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Thiocarbonyl, thiocarbyne and thiocarbene complexes of tungsten

Ruth Ann Doyle
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Doyle, Ruth Ann, Ph.D.

Iowa State University, 1989

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Thiocarbonyl, thiocarbyne and thiocarbene complexes of tungsten

by

Ruth Ann Doyle

A Dissertation Submitted to the
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In Charge of Major Work

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For the Major Department

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For the Graduate College

Iowa State University
Ames, Iowa
1989

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DEDICATION

To my family

PREFACE

This thesis consists of four sections. Each section represents research as it was submitted for journal publication. Literature citations, tables and figures pertain only to the sections in which they are included. Preceding the first section is a general introduction. Following the final section is a general summary.

GENERAL INTRODUCTION

TUNGSTEN THIOCARBONYL COMPLEXES

The similarity of carbon monosulfide (CS) to CO has stimulated much interest in the synthesis and reactivity of CS complexes.[1] Although a very large number of CO complexes are known, relatively few exist for CS. This can be attributed to the lack of stable molecular CS, which polymerizes above -160°C.[2] However, CS can be stabilized by coordination to transition metals; thus, many CS complexes are known. The CS group is found as a terminal ligand (e.g., $(CO)_5W(CS)$,[3] $CpFe(CO)_2(CS)^+$,[4] $CpMn(CO)_2(CS)$),[5] as a carbon-bridging ligand (e.g., bridging two metals as in $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CS)$,[6] $MnPt(\mu\text{-}CS)(CO)_2(PMePh_2)_2Cp$;[7] bridging three metals as in $Cp_3Co_3(\mu_3\text{-}S)(\mu_3\text{-}CS)$),[8] as an end-to-end bridging ligand (e.g., $(dppe)_2(CO)W\text{-}C{\equiv}S\text{-}W(CO)_5$,[9] $(\eta^6\text{-}C_6H_5Me)(CO)_2Cr\text{-}C{\equiv}S\text{-}Cr(CO)_5$)[10] and as a semibridging ligand (e.g., $[HB(pz)_3](CO)W(\mu\text{-}CO)(\mu\text{-}CS)Au(PR_3)$, R = Me, Ph).[11]

In its complexes, CS is a better σ-donor and π-acceptor than CO[12] and generally binds more strongly to metals than does CO. Moreover, in carbonyl thiocarbonyl complexes, the CS group always prefers bridging positions.[6, 7, 13] It has been proposed[13] that the reason for the preference is the low stability (i.e., high energy) of the 2p-3p π bonds between the carbon and sulfur atoms.[14] Thus, the migration of CS from a terminal ($-C{\equiv}S$) to a bridging ($>C{=}S$) position results in the loss of little C-S π-bond stabilization. The stabilization gained by forming a bond to another metal apparently more than compensates for the loss in C≡S π bonding.

The studies in this thesis involve tungsten thiocarbonyl complexes. Several tungsten thiocarbonyl complexes have been studied previously. The tungsten thiocarbonyl complex $W(CO)_5(CS)$ is prepared by the reaction of reduced metal carbonyl species (mainly $W_2(CO)_{10}^{2-}$) and thiophosgene (Cl_2CS) (eq 1).[3] In reactions similar to those of the hexacarbonyl

$$W(CO)_6 \xrightarrow[\text{(2) } Cl_2C{=}S]{\text{(1) Na/Hg, THF, 18 h}} \underset{6-9\%}{W(CO)_5(CS)} + \underset{9-48\%}{W(CO)_6} \qquad (1)$$

analog, $W(CO)_5(CS)$ reacts with donor ligands at elevated temperatures to yield substituted $W(CO)_4(CS)(L)$ complexes (Scheme 1).[3]

Primary amines react with $W(CO)_5(CS)$ to afford the corresponding isocyanide complex $W(CO)_5(CNR)$ (eq 2).[15]

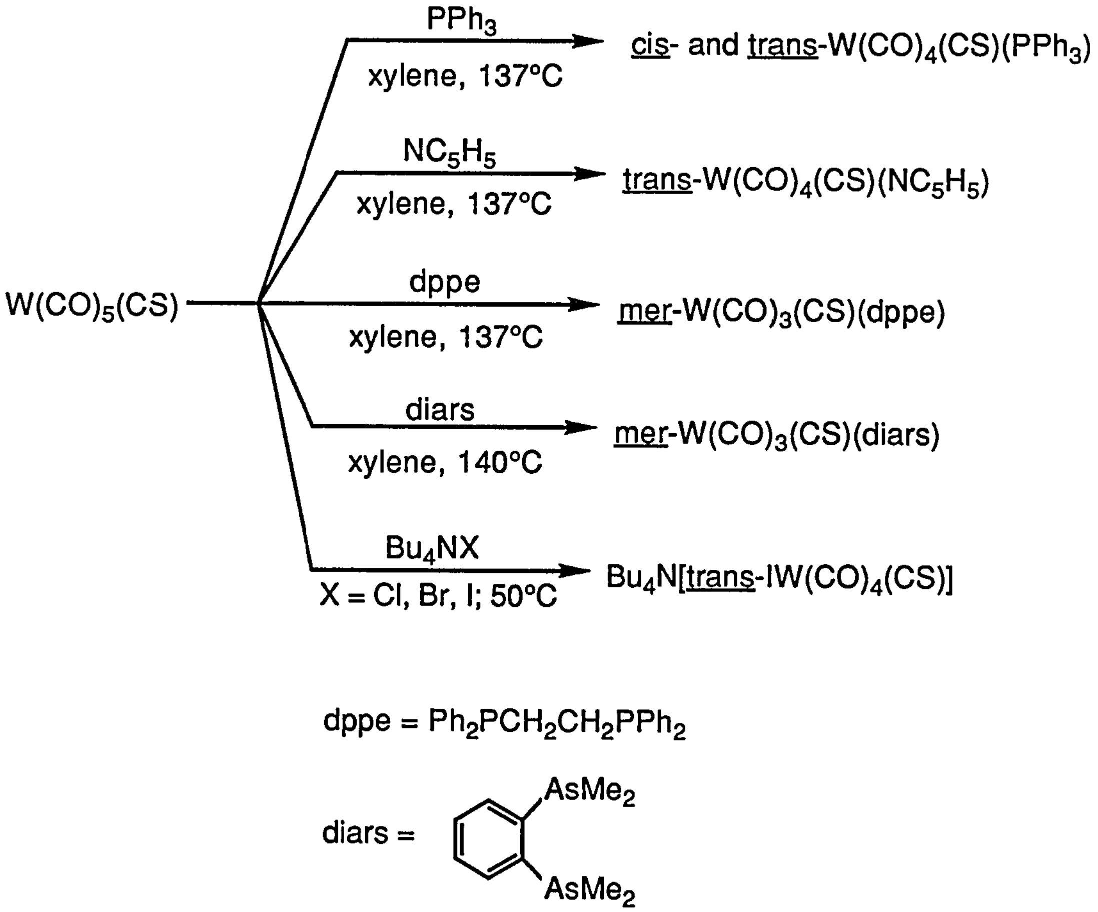
$$W(CO)_5(CS) + RNH_2 \xrightarrow{25^\circ C} W(CO)_5(C{\equiv}N\text{-}R) + H_2S \qquad (2)$$

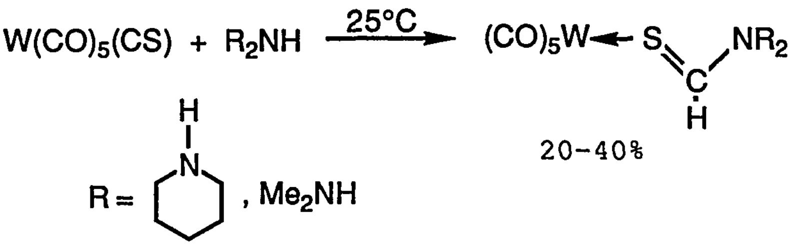
$$R = Me, C_6H_{11}$$

Secondary amines also react with $W(CO)_5(CS)$ in a process which involves rearrangement to give thioformamide complexes (eq 3).[15]

Electrophilic reagents react with tungsten(0) thiocarbonyl complexes to yield products which result from

Scheme 1

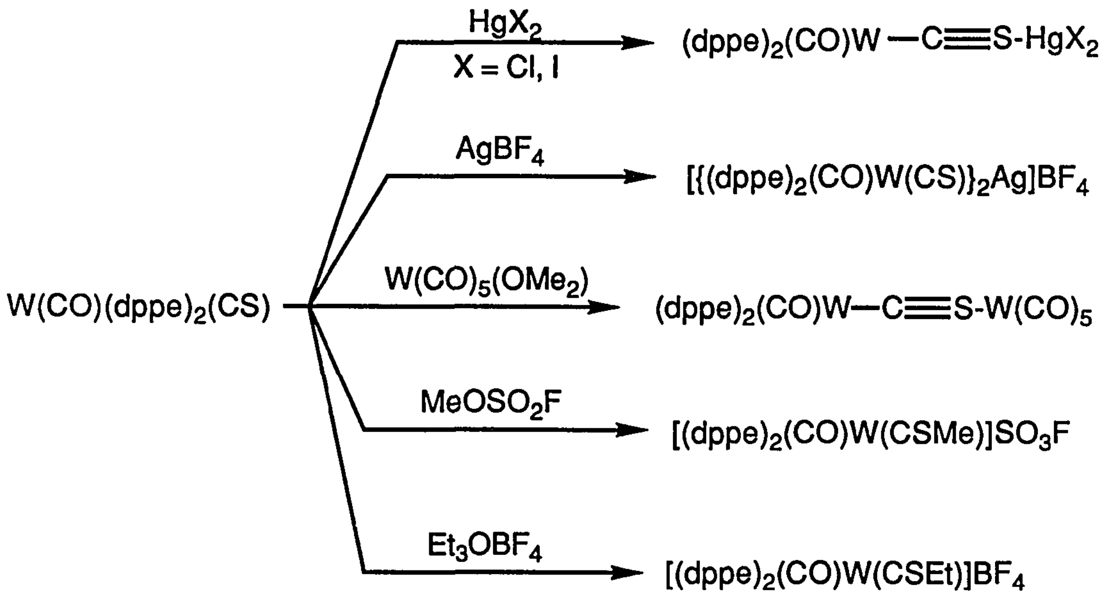

W(CO)$_5$(CS)
PPh$_3$
xylene, 137°C
cis- and trans-W(CO)$_4$(CS)(PPh$_3$)
NC$_5$H$_5$
xylene, 137°C
trans-W(CO)$_4$(CS)(NC$_5$H$_5$)
dppe
xylene, 137°C
mer-W(CO)$_3$(CS)(dppe)
diars
xylene, 140°C
mer-W(CO)$_3$(CS)(diars)
Bu$_4$NX
X = Cl, Br, I; 50°C
Bu$_4$N[trans-IW(CO)$_4$(CS)]
dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$
diars =
AsMe$_2$
AsMe$_2$



