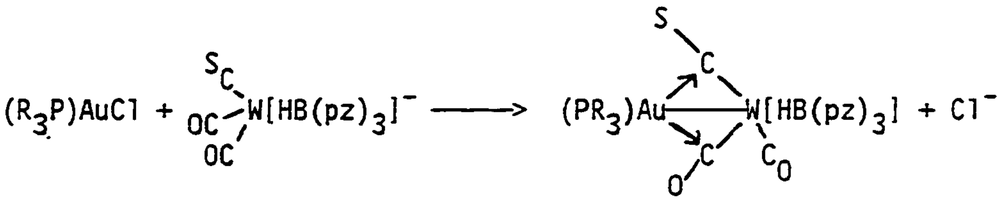
second metal atom (M') and the semibridging carbonyl ligand is a donation of electron density from M' into the CO π^* orbitals. As a result, the semibridging CO ligand shows a lower stretching frequency than a comparable terminal CO group.[9] Unlike CO, CS has not been found or suggested to be a side-on or semibridging ligand in any metal complexes until now.

RESULTS AND DISCUSSION

Syntheses and Characterization of $[HB(pz)_3](CO)_2(CS)W\text{-}Au(PR_3)$

Terminal CS groups in electron-rich complexes form adducts at the S with Lewis acids, e.g., $(diphos)_2(CO)W(CSHgCl_2)$,[11] and are also alkylated at the CS sulfur atom, e.g. $[HB(pz)_3](CO)_2W(CSR)$.[12] On the other hand, certain electrophiles add to the metal center as in the reactions of $CpW(CO)_2(CS)^-$ with HgI_2, $ClSnPh_3$, and $ClPbPh_3$.[13] We examined the reactions of $[HB(pz)_3](CO)_2W(CS)^-$ with $ClAu(PR_3)$ to determine whether the $Au(PR_3)$ group adds to the S or the W atom.[12b]

Reactions of $[HB(pz)_3](CO)_2W(CS)^-$ and $ClAu(PR_3)$ in CH_2Cl_2 at room temperature produce orange crystalline complexes $[HB(pz)_3](CO)_2(CS)W\text{-}Au(PR_3)$(eq 1); the low-yield (20-30%) is presumably due to incomplete separation of the products since no other CO-containing products are observed during the reaction. In the products, **1** and **2**, the $Au(PR_3)$ moiety has added to the W, as is found in other heterobimetallic Au



(1)

1, R = Ph

2, R = Me

compounds, e.g., $Cp(CO)_3W\text{-}Au(PPh_3)$,[14] $(CO)_4[P(OPh)_3]Mn\text{-}Au(PPh_3)$,[15] $(CO)_4Co\text{-}Au(PPh_3)$,[16] $(\eta^3\text{-}C_3H_5)(CO)_3Fe\text{-}Au(PPh_3)$.[17]

Compounds 1 and 2 are air-sensitive in solution, but relatively stable in the solid state. The IR spectrum of 2 (1920, 1830 cm^{-1}) shows lower CO stretching frequencies than that of 1 (1923, 1836 cm^{-1}), as expected for the more electron-donating PMe_3 group. The stretching frequency of the semibridging CO group is assigned to the lower band (1 (1836 cm^{-1}), 2 (1830 cm^{-1})), for reasons discussed in the Introduction. The stretching frequency of the semibridging CS group would also be expected to be lower than that of a comparable terminal CS group, e.g., $[HB(pz)_3](CO)_2W(CS)I$, ν CS = 1243 cm^{-1}.[13] Unfortunately, the ν(CS) band of the semibridging CS group has not been identified because the $HB(pz)_3^-$ and PPh_3 groups also have strong absorptions between 1300 - 1000 cm^{-1}.[18]

The ^{13}C NMR spectrum of 1 at room temperature shows three peaks corresponding to two different CO groups and a CS. The resonance at 226.88 ppm, which is assigned to the terminal CO, has a chemical shift which is similar to that of CO groups in related compounds, e.g., 224.0 ppm for $[HB(pz)_3](CO)_2W(CS)I$.[13] The semibridging CO is then assigned to the band at 295.80 ppm. The semibridging CO is shifted downfield more than the terminal CO, as is also found in $Cp(CO)_2W(\mu\text{-}C(tolyl){=}CH_2)Pt(PMe_3)_2$,[19] $Cp(CO)_2W(\mu\text{-}C(tolyl))Rh(PMe_3)(\eta^5\text{-}C_9H_7)$.[20] The instability of the compound does not allow high temperature ^{13}C NMR studies, which might provide information about scrambling of the semibridging and terminal CO groups.[6] The resonance at 301.05 ppm with J_{PC} = 34.18 Hz, which is assigned to the semibridging CS, has a similar chemical shift to that of the terminal CS in $[HB(pz)_3](CO)_2W(CS)I$ (300.0 ppm).[13] The J_{PC} coupling to the PPh_3 phosphorus for the CS (J_{PC} = 34.18 Hz) but not for the CO ($J_{PC} \cong 0$ Hz) in 1 suggests that there is a stronger interaction between Au and CS than CO. Also in 2, J_{PC} coupling to the PMe_3 phosphorus is greater for CS (J_{PC} = 29.60 Hz) than for CO (J_{PC} = 7.39 Hz). The larger J_{PC} (7.39 Hz) for the semibridging CO in the PMe_3 compound, as compared with the PPh_3 compound ($J_{PC} \cong 0$ Hz), suggests a stronger interaction of the semibridging CO with Au in 2 than in 1; these conclusions are supported by the structural results described below. In W-Pt dinuclear complexes with a semibridging CO interaction with the Pt, it has also been observed that J_{PC} coupling constants are larger for shorter Pt-CO (semibridging) bonds, e.g., $Cp(CO)_2W(\mu\text{-}\eta^1,\eta^3\text{-}CH(tolyl))Pt(PMe_3)_2$ (Pt-CO = 2.27 Å, J_{PC} = 22 Hz)[21] versus $Cp(CO)_2W(\mu\text{-}C(tolyl) = CH_2)Pt(PMe_3)_2$(Pt-CO = 2.54 Å, J_{PC} = 11 Hz).[19]