(3)

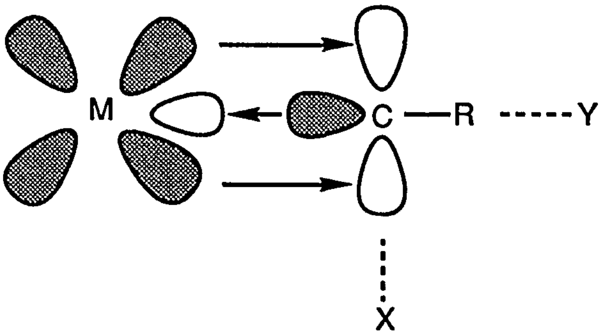
either oxidative addition to the metal atom or electrophilic addition to the thiocarbonyl sulfur atom. Thus, $W(CO)_5(CS)$ reacts with Br_2 and PPh_3 to yield $W(CO)_2(CS)(PPh_3)_2Br_2$.[9] Proton addition to the metal atom in $W(CO)(CS)(dppe)_2$ is observed with $HOSO_2CF_3$ to afford $[HW(CO)(CS)(dppe)_2]SO_3CF_3$.[9] In contrast, $W(CO)(CS)(dppe)_2$ reacts with a variety of Lewis acids to form the sulfur adduct (Scheme 2).[9]

Scheme 2



TUNGSTEN THIOCARBYNE COMPLEXES

The first compounds with a formal metal-carbon triple bond [$(X)(CO)_4M\equiv CR$; X = Cl, Br, I; M = Cr, Mo, W; R = Ph] were reported by E. O. Fischer *et al.* in 1973.[16] The carbyne bond consists of a σ and two π bonds, as shown below (another filled *d* orbital in the *yz* plane and the p_z orbital on carbon are omitted for clarity). In addition to phenylcarbynes, complexes with the following carbyne R groups are now known: alkyl, aryl, alkenyl, alkynyl, hydrido, silyl, amino, phosphino, thio, seleno and halogeno.[17] Addition of electrophiles to terminal thiocarbonyl ligands gives thiocarbynes (eq 4). The thiocarbonyl ligand can be alkylated in complexes that are sufficiently electron-rich (i.e., their ν(CS) values are less than approximately 1200 cm^{-1}). Thus, thiocarbyne complexes have been prepared from the electron-rich thiocarbonyl complexes $(dppe)_2(CO)W\text{-}C\equiv S$[9] (eq 5) and $Bu_4N[L(CO)_2W(CS)]$ (L = Cp (cyclopentadienyl) and $HB(pz)_3$ (hydrotris(1-pyrazolyl)borato) (eq 6).[18]



$$L_nM\text{-}C\equiv S: + E \longrightarrow L_nM\equiv C\text{-}S\text{-}E \qquad (4)$$

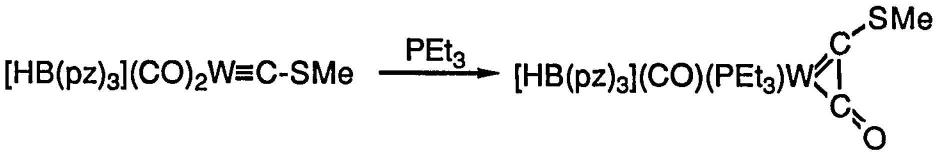
$$(\mathrm{dppe})_2(\mathrm{CO})\mathrm{W\text{-}C{\equiv}S}: \xrightarrow{\mathrm{MeOSO_2F}} [(\mathrm{dppe})_2(\mathrm{CO})\mathrm{W{\equiv}C\text{-}SMe}]\mathrm{SO_3F} \qquad (5)$$

$$\mathrm{L(CO)_2W\text{-}C{\equiv}S^-} \xrightarrow{\mathrm{RX}} \mathrm{L(CO)_2W{\equiv}C\text{-}SR} \quad + \mathrm{X^-} \qquad (6)$$

$$\mathrm{L = Cp;\ RX = 2,4\text{-}(NO_2)_2C_6H_3Cl}$$

$$\mathrm{L = HB(pz)_3;\ RX = MeI,\ EtI,\ 2,4\text{-}(NO_2)_2C_6H_3Cl}$$

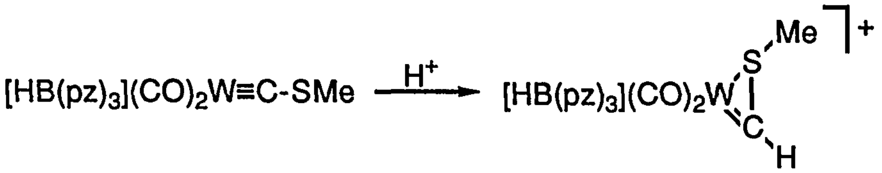
The thiocarbyne complex $[HB(pz)_3](CO)_2W{\equiv}C\text{-}SMe$ is similar in its reactivity to other electron-rich carbynes.[19] Treating the thiocarbyne with PEt_3 causes carbonylation of the carbyne to give the η^2-ketenyl compound (eq 7).[20] This is in contrast to Fischer-type cationic carbynes which are



$$\mathrm{[HB(pz)_3](CO)_2W{\equiv}C\text{-}SMe} \xrightarrow{\mathrm{PEt_3}} \mathrm{[HB(pz)_3](CO)(PEt_3)W}\!\overset{\mathrm{C\text{-}SMe}}{\underset{\mathrm{C{=}O}}{|}} \qquad (7)$$

electrophilic and are frequently observed to undergo attack at the carbyne carbon by a variety of nucleophiles.[21]

Electron-rich carbynes can also be protonated at the carbyne carbon. Thus, when $[HB(pz)_3](CO)_2W{\equiv}C\text{-}SMe$ is treated with $HOSO_2CF_3$, it leads to the C- and S-coordinated thiocarbene complex (eq 8).[22]

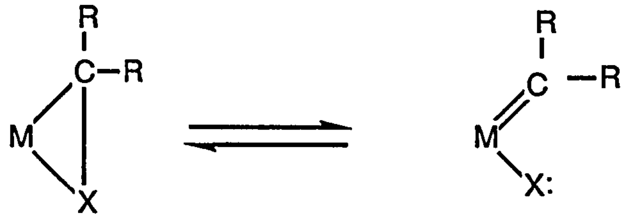


$$\mathrm{[HB(pz)_3](CO)_2W{\equiv}C\text{-}SMe} \xrightarrow{\mathrm{H^+}} \left[\mathrm{[HB(pz)_3](CO)_2W}\!\overset{\mathrm{S\text{-}Me}}{\underset{\mathrm{C\text{-}H}}{|}}\right]^+ \qquad (8)$$

TUNGSTEN THIOCARBENE COMPLEXES

Only a few η^2-thiocarbene complexes, $\{(PPh_3)_2[CN(4-C_6H_4Me)](Cl)Os[\eta^2-C(4-C_6H_4Me)SMe]\}ClO_4$,[23] $\{[HB(pz)_3](CO)_2W-[\eta^2-CH(SMe)]\}SO_3CF_3$[22] and $\{Cp(CO)_2W[\eta^2-C(4-C_6H_4Me)SMe]\}BF_4$,[24] in which the carbene ligand is coordinated to the metal via both the carbene carbon and sulfur atoms, have been reported in the literature. The thiocarbene complex $[HB(pz)_3](CO)_2W[\eta^2-CH(SMe)]^+$ reacts with a variety of nucleophiles to give a range of products (Scheme 3).[20,25] In those reactions where the carbene adduct $[HB(pz)_3](CO)_2W[\eta^2-CH(L)SMe]$ is formed, both the carbon and sulfur atoms remain coordinated to tungsten and the C-S bond remains intact.

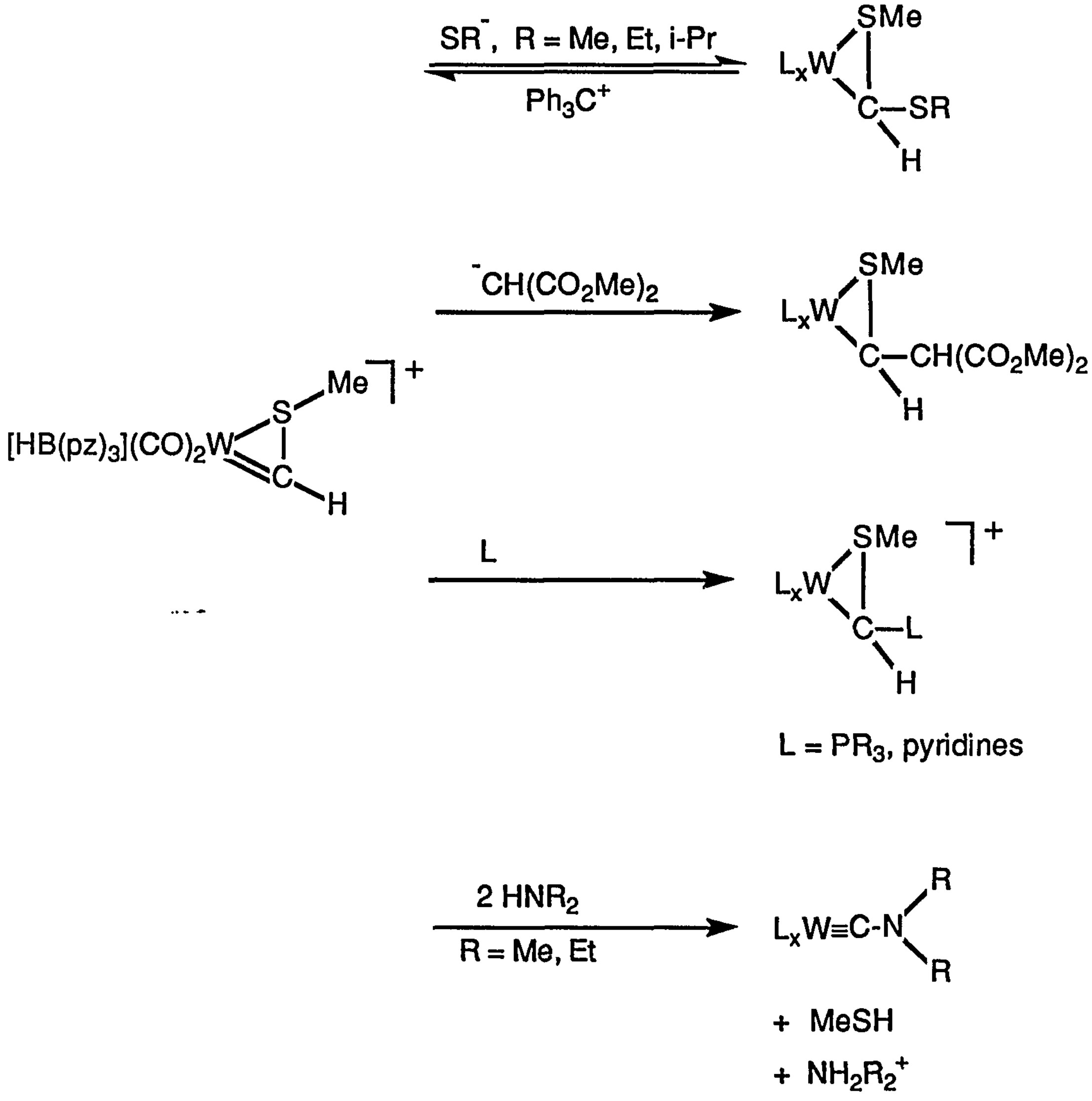
A variety of heteroatom-containing metallacyclopropane complexes of the form **A** in eq 9, where X = OR, SR, NR_2, PR_2, have been reported in the literature.[26] Cleavage of the C-X bond to give the carbene (**B** in eq 9) has been proposed in two cases. Headford and Roper[27a] and Collins and Roper[27b, 27c] have suggested that the reaction (eq 10) of $NaBH_4$ with the metallocyclopropane, **1**, to give **3** is promoted by the partial carbenic character of the CH_2 group as represented by

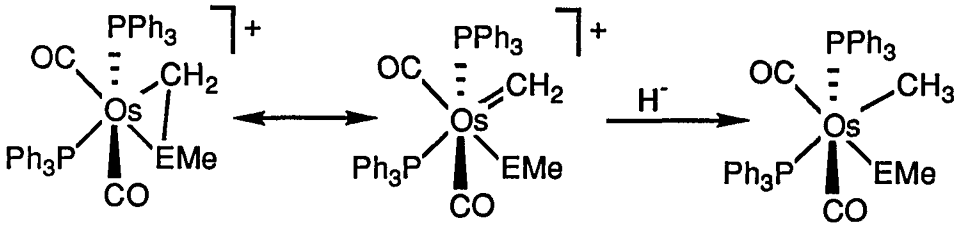


(9)

A **B**

Scheme 3


SR⁻, R = Me, Et, i-Pr
Ph3C+
LxW
SMe
C—SR
H
⁻CH(CO2Me)2
C—CH(CO2Me)2
[HB(pz)3](CO)2W
S
Me
C
H
+
L
C—L
L = PR3, pyridines
2 HNR2
R = Me, Et
LxW≡C-N
R
R
+ MeSH
+ NH2R2+

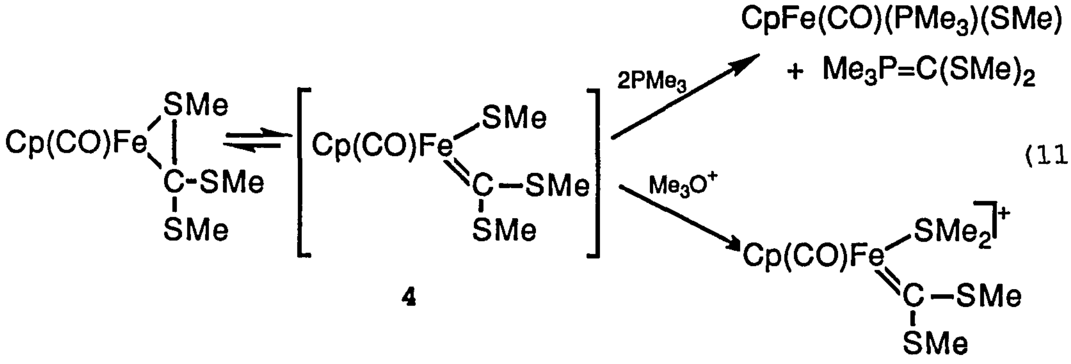


(10)

1 2 3

E = S, Se, Te

resonance form **2**; however, there were no other results which would support this proposal. Temperature-dependent ^{1}H NMR studies of a related iron complex, $Cp(CO)Fe[\eta^2\text{-}C(SMe)_2SMe]$, suggest that it is in rapid equilibrium with a carbene-mercaptide form $Cp(CO)(MeS)Fe{=}C(SMe)_2$.[28] The existence of the carbene-mercaptide form is also supported by chemical evidence (eq 11). Phosphines are known to react with carbenes[29] to form the carbene adducts. The reaction of the iron complex with PMe_3 is thought to occur via PMe_3 attack at the carbene carbon of the carbene mercaptide complex (**4** in eq 11) to give a $Cp(CO)(MeS)Fe[C(SMe)_2PMe_3]$ intermediate.



(11)

Subsequent substitution of the $Me_3PC(SMe)_2$ group by a second PMe_3 results in the formation of the final products. On the other hand, the SMe ligand in **4** can be alkylated to give the dimethylsulfide ligand.

The research contained in this thesis develops much further the novel reactivity of tungsten thiocarbonyl, thiocarbyne and thiocarbene complexes.

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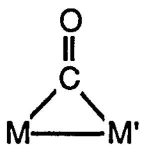
SECTION I. SYNTHESIS AND STRUCTURE OF THE FIRST EXAMPLE OF A FOUR-ELECTRON DONOR, SIDE-ON BRIDGING THIOCARBONYL LIGAND

ABSTRACT

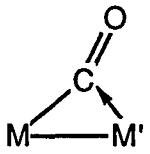
Treatment of $Bu_4N\{[HB(pz)_3](CO)_2W(CS)\}$ with $[(In)Mo(CO)_2(MeCN)_2]BF_4$, where $[HB(pz)_3]$ is the hydrotris(1-pyrazolyl)borato ligand and In is indenyl (η^5-C_9H_7), gives the neutral W-Mo bonded dimer $[HB(pz)_3](CO)_2W(\mu$-$CS)$-$Mo(In)(CO)_2$. A single-crystal X-ray diffraction study shows that the Mo atom obtains an 18-electron configuration by accepting π-electron density from the thiocarbonyl ligand which is also bonded via the carbon to the tungsten. This is the first example of a complex containing a four-electron donating, side-on bridging thiocarbonyl ligand. Studies of the analogous CO complex indicate that CS forms more stable bridged compounds of this type than does CO.