The C-bridging CS ligand in $Cp_2Fe_2(CO)_3(CS)$,[22] $Cp_2Fe_2(CO)_2(CS)_2$,[1f] $MnPt(\mu\text{-}CS)(CO)_2(PMePh_2)_2Cp$,[6] and $Cp(PMe_3)CoMnCp(CO)(\mu\text{-}CO)(\mu\text{-}CS)$,[23] can be alkylated ($R^+$) at the sulfur atom to give bridging thiocarbyne complexes, $M(\mu\text{-}CSR)M'$. However, methylation of 1 with $(Me_3O)PF_6$ in CH_2Cl_2 at room temperature for 20 min cleaves the W-Au bond to give the terminal thiocarbyne $[HB(pz)_3](CO)_2W(\equiv CSMe)$, a compound which was prepared earlier via the reaction of $[HB(pz)_3](CO)_2W(CS)^-$ with MeI.[12b]

Structure and Bonding Descriptions of $[HB(pz)_3](CO)_2(CS)W$-$Au(PR_3)$, 1 (R = Ph) and 2 (R = Me) Single-crystal X-ray diffraction studies of 1 and 2 show these molecules to have essentially the same structures (Fig. 1 and 2) with a W-Au bond bridged by semibridging CS and CO ligands; the major difference between the structures of 1 and 2 is the Au-C(1) distance, which is discussed later. Figure 3 contains bond distances and angles around the semibridging CS and CO and terminal CO ligands in complex 1. Selected bond distances and bond angles for 1 and 2 are given in Table I. Since the bond distances and angles are more precise for 1 (R = 3.1%) than 2 (R = 5.2%), complex 1 will be discussed in greater detail. First we compare the structure of 1 with that of the closely-related $Cp(CO)_3W$-$Au(PPh_3)$,[14] in which two of the CO groups are semibridging. The W-Au bond distance (2.8248(4) Å) in 1 is somewhat longer than those found in $Cp(CO)_3W$-$Au(PPh_3)$ (2.698(3) Å) and $Cp(CO)_2W$-$Au(PPh_3)(\mu$-$CH(tolyl))$ (2.729(1) Å).[24] Several features of the structure of 1 are consistent with the presence of a semibridging CO group. The W-C(2) bond distance (1.954(9) Å) is shorter than W-C(1) (2.000(8) Å), and the C(2)-O(2) bond distance (1.14(1) Å) appears to be shorter than C(1)-O(1) (1.16(1) Å). The W-C(2)-O(2) bond angle is 178.2(8)°, whereas the W-C(1)-O(1) bond angle (173.4 (7)°) deviates more from 180°; the W-C(1)-O(1) bond angle is close to those (172(4), 168(4)°) of the semibridging carbonyls in $Cp(CO)_3W$-$Au(PPh_3)$. The Au-C(1)-O(1) bond angle, 114.8(6)°, is much smaller than that of W-C(1)-

Table I. Comparison of Selected Distances and Angles between $[HB(pz)_3](CO)_2(CS)W\text{-}Au(PPh_3)$, **1**, and $[HB(pz)_3](CO)_2(CS)W\text{-}Au(PMe_3)$, **2**

(a) Distances (Å)[a]

1		2	
W-Au	2.8248(4)	W-Au	2.824(1)
W-C(1)	2.000(8)	W-C(1)	1.985(28)
W-C(2)	1.954(9)	W-C(2)	1.966(30)
W-C(3)	1.911(7)	W-C(3)	1.905(24)
W-N(1)	2.223(6)	W-N(1)	2.221(20)
W-N(2)	2.212(6)	W-N(2)	2.293(21)
W-N(3)	2.243(6)	W-N(3)	2.242(20)
Au-S	3.054(2)	Au-S	3.005(9)
Au-P	2.270(2)	Au-P	2.269(7)
Au-C(1)	2.720(8)	Au-C(1)	2.546(28)
Au-C(3)	2.162(7)	Au-C(3)	2.151(24)
Au-O(1)	3.374(7)	Au-O(1)	3.212(20)

---

[a] Estimated standard deviations are given in parentheses.

Table I (Continued)

1		2	
S-C(3)	1.630(8)	S-C(3)	1.631(25)
P-C(41)	1.814(8)	P-C(4)	1.773(43)
P-C(51)	1.796(8)	P-C(5)	1.850(37)
P-C(61)	1.806(9)	P-C(6)	1.766(43)
C(1)-O(1)	1.159(11)	C(1)-O(1)	1.173(34)
C(2)-O(2)	1.141(12)	C(2)-O(2)	1.136(39)
N(11)-B	1.511(12)	N(11)-B	1.493(38)
N(21)-B	1.560(12)	N(21)-B	1.505(39)
N(31)-B	1.533(12)	N(31)-B	1.508(38)

(b) Angles (°)[b]

1		2	
Au-W-C(1)	66.1(2)	Au-W-C(1)	61.0(8)
Au-W-C(2)	105.6(3)	Au-W-C(2)	97.1(9)

---

[b] Estimated standard deviations are given in parentheses.

Table I (Continued)

1		2	
Au-W-C(3)	49.9(2)	Au-W-C(3)	49.6(7)
Au-W-N(1)	124.0(2)	Au-W-N(1)	135.2(5)
Au-W-N(2)	150.1(2)	Au-W-N(2)	142.8(5)
Au-W-N(3)	85.3(2)	Au-W-N(3)	90.7(5)
C(1)-W-C(2)	85.9(3)	C(1)-W-C(2)	90.9(12)
C(1)-W-C(3)	105.0(3)	C(1)-W-C(3)	108.4(11)
C(1)-W-N(1)	167.9(3)	C(1)-W-N(1)	162.7(10)
C(1)-W-N(2)	88.7(3)	C(1)-W-N(2)	83.1(10)
C(1)-W-N(3)	95.5(3)	C(1)-W-N(3)	95.0(10)
C(2)-W-C(3)	78.7(3)	C(2)-W-C(3)	82.7(11)
C(2)-W-N(1)	96.7(3)	C(2)-W-N(1)	92.3(10)
C(2)-W-N(2)	87.3(3)	C(2)-W-N(2)	92.7(10)
C(2)-W-N(3)	168.6(3)	C(2)-W-N(3)	171.9(10)
C(3)-W-N(1)	87.2(3)	C(3)-W-N(1)	88.9(9)
C(3)-W-N(2)	159.5(3)	C(3)-W-N(2)	167.5(9)
C(3)-W-N(3)	111.8(3)	C(3)-W-N(3)	100.8(9)
N(1)-W-N(2)	79.6(2)	N(1)-W-N(2)	79.7(7)
N(1)-W-N(3)	79.6(2)	N(1)-W-N(3)	80.5(7)
N(2)-W-N(3)	81.4(2)	N(2)-W-N(3)	82.5(7)

Table I (Continued)

1		2	
W-Au-P	154.6(1)	W-Au-P	151.7(2)
W-Au-C(1)	42.2(2)	W-Au-C(1)	43.0(6)
W-Au-C(3)	42.5(2)	W-Au-C(3)	42.4(6)
P-Au-C(1)	119.3(2)	P-Au-C(1)	109.9(7)
P-Au-C(3)	162.1(2)	P-Au-C(3)	166.0(7)
C(1)-Au-C(3)	78.0(3)	C(1)-Au-C(3)	83.9(9)
Au-P-C(41)	109.1(3)	Au-P-C(4)	115.3(14)
Au-P-C(51)	114.1(3)	Au-P-C(5)	111.3(12)
Au-P-C(61)	114.1(3)	Au-P-C(6)	113.9(14)
C(41)-P-C(51)	106.5(4)	C(4)-P-C(5)	103.8(18)
C(41)-P-C(61)	106.8(4)	C(4)-P-C(6)	108.5(20)
C(51)-P-C(61)	105.8(4)	C(5)-P-C(6)	102.8(18)
W-C(1)-Au	71.7(2)	W-C(1)-Au	76.0(9)
W-C(1)-O(1)	173.4(7)	W-C(1)-O(1)	169.6(24)
Au-C(1)-O(1)	114.8(6)	Au-C(1)-O(1)	114.3(20)
W-C(2)-O(2)	178.2(8)	W-C(2)-O(2)	178.3(27)
W-C(3)-Au	87.6(3)	W-C(3)-Au	88.0(9)
W-C(3)-S	165.9(5)	W-C(3)-S	167.3(16)
Au-C(3)-S	106.4(4)	Au-C(3)-S	104.4(12)

Table II. Summary of Crystal Data and Intensity Data Collection for $[HB(pz)_3](CO)_2(CS)W\text{-}Au(PPh_3)$, 1, and $[HB(pz)_3](CO)_2(CS)W\text{-}Au(PMe_3)$, 2

	1	2
Formula unit	$C_{30}H_{25}AuBN_6O_2PSW$	$C_{15}H_{19}AuBN_6O_2PSW$
Molecular weight	956.23	770.02
Space group	$P2_1/n$	Pbca
a, Å	15.062(4)	16.956(3)
b, Å	18.103(3)	17.173(3)
c, Å	11.887(2)	15.053(2)
α, °	90	90
β, °	103.53(2)	90
γ, °	90	90
Volume, $Å^3$	3151.2(12)	4383.4(14)
Z	4	8
ρ_{calc} g/cm^3	2.015	2.333
Crystal dimensions, cm	0.05x0.05x0.045	0.02x0.02x0.02
Diffractometer	DATEX	Syntex $P2_1$
Radiation, Å	0.70966	0.71069
Monochromator	oriented graphite crystal	
Absorption coeff, cm^{-1} (corr.appl.)	85.12	122.09

Table II (Continued)

	1	2
Ratio min/max transmission	0.544	0.433
ω step scan mode	0.5 sec per 0.01°	1° per min.
Scan width	1.2°	1.0°
Background measurement	total 10 sec	same as the scan
$2\theta_{max}$, °	50	45
Octants measured	±h,±k,l	h,k,l
Reflections measured	5392	3443
Independent observed (I $3\sigma_I$)	3900	1905
R[a]	0.031	0.052
Rw[b]	0.038	0.062
S[c]	1.258	1.689
Secondary extinction[d]	$0.259(22)\text{x}10^4$	$0.070(19)\text{x}10^4$

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

[b] $Rw \equiv [\Sigma\omega(|F_o|-|F_c|)^2/\Sigma\omega|F_o|^2]^{1/2}$, where $\omega=1/\sigma_F{}^2$.

[c] $S \equiv [\Sigma\omega(|F_o|-|F_c|)^2/(N_o-N_v)]^{1/2}$, where N_o and N_v being numbers of observations and varied parameters, respectively.

[d] Isotropic parameter applied to Fc, based on P. Coppens and W. C. Hamilton (Acta Cryst. 1970, A26, 71) with a polarization factor for the case of a monochromator in the diffracted beam.