COMMUNICATION

The similarity of carbon monosulfide (CS) to CO has stimulated much interest in the synthesis and reactivity of CS complexes.[1] There are four types of CO bridging ligand:[2] carbon bridging (**A**), semibridging (**B**), in which a filled orbital on M' donates into the empty π^* orbital of the CO ligand, side-on bonding (**C**), involving donation from the filled π-orbital of the CO ligand into an empty orbital on M', and end-on (**D**). Unlike CO, CS has not been found or suggested to be a side-on bridging ligand in any metal complexes. The C-S group is known as a carbon-bridging ligand (e.g., $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CS)$,[3] $MnPt(\mu\text{-}CS)(CO)_2(PMePh_2)_2Cp$),[4] as an end-to-end bridging ligand (e.g., $(dppe)_2(CO)W\text{-}C{\equiv}S\text{-}W(CO)_5$,[5] $(\eta^6\text{-}C_6H_5Me)(CO)_2Cr\text{-}C{\equiv}S\text{-}Cr(CO)_5$)[6] and as a semibridging ligand (e.g., $[HB(pz)_3](CO)W(\mu\text{-}CO)(\mu\text{-}CS)Au(PR_3)$, R = Me, Ph).[7] In all of these types of complexes, the CS ligand has a greater preference for the bridging position than CO. In this communication, we describe the synthesis and structure of $[HB(pz)_3](CO)_2W(\mu\text{-}CS)Mo(CO)_2(In)$ (**I**; In = $\eta^5\text{-}C_9H_7^-$, indenyl;



A



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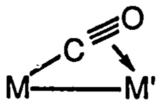
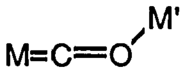


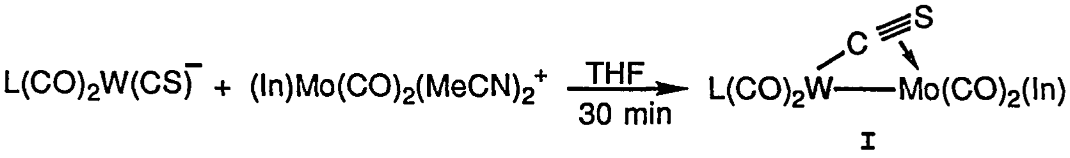
C



D

$HB(pz)_3^-$, hydrotris(1-pyrazolyl)borate), the first example of a complex containing a side-on bridging CS ligand. In this type of bridging situation, the CS ligand also forms a more stable complex than CO.

Addition of one equivalent of $[(In)Mo(CO)_2(MeCN)_2]BF_4$[8] to a THF solution of $Bu_4N\{[HB(pz)_3](CO)_2W(CS)\}$[9] (0.553 mmol) at 25°C produces a brown solution of **I** in 30 min. After the solvent is removed *in vacuo*, the resulting brown residue is recrystallized several times from THF/Et_2O. A final



$L = [HB(pz)_3]$, $In = \eta^5\text{-}C_9H_7$

recrystallization from CH_2Cl_2/hexanes at -20°C gives **I** as a brown crystalline solid in 64% yield. The compound is characterized by elemental analysis, IR, ^1H and $^{13}C\{H\}$ NMR and mass spectra.[10]

An X-ray structure determination[13] of a red-brown single crystal of **I** reveals a side-on bonded bridging CS ligand which is carbon-bonded to tungsten and π-donating to molybdenum as shown in Figure 1. The Mo-C(1) bond distance (2.229(4) Å) is within experimental error of the Mo-C distance (2.237(7) Å) in the side-on bonded isonitrile complex $[Mo_2(\mu\text{-}\eta^2\text{-}(CN\text{-}t\text{-}Bu))(CO)_4Cp_2]$.[14] Moreover, it is ~0.1 Å shorter than the Mo-C distances to the side-on

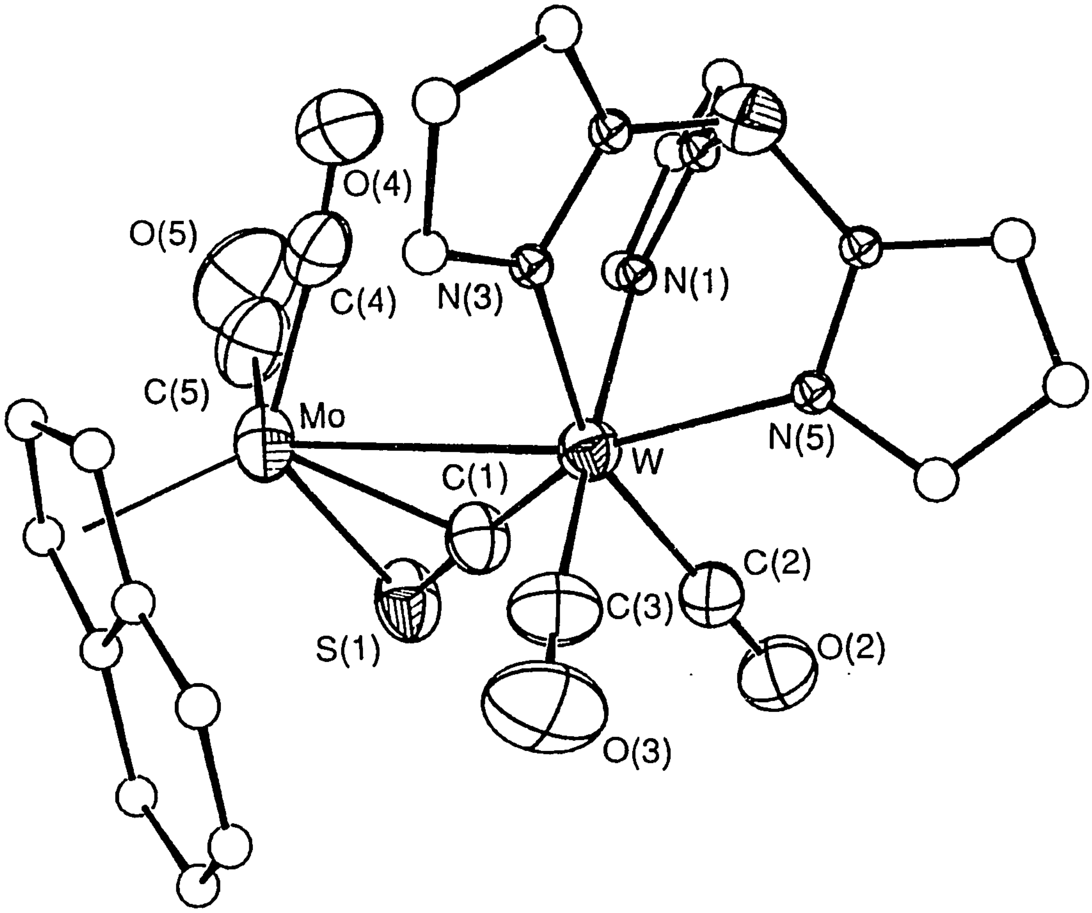


Figure 1. ORTEP plot of $[HB(pz)_3](CO)_2W(\mu\text{-}CS)Mo(CO)_2(In)$, I. Selected bond distances (Å) and angles (deg) are W-Mo = 3.3102(4), W-C(1) = 1.895(5), C(1)-S(1) = 1.640(6), W-N(1) = 2.194(4), W-N(3) = 2.205(4), W-N(5) = 2.229(4), W-C(2) = 2.001(5), W-C(3) = 1.969(5), Mo-C(1) = 2.229(4), Mo-S(1) = 2.511(2), Mo-C(4) = 1.956(6), Mo-C(5) = 1.917(7), W-C(1)-S(1) = 170.8(3), C(1)-W-Mo = 40.2(1), Mo-W-N(5) = 165.4(1).

bridging CO's in $[MoW_2[\mu\text{-}C(4\text{-}C_6H_4Me)]_2(\mu\text{-}CO)_2(CO)_4Cp_2]$ (2.355(12) and 2.348(14) Å).[15] The Mo-S(1) distance (2.511(2) Å) is clearly bonding and compares well with other M-S bond distances in such diverse compounds as $Mo(CO)_3(phen)(\eta^2\text{-}SO_2)$ (2.532(3) Å),[16] $Et_4N[W_2(CO)_{10}(\mu\text{-}SC_6Cl_5)]$ (2.568(4) Å)[17] and $[Na(18\text{-crown-}6)][W(CO)_5(SH)]$ (2.567(5) Å).[18] The W-C(1) distance (1.895(5) Å) is similar to the W-CS bond distances in the semibridging CS complex $[HB(pz)_3](CO)W(\mu\text{-}CO)(\mu\text{-}CS)Au(PPh_3)$ (1.911(7) Å)[7] and the terminal CS complex *trans*-$[W(CO)_4(CS)(CNCy)]$ (1.944(19) Å).[19] The C(1)-S(1) distance (1.640(6) Å) is ~0.1 Å longer than the C-S distances in the terminal thiocarbonyl complexes $[(\eta^5\text{-}C_5H_4Me)Mn(CS)(NO)I]$ (1.513(6) Å),[20] *trans*-$[RhCl(CS)(PPh_3)_2]$ (1.54(1) Å)[21] and *trans*-$[W(CO)_4(CS)(CNCy)]$ (1.56(2) Å).[19] This bond lengthening may be attributed to the donation of electron density from a CS π-bonding orbital to an empty orbital on molybdenum. The W-Mo bond distance (3.3102(4) Å) is ~0.1 Å longer than the M-M bond distances in $[CpM(CO)_3]_2$ (M = Mo, W; 3.235(1) and 3.222(1) Å, respectively)[22] and $[Mo_2(\mu\text{-}\eta^2\text{-}(CN\text{-}t\text{-}Bu))(CO)_4Cp_2]$ (3.2152(10) Å).[14] A similar lengthening of the W-Au bond was observed in the semibridging CS complex $[HB(pz)_3](CO)W(\mu\text{-}CO)(\mu\text{-}CS)Au(PPh_3)$ (2.824(4) Å)[7] as compared with that in the semibridging CO complex $Cp(CO)W(\mu\text{-}CO)_2Au(PPh_3)$ (2.698(3) Å)[15].

To compare the bond distances and angles of the side-on bonded CS ligand in **I** with those of the semibridging CS complex $[HB(pz)_3](CO)W(\mu\text{-}CO)(\mu\text{-}CS)Au(PPh_3)$[7], these data are summarized in Figure 2. In both complexes, the bridging CS carbon is bonded to both metals, although somewhat more strongly to the tungsten atom. One the other hand, the sulfur in the semibridging CS does not bond to either metal, but the side-on CS sulfur is within normal bonding distance of the molybdenum. It is the bonding of the sulfur atom which clearly distinguishes these two types of bridging CS ligands.