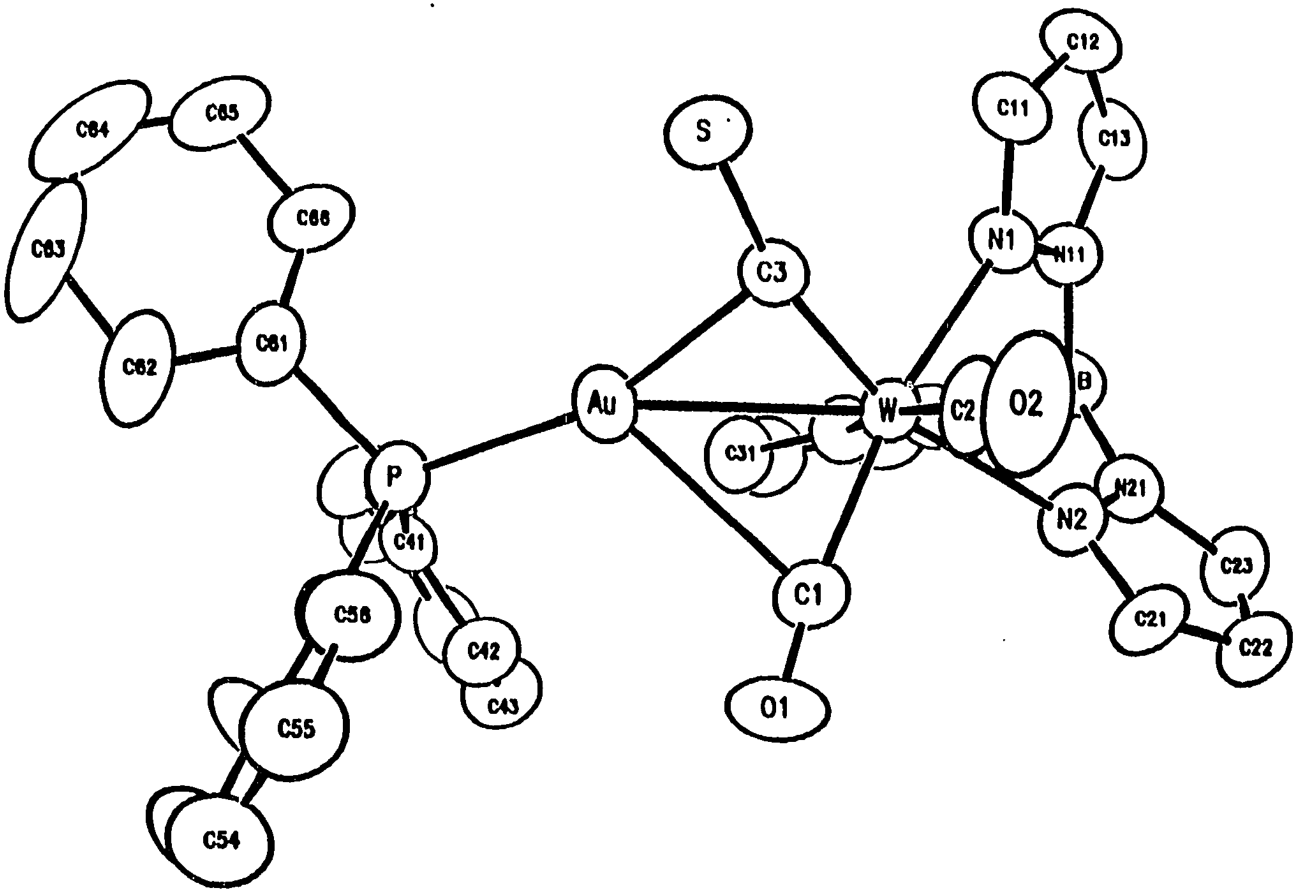


Figure 1. ORTEP plot of $[HB(pz)_3](CO)_2(CS)W—Au(PPh_3)$, 1

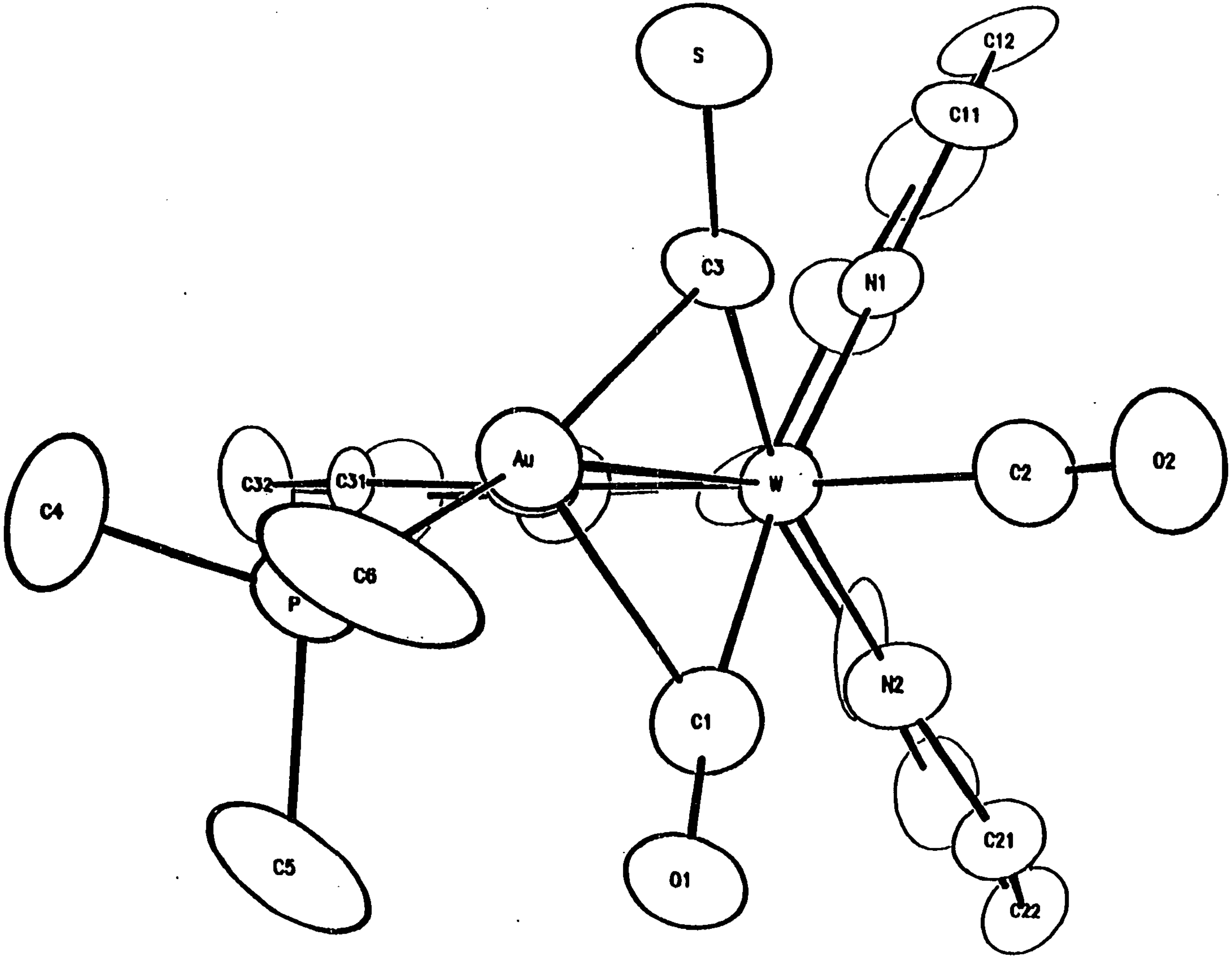


Figure 2. ORTEP plot of $[HB(pz)_3](CO)_2(CS)W—Au(PMe_3)$, 2, view down the B—W bond