The side-on carbonyl analog of **I**, $[HB(pz)_3](CO)_2W(\mu\text{-}CO)\text{-}Mo(CO)_2(In)$, was observed by IR spectroscopy (ν(CO) 1957m, 1884s, 1827s, 1815sh, 1630vw (br) cm^{-1}) when a CH_2Cl_2 solution of $Et_4N\{[HB(pz)_3]W(CO)_3\}$[23] was treated with $[(In)Mo(CO)_2(MeCN)_2]BF_4$.[8] Attempts to grow single crystals of the complex were unsuccessful because it decomposed in solution in ~8 h. This result suggests that CO is a less stable side-on bridging ligand than CS. Also the fact that complex **I** contains a side-on bonded CS rather than CO indicates that CS has a greater preference for a side-on bridging site than CO. Thus, in all four types of bridging situations (**A**, **B**, **C** and **D**), the CS is favored over CO as the bridging ligand.

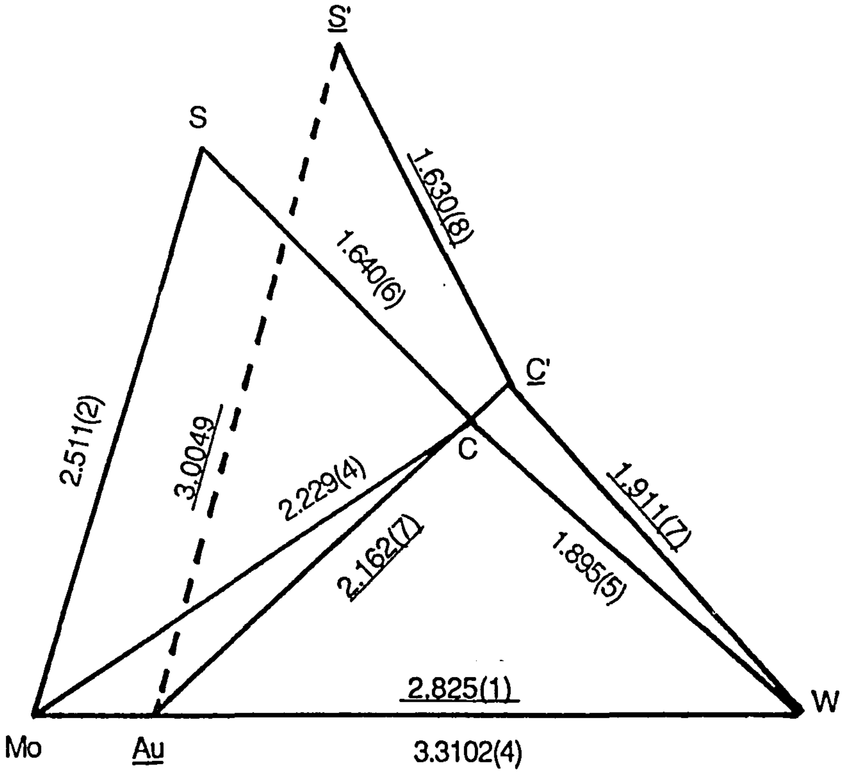


Figure 2. Comparison of bond distances (Å) and angles (deg) in the side-on bonded CS in I with the semibridging CS in [HB(pz)3](CO)W(μ-CO)(μ-CS)Au(PPh3). Selected bond angles are C-W-Mo = 40.2(1), C'-W-Au = 49.9(2), W-C-S = 170.8(3), W-C'-S' = 165.9(5).

ACKNOWLEDGMENT

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10. $[HB(pz)_3](CO)_2W(\mu\text{-}CS)Mo(CO)_2(In)$, **I:** IR (THF): ν(CO) 1984m, 1938vs, 1893m, 1862m cm^{-1}. ν(CS) is not

observed. ^{1}H NMR (CD_2Cl_2) δ 7.72(d, J = 2.2, H3 and H5 of pz); 7.19, 7.06 and 6.77 (m, H4-7 of In); 6.47, 5.91 (m, H1 and H3 of In); 6.28 (s, H4 of pz); 5.56 (t, J = 2.8, H2 of In). The assignments for In and $HB(pz)_3$ are based on those for $InRh(C_2H_4)_2$[11] and $[HB(pz)_3](CO)_2W{\equiv}CMe$[12], respectively. ^{13}C NMR δ (CD_2Cl_2) 285.8 (CS); 243.2, 242.8, 223.7, 221.5 (CO); 145.8 (C3 of pz); 136.4 (C5 of pz); 106.5 (C4 of pz); 127.2, 126.6, 124.6, 124.4, 119.1, 117.8, 93.9, 82.8, 78.5 (In). EIMS (70 eV): m/e 764 (M^+), 708 (M^+-2CO), 680 (M^+-3CO). Anal. Calcd for $C_{23}H_{17}BMoN_6O_4SW$: C, 36.15; H, 2.24; N, 11.00. Found: C, 36.10; H, 2.33; N, 10.90.

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13. Crystallographic data for **I**: mol wt 764.09; triclinic, space group $P\bar{1}$; a = 11.062(2) Å, b = 13.904(2) Å, c = 8.889(2) Å, α = 97.43(2)°, β = 108.58(2)°, γ = 78.03(1)°, V = 1264.8(8) $Å^3$, ρ_{calcd} = 2.006 g/cm^3 for Z = 2 at 22 ± 1°C, μ = 52.47 cm^{-1} (Mo Kα). Diffraction data were collected at 22 ± 1°C using an Enraf-Nonius CAD4 automated diffractometer. A total of 6088 reflections were collected. Of the 5788 unique data, 5197 were considered observed, having $F_{obs}^2 > 3\sigma(F_{obs}^2)$.

The positions of the metal atoms and most of the coordination sphere atoms were given by an automated Patterson interpretation method (SHELXS-86, G. M. Sheldrick, Institut für Anorganische Chemie der Universität, Göttingen, F.R.G.). The remainder of the non-hydrogen atoms were located in difference Fourier maps following least-squares refinement of the known atoms. $R = 0.0358$ and $R_w = 0.0495$.

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SUPPLEMENTARY MATERIAL

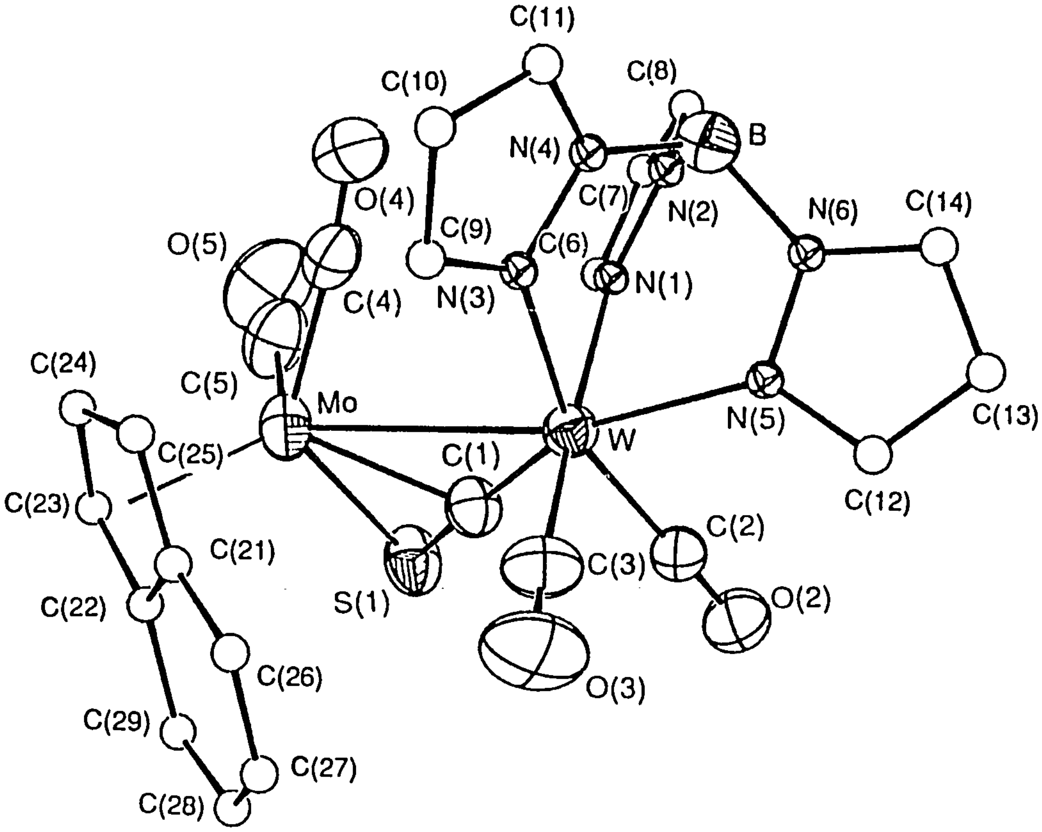

Figure 1. ORTEP drawing of $[HB(pz)_3](CO)_2W(\mu\text{-}CS)Mo(CO)_2(In)$ (I), with major ellipsoids scaled to enclose 50% of the electron density. The ring carbon and nitrogen atoms have been drawn as arbitrarily-sized spheres for clarity.

Table 1. Crystal Data for $[HB(pz)_3](CO)_2W(\mu\text{-}CS)Mo(CO)_2(In)$ (**I**)

Formula	$WMoSO_4N_6C_{23}BH_{17}$
Formula weight	764.09
Space group	P1
a, Å	11.062(2)
b, Å	13.904(2)
c, Å	8.889(2)
α, deg	97.43(2)
β, deg	108.58(2)
γ, deg	78.08(1)
V, $Å^3$	1264.8(8)
Z	2
d_{calc}, g/cm^3	2.006
Crystal size, mm	0.25 x 0.28 x 0.50
$\mu(MoK\alpha)$, cm^{-1}	52.47
Data collection instrument	Enraf-Nonius
Radiation (monochromated in incident beam)MoK_α	MoK_α (λ = 0.71073 Å)
Orientation reflections, number, range (2θ)	25, 20-35°
Temperature, °C	22 ± 1
Scan method	ω-2θ
Data collection range, 2θ, deg	0-55

No. unique data, total:	5788
with $F_o^2 > 3\sigma(F_o^2)$:	5197
Number of parameters refined	335
Trans. factors, max., min. (psi-scans)	1.000, 0.930
R^a	0.0358
$R_w{}^b$	0.0495
Quality-of-fit indicator[c]	1.897
Largest shift/esd, final cycle	0.03
Largest peak, e/Å^3	2.57

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

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

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

Table 2. Positional Parameters and Their Estimated Standard Deviations for $[HB(pz)_3](CO)_2W-(\mu-CS)Mo(CO)_2(In)$ (I)[a]

Atom	x	y	z	B(Å^2)
W	0.16864(1)	0.31708(1)	0.19788(2)	2.601(3)
Mo	0.46090(4)	0.20020(3)	0.19493(6)	3.495(9)
S(1)	0.4379(1)	0.3718(1)	0.1167(2)	4.10(3)
O(2)	0.1208(4)	0.5421(3)	0.1476(6)	4.7(1)
O(3)	0.2339(5)	0.3814(4)	0.5586(5)	6.4(1)
O(4)	0.2721(4)	0.0567(3)	0.0226(6)	5.7(1)
O(5)	0.4921(6)	0.1330(5)	-0.1346(7)	8.3(2)
N(1)	0.0946(3)	0.2677(3)	-0.0542(5)	2.97(8)
N(2)	-0.0089(4)	0.2209(3)	-0.1102(5)	3.43(9)
N(3)	0.1225(4)	0.1778(3)	0.2393(5)	3.22(8)
N(4)	0.0171(4)	0.1421(3)	0.1396(5)	3.45(8)
N(5)	-0.0417(4)	0.3586(3)	0.1759(5)	3.36(8)
N(6)	-0.1275(4)	0.3032(3)	0.0804(5)	3.42(9)
C(1)	0.3213(4)	0.3423(4)	0.1685(6)	3.20(9)
C(2)	0.1375(4)	0.4608(3)	0.1640(7)	3.4(1)
C(3)	0.2162(5)	0.3562(4)	0.4272(6)	4.0(1)
C(4)	0.3360(5)	0.1128(4)	0.0915(7)	4.2(1)
C(5)	0.4814(6)	0.1608(5)	-0.0115(8)	5.3(2)
C(6)	0.1302(5)	0.2801(4)	-0.1790(6)	3.9(1)
C(7)	0.0465(7)	0.2425(5)	-0.3183(7)	5.0(1)
C(8)	-0.0389(6)	0.2070(5)	-0.2689(8)	4.8(1)

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

Table 2 (continued)

Atom	x	y	z	B(Å^2)
C(9)	0.1744(6)	0.1179(4)	0.3572(7)	4.2(1)
C(10)	0.1045(7)	0.0437(4)	0.3389(8)	5.2(1)
C(11)	0.0058(5)	0.0610(4)	0.2009(7)	4.3(1)
C(12)	-0.1122(5)	0.4399(4)	0.2274(7)	4.4(1)
C(13)	-0.2433(5)	0.4366(5)	0.1609(8)	4.8(1)
C(14)	-0.2487(5)	0.3499(5)	0.0723(7)	4.4(1)
C(21)	0.5631(7)	0.2043(6)	0.4851(8)	6.0(2)
C(22)	0.6489(6)	0.2347(6)	0.4216(8)	6.1(2)
C(23)	0.6816(6)	0.1600(7)	0.315(1)	7.6(2)
C(24)	0.6261(8)	0.0822(6)	0.317(1)	8.2(2)
C(25)	0.5416(7)	0.1108(5)	0.4171(9)	7.1(2)
C(26)	0.5158(9)	0.2667(9)	0.5986(9)	8.7(3)
C(27)	0.551(1)	0.355(1)	0.637(1)	12.7(4)
C(28)	0.631(1)	0.3864(8)	0.580(1)	10.4(3)
C(29)	0.6848(8)	0.3335(8)	0.470(1)	9.2(2)
B	-0.0793(5)	0.2018(4)	0.0033(8)	3.8(1)

Table 3. Bond Distances for $[HB(pz)_3](CO)_2W(\mu\text{-}CS)\text{-}Mo(CO)_2(In)$ (**I**), (Å)[a]

W-Mo	3.3102(4)	C(10)-C(9)	1.38(1)
W-N(1)	2.197(4)	C(10)-C(11)	1.36(8)
W-N(3)	2.205(4)	C(11)-N(4)	1.358(8)
W-N(5)	2.229(4)	C(13)-C(12)	1.388(7)
W-C(1)	1.895(5)	C(13)-C(14)	1.353(9)
W-C(2)	2.001(5)	C(14)-N(6)	1.347(6)
W-C(3)	1.969(5)	B-N(2)	1.534(9)
Mo-S(1)	2.511(2)	B-N(4)	1.537(7)
Mo-C(1)	2.229(4)	B-N(6)	1.554(7)
Mo-C(4)	1.956(6)	Mo-C(21)	2.463(6)
Mo-C(5)	1.917(7)	Mo-C(22)	2.471(6)
S(1)-C(1)	1.640(6)	Mo-C(23)	2.310(6)
N(1)-N(2)	1.359(6)	Mo-C(24)	2.273(8)
N(1)-C(6)	1.330(8)	Mo-C(25)	2.301(8)
N(3)-N(4)	1.364(5)	C(21)-C(22)	1.40(1)
N(3)-C(9)	1.328(7)	C(21)-C(25)	1.40(1)
N(5)-N(6)	1.354(5)	C(21)-C(26)	1.40(1)
N(5)-C(12)	1.351(7)	C(22)-C(23)	1.39(1)
C(2)-O(2)	1.128(6)	C(22)-C(29)	1.48(1)
C(3)-O(3)	1.141(7)	C(23)-C(24)	1.36(1)
C(4)-O(4)	1.146(7)	C(24)-C(25)	1.45(1)
C(5)-O(5)	1.146(9)	C(26)-C(27)	1.33(2)
C(7)-C(6)	1.402(8)	C(27)-C(28)	1.32(2)
C(7)-C(8)	1.36(1)	C(28)-C(29)	1.36(1)
C(8)-N(2)	1.340(8)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 4. Bond Angles for $[HB(pz)_3](CO)_2W(\mu\text{-}CS)Mo(CO)_2(In)$ (I), (deg)^a

Mo-W-N(1)	88.7(1)	S(1)-Mo-C(4)	123.8(2)
Mo-W-N(3)	89.6(1)	S(1)-Mo-C(5)	84.4(2)
Mo-W-N(5)	165,4(1)	C(1)-Mo-C(4)	97.7(2)
Mo-W-C(2)	113.5(1)	C(1)-Mo-C(5)	105.9(2)
Mo-W-C(3)	96.3(2)	C(4)-Mo-C(5)	73.8(3)
W-Mo-C(1)	33.3(1)	Mo-S(1)-C(1)	60.7(2)
W-Mo-C(4)	71.3(2)	W-N(1)-N(2)	122.2(3)
W-Mo-C(5)	115.5(2)	W-N(1)-C(6)	130.6(3)
W-Mo-S(1)	73.06(3)	N(2)-N(1)-C(6)	107.0(4)
N(1)-W-N(3)	83.8(2)	W-N(3)-N(4)	120.9(3)
N(1)-W-N(5)	82.7(1)	W-N(3)-C(9)	132.2(3)
N(1)-W-C(1)	91.7(2)	N(4)-N(3)-C(9)	106.7(4)
N(1)-W-C(2)	96.2(2)	W-N(5)-N(6)	120.8(3)
N(1)-W-C(3)	172.9(2)	W-N(5)-C(12)	132.3(3)
N(3)-W-N(5)	77.8(1)	N(6)-N(5)-C(12)	106.5(4)
N(3)-W-C(1)	129.8(2)	W-C(1)-Mo	106.5(2)
N(3)-W-C(2)	156.8(2)	W-C(1)-S(1)	170.8(3)
N(3)-W-C(3)	91.1(2)	M0-C(1)-S(1)	79.3(2)
N(5)-W-C(1)	151.2(2)	W-C(2)-O(2)	178.8(5)
N(5)-W-C(2)	79.2(2)	W-C(3)-O(3)	174.8(5)
N(5)-W-C(3)	91.3(2)	Mo-C(4)-O(4)	172.7(6)
C(1)-W-C(2)	73.3(2)	Mo-C(5)-O(5)	176.8(7)
C(1)-W-C(3)	95.4(2)	N(1)-N(2)-C(8)	109.2(5)
C(2)-W-C(3)	86.5(2)	N(1)-N(2)-B	120.1(4)
S(1)-Mo-C(1)	39.9(1)	C(8)-N(2)-B	130.4(5)
N(3)-N(4)-B	121.0(4)	C(4)-Mo-C(24)	96.9(3)
N(3)-N(4)-C(11)	108.3(4)	C(4)-Mo-C(25)	91.4(3)