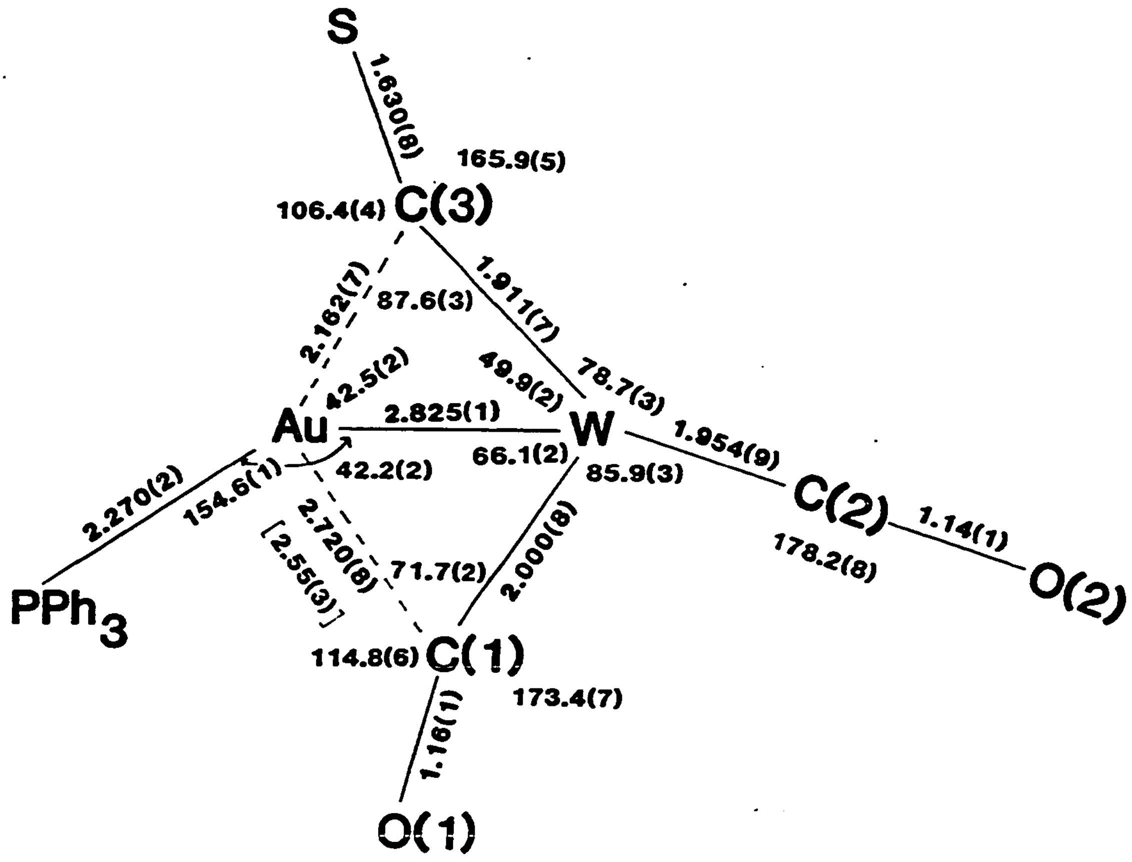


Figure 3. Bond distances and angles around the semibridging CS and CO and terminal CO ligands in the complex $[HB(pz)_3](CO)_2W$-$AuPPh_3$, 1. The significant difference between 1 and 2 is in the Au-C(1) distance; this distance in complex 2 is shown in square brackets.

O(1) (173.4(7)°). The Au-C(1) bond distance is 2.720(8) Å, which compares with the distances (2.51(5) Å and 2.79(5) Å) of the semibridging CO carbons to Au in $Cp(CO)_3W$-$Au(PPh_3)$. The bond distances of the semibridging CO carbons to Au in $(\eta^3$-$C_3H_5)(CO)_3Fe$-$Au(PPh_3)$ are 2.595(7) Å and 2.569(7) Å.[17] The Au-O(1) distance is 3.374(7) Å, too long to be considered a side-on bonding CO.[9] Thus, C(1)-O(1) may be described as a semibridging CO group; the Au back-bonds to the semibridging CO ligand by donating electron density into the π^* orbitals of CO, competing against π-back donation from the W-atom. The geometry of the semibridging carbonyl ligand in 1 is similar to that in $(\eta^3$-$C_3H_5)(CO)_3Fe$-$Au(PPh_3)$,[17] $Cp(CO)_3W$-$Cu(PPh_3)_2$,[25] and $Cp(CO)_2W(\mu$-$C(tolyl)=CH_2)Pt(PMe_3)_2$.[19] Although the 14-electron gold(I) center has been considered a poor π-electron donor,[26] the much shorter Au-C(1) distance in the PMe_3 (2.55(3) Å) compound 2 as compared with the PPh_3 (2.720(8) Å) complex 1 strongly supports the idea that Au donates electron density into the CO π^* orbitals.

The CS ligand in 1 is also in a semibridging position; the Au-S distance is 3.054(2) Å, long for a side-on bonding CS. As in terminal and C-bridging CS complexes, CS behaves as if it were a better σ-donor and π-acceptor ligand than CO. Thus, the W-C(3) bond distance (1.911(7) Å) is shorter than both the W-C(1) (2.000(8) Å) and W-C(2) (1.954(9) Å) bond distances; it is also somewhat shorter than the W-C bond distance (1.94(2) Å) to the terminal CS in $(CO)_4(CNC_6H_{11})W(CS)$,[18] although this is a much less electron-rich system. The W-C(3)-S bond angle (165.9(5)°) deviates significantly from 180° and is smaller than that of W-C(1)-O(1) (173.4(7)°) but is similar to those of the semibridging carbonyls in $Cp(CO)_3W\text{-}Au(PPh_3)$ (168(4)°, 172(4)°).[10b] The M-C-O angles[10b] in other semibridging CO compounds[8,9,19-21,25] range from 154° ($MnPt(\mu\text{-}CS)(CO)_2(PMePh_2)_2Cp$)[6] to 177° ($(\eta^3\text{-}C_3H_5)(CO)_3Fe\text{-}Au(PPh_3)$.[17] The Au-C(3) distance (2.162(7) Å) is longer than the Au-C(sp) single bond distance (1.94(2) Å) in $(i\text{-}propyl)NH_2AuC{\equiv}CC_6H_5$,[27] the Au-C($sp^2$) single bond distance (2.07(2) Å) in $Ph_3PAuC_6F_5$,[28] and the Au-C(sp^3) single bond distance (2.12(3) Å) in Ph_3PAuMe.[29] Thus, the Au-C(3) interaction is weaker than a full bond. The Au-C(3)-S bond angle, 106.4(4)°, is much smaller than W-C(3)-S (165.9(5)°), as expected for a semibridging CS group. The Au-C(3) bond distance (2.162(7) Å) is substantially shorter than the Au-C(1) bond distance (2.720(8) Å), which is consistent with the better π acceptor ability of CS over CO.[1b] It is interesting that the Au-CS bond distance is essentially the same in **1** and **2**, whereas the Au-CO distance is considerably shorter in the PMe_3 complex **2**. This suggests that the semibridging CS ligand is less capable of accepting the additional electron density in **2**, whereas the Au-CO bond is considerably strengthened by it.