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[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 4 (continued)

C(11)-N(4)-B	129.7(4)	C(5)-Mo-C(21)	147.1(2)
N(5)-N(6)-C(14)	109.2(4)	C(5)-Mo-C(22)	120.1(3)
N(1)-C(6)-C(7)	109.6(6)	C(5)-Mo-C(23)	91.4(3)
C(6)-C(7)-C(8)	105.0(6)	C(5)-Mo-C(24)	93.8(3)
N(2)-C(8)-C(7)	109.1(5)	C(5)-Mo-C(25)	127.3(3)
N(3)-C(9)-C(10)	111.3(5)	C(21)-Mo-C(22)	33.0(3)
C(9)-C(10)-C(11)	104.6(6)	C(21)-Mo-C(23)	56.2(3)
N(4)-C(11)-C(10)	109.1(5)	C(21)-Mo-C(24)	56.9(3)
N(5)-C(12)-C(13)	109.6(5)	C(21)-Mo-C(25)	33.9(3)
C(12)-C(13)-C(14)	105.4(5)	C(22)-Mo-C(23)	33.5(3)
N(6)-C(14)-C(13)	109.2(5)	C(22)-Mo-C(24)	56.0(3)
N(2)-B-N(4)	109.7(4)	C(22)-Mo-C(25)	56.8(3)
N(2)-B-N(6)	107.4(5)	C(23)-Mo-C(24)	34.4(4)
N(4)-B-N(6)	106.5(4)	C(23)-Mo-C(25)	59.2(3)
C(1)-Mo-C(4)	97.7(2)	C(24)-Mo-C(25)	37.0(3)
C(1)-Mo-C(5)	105.9(2)	C(22)-C(21)-C(25)	108.9(7)
C(1)-Mo-C(21)	101.5(2)	C(22)-C(21)-C(26)	119.5(8)
C(1)-Mo-C(22)	104.6	C(25)-C(21)-C(26)	131.7(9)
C(1)-Mo-C(23)	133.2(3)	C(21)-C(22)-C(23)	107.9(7)
C(1)-Mo-C(24)	158.1(3)	C(21)-C(22)-C(29)	120.0(7)
C(1)-Mo-C(25)	126.3(2)	C(23)-C(22)-C(29)	132.2(9)
C(4)-Mo-C(5)	73.8(3)	C(22)-C(23)-C(24)	109.1(9)
C(4)-Mo-C(21)	120.2(3)	C(23)-C(24)-C(25)	108.5(8)
C(4)-Mo-C(22)	148.0(3)	C(21)-C(25)-C(24)	105.2(8)
C(4)-Mo-C(23)	129.0(3)	C(21)-C(26)-C(27)	118.(1)
C(26)-C(27)-C(28)	124.(1)	C(22)-C(29)-C(28)	114.(1)
C(27)-C(28)-C(29)	124.(1)		

Table 5. Least-Squares Planes for $[HB(pz)_3](CO)_2W(\mu\text{-}CS)Mo(CO)_2(In)$ (I)

The equation of the plane is of the form:

$$A^*x + B^*y + C^*z - D = 0$$

where A, B, C and D are constants and x, y and z are orthogonalized coordinates.

Plane No.	A	B	C	D	Atom	x	y	z
1	-0.0993	-0.1663	-0.9811	-2.5506	W	2.2193	4.1992	1.6635
					Mo	5.1238	2.6111	1.6388
					C(1)	4.0612	4.5606	1.4158
2	-0.2090	-0.2228	-0.9522	-3.2129	Mo	5.1238	2.6111	1.6388
					C(1)	4.0612	4.5606	1.4158
					S(1)	5.5859	4.9900	0.9807

Dihedral Angles Between Planes:

Plane No.	Plane No.	Dihedral Angle
1	2	7.27 ± 0.59

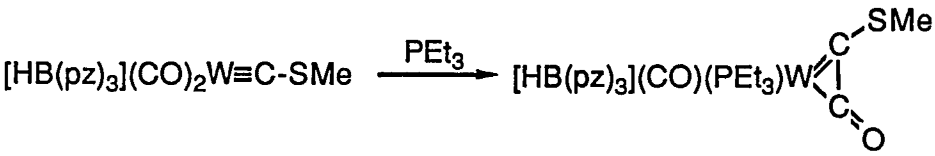
SECTION II. SYNTHESIS AND REACTIONS OF THE CATIONIC THIOCARBYNE $[HC(pz)_3](CO)_2W{\equiv}C{-}SMe^+$. REACTIONS OF THE THIOCARBENE $[HC(pz)_3](CO)_2W[\eta^2{-}CH(SMe)]^{2+}$ WITH NUCLEOPHILES

ABSTRACT

The thiocarbonyl complex $[HC(pz)_3](CO)_2W(CS)$ **(I)** is prepared by reaction of *trans*-$IW(CO)_4(CS)^-$ with $HC(pz)_3$, tris(1-pyrazolyl)methane. The nucleophilic sulfur atom of the CS ligand is methylated with Me_3O^+ to give the thiocarbyne $[HC(pz)_3](CO)_2W{\equiv}C{-}SMe^+$ **(II)**. Reaction of the carbyne **(II)** with phosphorus nucleophiles (PR_3) gives the η^2-ketenyl derivatives $[HC(pz)_3](CO)(PR_3)\overline{W[C(O)C}SMe]^+$. Methylation of $[HC(pz)_3](CO)(PMe_3)\overline{W[C(O)C}SMe]^+$ at the ketenyl oxygen atom yields the acetylene complex $[HC(pz)_3](CO)(PMe_3)$-$W(MeOC{\equiv}CSMe)^{2+}$. The title thiocarbene complex $[HC(pz)_3](CO)_2W[\eta^2{-}CH(SMe)]^{2+}$ **(III)** is prepared by protonation of the carbyne carbon atom in $[HC(pz)_3](CO)_2W{\equiv}C{-}SMe^+$ with $HBF_4{\bullet}Et_2O$. Reactions of **III** with PR_3, SR^-, and $NaBH_4$ nucleophiles give the carbene adducts $[HC(pz)_3](CO)_2W$-$[\eta^2{-}CH(L)SMe]^{2+,\ 1+}$. These studies show that the reactivity of $[HC(pz)_3](CO)_2W{\equiv}C{-}SMe^+$ **(II)** is similar to that of electron-rich carbynes like $[HB(pz)_3](CO)_2W{\equiv}C{-}SMe$ rather than to the reactivity of cationic Fischer carbynes.

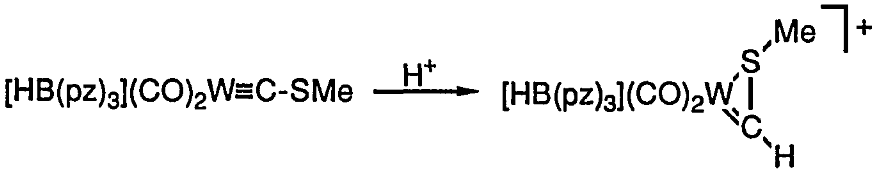
INTRODUCTION

In recent years, the preparations and reactions of thiocarbene[1] and thiocarbyne[2] complexes have been studied extensively in this laboratory. The thiocarbyne complex [HB(pz)$_3$](CO)$_2$W≡C-SMe,[3] where HB(pz)$_3^-$ is the hydrotris(1-pyrazolyl)borato ligand, is similar in its reactivity to other electron rich carbynes.[4] Treating the thiocarbyne with PEt$_3$ causes carbonylation of the carbyne to give the η^2-ketenyl compound (eq 1).[5] Electron-rich carbynes can also be



$$[HB(pz)_3](CO)_2W{\equiv}C\text{-}SMe \xrightarrow{PEt_3} [HB(pz)_3](CO)(PEt_3)W[\eta^2\text{-}C(SMe)CO] \quad (1)$$

protonated at the carbyne carbon. Clark and coworkers[6] reported the reaction of Os[≡C(4-C$_6$H$_4$Me)](Cl)(CO)(PPh$_3$)$_2$ with HCl that resulted in the formation of Os[=CH(4-C$_6$H$_4$Me)]-(Cl)$_2$(CO)(PPh$_3$)$_2$. Similarly, reactions of Cp(CO)$_2$W≡CR (R = Me, tolyl) with HI give neutral carbenes Cp(CO)$_2$IW=CHR.[7] When [HB(pz)$_3$](CO)$_2$W≡C-SMe is treated with HOSO$_2$CF$_3$, it leads to the C- and S-coordinated thiocarbene complex (eq 2).[8] The



$$[HB(pz)_3](CO)_2W{\equiv}C\text{-}SMe \xrightarrow{H^+} [HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]^+ \quad (2)$$