The C(3)-S bond distance (1.630(8) Å) is longer than those of other terminal CS ligands (1.50 - 1.59 Å);[1e,18] this lengthening presumably results from the donation of electron density from the Au to the π^* orbitals of CS. The C(3)-S bond distance is even longer than those of the C-bridged CS ligands in $[CpFe(CS)(CO)]_2$ (avg. 1.590(8) Å)[30] and $Cp_2Fe_2(CO)_3CS$ (avg. 1.601(9) Å).[31]

The W-Au-P bond angle (154.6(1)°) deviates noticeably from the 180° found in most Au(I) complexes,[27-29] and is substantially smaller than that found in $Cp(CO)_3W-AuPPh_3$ (173.8(3)°). If one assumes Au to prefer linear coordination and one of its ligands is the phosphine, the second ligand should lie on an extension of the P-Au vector. It is interesting that this extension intersects the W-C(3) bond at about its midpoint; however, it is not clear what significance this has for the bonding in the semibridging CS complexes. The Au atom adopts an approximately planar geometry; the W atom deviates (0.8 Å) from the least-squares plane, defined by Au, P, C(1), and C(3). The interplanar angle between W-C(1)-Au and W-C(3)-Au is 138° and 161° in **1** and **2**, respectively. The C(1)→O(1) bond vector lies in the W-C(1)-Au plane (within 0.03°) in **1**, but is out of this plane slightly (2.04°) pointing toward the semibridging CS in **2**. The C(3)→S bond vector points away from the W-C(3)-Au plane toward the semibridging CO in both **1** (2.29°) and **2** (2.76°).

The geometry around the W atom can be viewed as a distorted pentagonal bipyramid; C(2) and N(3) are in the axial positions, and Au, C(1), C(3), N(1), and N(2) are in the equatorial plane. The angle C(2)-W-N(3) is 168.6° and 171.9° in **1** and **2**, respectively. The angles L(axial)-W-L (equatorial) range from 79-112°, where L represents ligands including Au. This 7-coordination geometry, distinctly different from either capped octahedral or capped trigonal prismatic structure, has also been observed in other $[HB(pz)_3]$ complexes such as $[HB(pz)_3](CO)_2W[\eta^2\text{-CH(SMe)}]^+$,[32] $[HB(pz)_3](CO)_2W[\eta^2\text{-CH(SMe)(PPh}_2)]$,[33] and $[HB(pz)_3](CO)_2Mo[\eta^2\text{-}COR]$ (R = Ph, Me),[34] in which the L(ax)-M-L(ax) angles range from 171.4° to 176.7° and the L-(ax)-M-L(eq) angles vary from 72.6° to 109.3°.

In conclusion, CS is a better semibridging ligand than CO as suggested by the fact that the CS instead of a second CO is involved in semibridging in **1** and **2**. This conclusion is supported by the much shorter Au-C distance for Au-CS than Au-CO. The more favorable semibridging ability of the CS group appears to be due to its better π^*-acceptor ability as compared with CO, which allows it to interact more strongly with the π-donating Au atom.

EXPERIMENTAL SECTION

General Procedures All reactions were carried out under an N_2 atmosphere. Methylene chloride and hexane were dried over CaH_2 and distilled under N_2. Diethyl ether was distilled from Na-benzophenone under N_2. Reagent grade benzene was stored over type 4A molecular sieves. Products were crystallized using a layering technique, whereby the compound (30 mg) dissolved in CH_2Cl_2 (2 mL) was layered with hexane (10 mL) and allowed to sit at 0°C under a constant N_2 atmosphere. Infrared spectra were recorded on a Perkin-Elmer 681 spectrometer; the band positions were calibrated against gaseous CO. ^{1}H NMR spectra were obtained with a Nicolet NT-300 (300 MHz) spectrometer. Proton-decoupled ^{13}C NMR spectra were measured on the same instrument (75.46 MHz). To reduce ^{13}C NMR data collection times, $Cr(acac)_3$ (ca. 0.1 M) was added to the solutions.[35] Chemical shifts of ^{13}C nuclei are reported in δ units using CD_2Cl_2 (δ = 53.80) as the internal standard. Electron impact mass spectra (EIMS) were obtained on a Finnigan 4000 spectrometer. Elemental microanalyses were performed by Galbraith Laboratories Inc., Knoxville, Tennessee.

Solutions of $[(n\text{-}Bu)_4N]\{[HB(pz)_3](CO)_2W(CS)\}$[13] were prepared using previously described procedures. Ph_3PAuCl and Me_3PAuCl were purchased from Strem Chemical, Inc.

$[HB(pz)_3](CO)_2(CS)W\text{-}AuPPh_3$, 1 A reaction solution containing $[(n\text{-}Bu)_4N]\{[HB(pz)_3](CO)_2W(CS)\}$ (0.22 mmol) and $ClAuPPh_3$ (109 mg, 0.22

mmol) in 20 mL of CH_2Cl_2 was stirred at room temperature for 15 min, yielding a red solution, which was evaporated to dryness under reduced pressure. The resulting oily residue was extracted with diethyl ether until the extract was colorless. The extract was filtered through Celite, and the filtrate was evaporated to give an orange solid; recrystallization from CH_2Cl_2/hexane at 0°C gave red crystals of 1 (63 mg, 30%). Microscopic crystals were found which were suitable for X-ray analysis. Anal. Calcd for $C_{30}H_{25}AuBN_6O_2PSW$: C, 37.68; H, 2.64; N, 8.79. Found: C, 37.61; H, 2.63; N, 8.65. EIMS (19 eV): m/e 956(M^+), 900 (M^+-2CO). IR (CH_2Cl_2): 1923(s), 1836(s) cm^{-1}. ^1H NMR (CD_2Cl_2): 8.20 (br, H3 of pz), 7.60 (m, H5 of pz and Ph), 6.16 (br, H4 of pz). ^{13}C NMR (CD_2Cl_2): 301.05 (d, J_{PC} = 34.18 Hz, CS), 295.80 (semibridging CO), 226.88 (CO), 145.87 (C3 of pz), 135.54 (C5 of pz), 105.80 (C4 of pz), [134.38 (d, J_{PC} = 13.47 Hz), 131.86, 130.60, 129.88, 129.43 (d, J_{PC} = 8.54 Hz), Ph].

[HB(pz)$_3$](CO)$_2$(CS)W-AuPMe$_3$, 2   In a procedure similar to that used for 1, (Me_3P)AuCl (160 mg, 0.52 mmol) was allowed to react with [(n-Bu)$_4$]{[HB(pz)$_3$](CO)$_2$W(CS)} (0.52 mmol) in CH_2Cl_2 (50 mL) at room temperature for 15 min. The solution was diluted with 70 mL of ether; slow evaporation under reduced pressure furnished an orange precipitate. After the solution was decanted, the resulting orange solid was extracted with benzene. The benzene extract was filtered through Celite, and the solution was evaporated to dryness; recrystallization of the residue from CH_2Cl_2/hexane at 0°C gave red crystals of 2 (80 mg, 20%) some of which were suitable for X-ray analysis. Anal. Calcd for $C_{15}H_{19}AuBN_6O_2PSW$: C, 23.40; H, 2.49; N, 10.91. Found: C, 22.83; H, 2.57; N, 10.30. EIMS (70 eV): m/e 770 (M^+), 714 (M^+-2 CO). IR (CH_2Cl_2): 1920(s), 1830(s) cm^{-1}. ^1H NMR (CD_2Cl_2): 8.17 (br, H3 of Pz), 7.68 (br, H5 of pz), 6.23 (br, H4 of pz), 1.78 (d, J_{PH} = 9.72 Hz, Me). ^{13}C NMR (CD_2Cl_2): 295.70 (d, J_{PC} = 29.60 Hz, CS), 293.20 (d, J_{PC} = 7.39 Hz, semibridging CO), 228.11 (CO), 145.81 (C3 of pz), 135.61 (C5 of pz), 105.91 (C4 of pz), 17.81 (d, J_{PC} = 34.61 Hz, Me).

X-ray Crystallography   The general procedures for data collection and reduction have been published elsewhere.[36] Details of the data processing and relevant crystallographic data are given in Table II. Computer programs used in this study are summarized in reference 37.

The structures were determined using Patterson and electron density function calculations. Hydrogen atoms were included in the structure factor calculations at their calculated positions. The positional and anisotropic thermal parameters were refined by block-matrix/full-matrix procedures.

The atomic scattering factors were those from reference 38 modified for the real and imaginary parts of anomalous dispersion.

REFERENCES

1. (a) Butler, I. S.; Fenster, A. E. J. Organometal. Chem. 1974, 66, 161. (b) Butler, I. S. Acc. Chem. Res. 1977, 10, 359. (c) Collins, T. J.; Roper, W. R. J. Organometal. Chem. 1978, 159, 73. (d) Quick, M. H.; Angelici, R. J. Inorg. Chem. 1982, 21, 1674. (e) Bird, P. H.; Ismail, A. A.; Butler, I. S. Inorg. Chem. 1985, 24, 2911. (f) Angelici, R. J.; Dunker, J. W. Inorg. Chem. 1985, 24, 2209. (g) Broadhurst, P. V. Polyhedron 1985, 4, 1801.
2. Dombek, B. D.; Angelici, R. J. Inorg. Chem. 1976, 15, 1089.
3. Busetto, L.; Belluco, U.; Angelici, R. J. J. Organometal. Chem. 1969, 18, 213.
4. Fenster, A. E.; Butler, I. S. Can. J. Chem. 1972, 50, 598.
5. (a) Quick, M. H.; Angelici, R. J. J. Organometal. Chem. 1978, 160, 231. (b) Wagner, R. E.; Jacobson, R. A.; Angelici, R. J.; Quick, M. H. J. Organometal. Chem. 1978, 148, C35.
6. Jeffery, J. C.; Razay, H.; Stone, F. G. A. J. Chem. Soc., Dalton Trans. 1982, 1733.
7. Dombek, B. D.; Angelici, R. J. J. Am. Chem.Soc. 1974, 96, 7568.
8. (a) Cotton, F. A. Prog. Inorg. Chem. 1976, 21, 1. (b) Colton, R.; McCormick, M. J. Coord. Chem. Rev. 1980, 31, 1.
9. Horwitz, C.; Shriver, D. Adv. Organomet. Chem. 1984, 23, 219.

10. (a) Jemmis, E. D.; Pinhas, A. R.; Hoffmann, R. J. Am. Chem. Soc. **1980**, 102, 2576. (b) Morris-Sherwood, B. J.; Powell, C. B.; Hall, M. B. J. Am. Chem. Soc., **1984**, 106, 5079.
11. Dombek, B. D.; Angelici, R. J. Inorg. Chem. **1976**, 15, 2397.
12. (a) Dombek, B. D.; Angelici, R. J. J. Am. Chem. Soc. **1975**, 97, 1261. (b) Greaves, W. W.; Angelici, R. J. Inorg. Chem. **1981**, 20, 2983.
13. Greaves, W. W.; Angelici, R. J. J. Organometal. Chem. **1980**, 191, 49.
14. Wilford, J. B.; Powell, H. M. J. Chem. Soc. A **1969**, 8.
15. Mannan, Kh. A I. F. M. Acta Cryst. **1967**, 23, 649.
16. Blundell, T. L.; Powell, H. M. J. Chem. Soc. A **1971**, 1685.
17. Simon, F. E.; Lauher, J. W. Inorg. Chem. **1980**, 19, 2338.
18. Woodard, S. S.; Jacobson, R. A.; Angelici, R. J. J. Organometal. Chem. **1976**, 117, C75.
19. Barr, R. D.; Green, M.; Howard, J. A. K.; Marder, T. B.; Moore, I.; Stone, F. G. A. J. Chem. Soc., Chem. Commun. **1983**, 746.
20. Jeffery, J. C.; Sambale, C.; Schmidt, M. F.; Stone, F. G. A. Organometallics **1982**, 1, 1597.
21. Jeffery, J. C.; Moore, I.; Razay, H.; Stone, F. G. A. J. Chem. Soc., Chem. Commun. **1981**, 1255.
22. Quick, M. H.; Angelici, R. J. Inorg. Chem. **1981**, 20, 1123.
23. Kolb, V. S.; Werner, H. Angew. Chem. **1982**, 94, 207.

24. Carriedo, G. A.; Hodgson, D.; Howard, J. A. K.; Marsen, K.; Stone, F. G. A.; Went, M. J.; Woodward, P. J. Chem. Soc., Chem. Commun. 1982, 1006.

25. Carlton, L.; Lindsell, W. E.; McCullough, K. J.; Preston, P. N. J. Chem. Soc., Chem. Commun. 1983, 216.

26. (a) Graham, W. A. G. Inorg. Chem. 1968, 7, 315. (b) Johnson, B. F. G.; Davis, R. In "Comprehensive Inorganic Chemistry"; Bailar, J. C., Ed.; Pergamon Press: Oxford, 1973; Vol. 3, Chapter 3. (c) Browning, J.; Goggin, P. L.; Goodfellow, R. J.; Norton, M. G.; Rattray, A. J. M.; Taylor, B. F.; Mink, J. J. Chem. Soc., Dalton Trans. 1977, 2061.

27. Corfield, P. W. R.; Shearer, H. M. M. Acta Cryst. 1967, 23, 156.

28. Baker, R. W.; Pauling, P. Y. J. Chem. Soc., Dalton Trans. 1972, 2264.

29. Gavens, P. D.; Guy, J. J.; Mays, M. J.; Sheldrick, G. M. Acta Cryst. 1977, B33, 137.

30. Dunker, J. W.; Finer, J. S.; Clardy, J.; Angelici, R. J. J. Organomet. Chem. 1976, 114, C49.

31. Beckman, D. E.; Jacobson, R. A. J. Organomet. Chem. 1979, 179, 187.

32. Kim, H. P.; Kim, S.; Jacobson, R. A.; Angelici, R. J. Organometallics 1984, 3, 1124.

33. Kim, H. P.; Kim, S.; Jacobson, R. A.; Angelici, R. J. to be published.

34. Curtis, M. D.; Shiu, K-B.; Butler, W. M. *Organometallics* 1983, **2**, 1475.

35. Gansow, O. A.; Burke, A. R.; LaMar, G. N. *J. Chem. Soc., Chem. Commun.* 1972, 456.

36. Lindsay, A. J.; Kim, S.; Jacobson, R. A.; Angelici, R. J. *Organometallics* 1984, **3**, 1523.

37. Indexings of the crystals were done using the program BLIND (Jacobson, R. A. *J. Appl. Cryst.* 1976, **9**, 115). Structure factor calculations and least squares refinements were done using the program ALLS (Lapp, R. L.; Jacobson, R. A. U.S. Department of Energy Report IS-4708; Iowa State University: Ames, Iowa, 1979). Fourier series calculations were done using the program FOUR (Powell, D. R.; Jacobson, R. A. U.S. Department of Energy Report IS-4737; Iowa State University: Ames,Iowa, 1980), Patterson Harker analyses were done using the program ALCAMPS (Richardson, J. W. Jr. Ph.D. Dissertation, Iowa State University: Ames, Iowa, 1984), and for molecular drawing the program ORTEP (Johnson, C. K. U.S. Atomic Energy Commission Report ORNL-3794; Oak Ridge National Laboratory: Oak Ridge, Tenn., 1970) was used. An empirical absorption correction was carried out using diffractometer ϕ-scan data.

38. Cromer, D. T.; Waber, J. T. "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2A, pp 71-79. Templeton, D. H. "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1962; Vol. III, Table 3.3.2.c, pp 215-216.

SUMMARY

Studies of $[HB(pz)_3](CO)_2W(\equiv CSMe)$ and $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]$ demonstrate that they are highly reactive toward certain nucleophiles and electrophiles. CS is a better semibridging ligand than CO as suggested by the fact that the CS instead of a second CO is involved in semibridging in $[HB(pz)_3](CO)_2(CS)W\text{-}Au(PR_3)$, R = Ph or Me. This conclusion is supported by the much shorter Au-C distance for Au-CS than Au-CO. The more favorable semibridging ability of the CS group appears to be due to its better π^*-acceptor ability as compared with CO, which allows it to interact more strongly with the electron-donating Au atom. Further evidence of the electron donor ability of the Au is seen in the shorter Au-C distance for the semibridging CO in the more electron rich PMe_3 complex as compared with the PPh_3 analogue.

ACKNOWLEDGEMENTS

I am deeply indebted to Dr. Robert J. Angelici for his guidance, encouragement, and support during the course of this work. I wish to thank Dr. James H. Espenson, Dr. Robert E. McCarley, Dr. R. C. Larock, and Dr. Glenn L. Schrader for their service on my Ph.D. committee and their review of this dissertation. I would also like to express my gratitude to Dr. Robert A. Jacobson for his assistance on X-ray structural studies. I gratefully acknowledge Professor Taeyoung Lee, Professor Wonsick Lee, and Professor Myunghyun P. Suh for introducing me to chemical research and for encouraging me to pursue an advanced degree. It has been a distinct pleasure working with Dr. Yeung Yu, Dr. John Matachek, Ms. Nan Sauer, Dr. George Spies, Dr. Mohan Singh, and others in my research group. I would like to thank Missy Jacobson, Dr. and Mrs. Stanford, Dr. and Mrs. Malmquist, Mr. and Mrs. Potter, and my many other friends here in Ames for their fellowship and for making my stay more meaningful and joyful. I am very grateful for the constant love and support provided by my entire family. My special thanks go to Sangsoo Kim, my husband, for his understanding, sustained support, encouragement, and crystallographic expertise. I would like to also express my appreciation to Ms. Dawn Baksh for typing this manuscript.