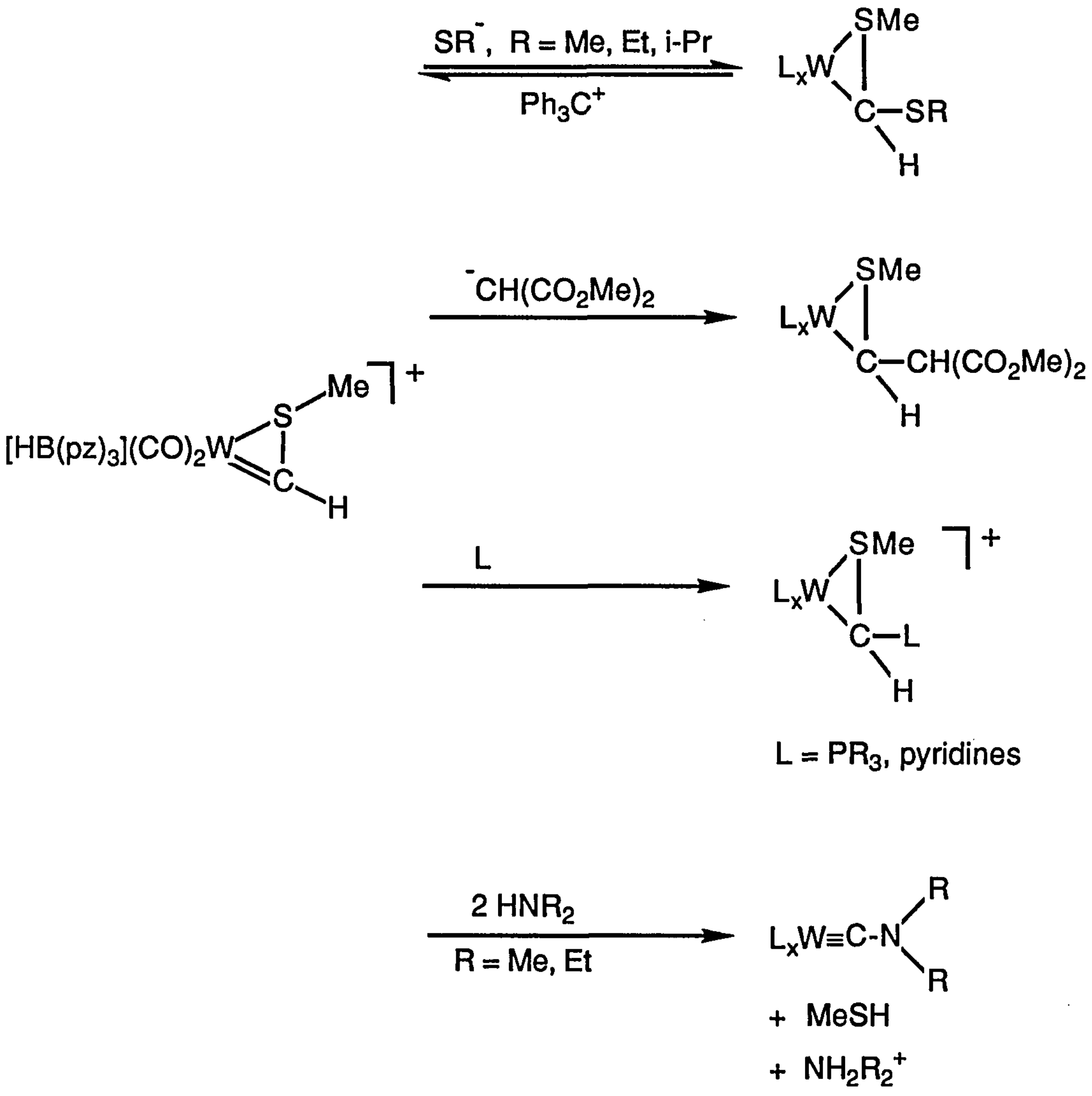
η^2-thiocarbene [HB(pz)$_3$](CO)$_2$W [η^2-CH(SMe)]$^+$ is attacked at the carbene carbon by a variety of nucleophiles (Scheme 1).[5,9]

In contrast, Fischer-type cationic carbynes are electrophilic and are frequently observed to undergo attack at the carbyne carbon by a variety of nucleophiles.[10] The carbyne complex $(C_6H_6)(CO)_2Cr{\equiv}C(Ph)^+$ reacts with PMe_3 to produce the ylide (eq 3).[11] Other examples of nucleophilic addition are the reactions of $Cp(CO)_2M{\equiv}C\text{-}Ph^+$ (M = Mn, Re)

$$(C_6H_6)(CO)_2Cr{\equiv}C\text{-}Ph^+ \xrightarrow{PMe_3} (C_6H_6)(CO)_2Cr{=}C(Ph)(PMe_3)^+ \quad (3)$$

with F^-, Cl^-, Br^-, I^- and $C_{10}H_7Se^-$ to give the corresponding neutral carbene compounds $Cp(CO)_2M[{=}C(Nu)(Ph)]$.[12] In this paper, we describe the preparation and reactions of the cationic carbyne $[HC(pz)_3](CO)_2W{\equiv}C\text{-}SMe^+$ (an analog of the neutral $[HB(pz)_3](CO)_2W{\equiv}C\text{-}SMe$), where $HC(pz)_3$ is the tris(1-pyrazolyl)methane ligand. One goal of this study was to determine whether $[HC(pz)_3](CO)_2W{\equiv}C\text{-}SMe^+$ reacts like a cationic Fischer-type carbyne or like electron-rich carbynes such as $[HB(pz)_3](CO)_2W{\equiv}C\text{-}SMe$.

Scheme 1


SR$^-$, R = Me, Et, i-Pr
Ph$_3$C$^+$
$^-$CH(CO$_2$Me)$_2$
L
2 HNR$_2$
R = Me, Et
[HB(pz)$_3$](CO)$_2$W
SMe
L$_x$W
C—SR
H
C—CH(CO$_2$Me)$_2$
C—L
L = PR$_3$, pyridines
L$_x$W≡C-N
R
+ MeSH
+ NH$_2$R$_2$$^+$

EXPERIMENTAL

General Procedures

All reactions, filtrations, distillations and recrystallizations were carried out under an atmosphere of prepurified N_2 using standard inert atmosphere and Schlenk techniques[13,14] unless stated otherwise. Hexanes and CH_2Cl_2 were distilled from CaH_2. Diethyl ether was distilled from Na/benzophenone. Nitromethane was distilled from $CaCl_2$. Reagent grade acetone was stored over type 4A molecular sieves and degassed with N_2 before use. Reactions were carried out at room temperature unless stated otherwise. All solutions were air-sensitive, and the products slowly decomposed in solution even when under N_2. As solids, the products could be handled in air; however, they were best stored under an atmosphere of N_2 or Ar. The products were characterized by comparing their IR (Table 1), ^{1}H NMR (Table 2), and $^{13}C\{H\}$ NMR (Table 3) spectra with those of their hydrotris(pyrazolyl)borato analogs.[5,9] In many cases, elemental analyses could not be obtained because the compounds partially decompose during recrystallization. Fast precipitation of the products by adding large amounts of Et_2O often trapped impurities in the solids.

Infrared spectra were obtained using a Perkin-Elmer 681 spectrophotometer, and spectra were referenced to the 1601.0 cm^{-1} band of polystyrene. The ^{1}H and $^{13}C\{H\}$ NMR spectra were recorded on a Nicolet-NT-300 MHz spectrometer, using the deuterated solvent as the internal reference. Fast atom bombardment (FAB, 3-nitrobenzyl alcohol matrix) mass spectra were obtained using a Kratos MS-50 spectrometer. Elemental microanalyses were performed by Galbraith Laboratories Inc., Knoxville, TN. Conductivity measurements were made by using a Markson 4402 conductivity meter and dip cell.

The compounds $Bu_4N[IW(CO)_4(CS)]$[15] and NaSR[9] were prepared by using previously described procedures. The ligand $HC(pz)_3$ was purchased from Columbia Organic Chemicals. All other chemicals were used as received from commercial sources.

$[HC(pz)_3](CO)_2W(CS)$, I

A solution of $Bu_4N[IW(CO)_4(CS)]$ (3.43 g, 4.84 mmol) in acetone (100 mL) was cooled to 0°C. Silver tetrafluoroborate (0.941 g, 4.83 mmol) was then added and the mixture stirred for 1 h. The resulting orange solution was filtered under vacuum using a coarse Schlenk frit containing Celite (2 x 7 cm) into a flask containing a solution of $HC(pz)_3$ (1.04 g, 4.85 mmol) in acetone (20 mL). Refluxing for 5 h caused a gold precipitate to form. The solution was then cooled to room temperature and the precipitate collected by suction filtration and washed with acetone (30 mL). Yield: 1.78 g, (74%). This complex was insoluble in all organic solvents

Table 1. IR Data for the complexes in CH_2Cl_2 Solvent

complex	IR $\nu(CO)$, cm^{-1}
$[HC(pz)_3](CO)_2W{-}C{\equiv}S$, **I**	1885 s, 1794 s[a]
$\{[HC(pz)_3](CO)_2W{\equiv}CSMe\}PF_6$, **II**-$PF_6$	1991 s, 1906 s
$\{[HC(pz)_3](CO)_2W[\eta^2{-}CH(SMe)]\}(BF_4)_2$, **III**-$2BF_4$	2079 s, 2010 s[b]
$\{[HC(pz)_3](CO)(PMe_3)W[C(O)CSMe]\}BF_4$, **IV**-$BF_4$	1902 s, 1680 m
$\{[HC(pz)_3](CO)(PEt_3)W[C(O)CSMe]\}BF_4$, **V**-$BF_4$	1881 s, 1665 m
$\{[HC(pz)_3](CO)(PEt_2H)W[C(O)CSMe]\}BF_4$, **VI**-$BF_4$	1905 s, 1680 m
$\{[HC(pz)_3](CO)(PMe_2Ph)W[C(O)CSMe]\}BF_4$, **VII**-$BF_4$	1904 s, 1683 m
$\{[HC(pz)_3](CO)(PMe_3)W(\eta^2{-}MeOC{\equiv}CSMe)\}(BF_4)_2$, **VIII**-$2BF_4$	1970 s[b]
$\{[HC(pz)_3](CO)_2W[\eta^2{-}CH(PPh_3)SMe]\}(BF_4)_2$, **IX**-$2BF_4$	1960 s, 1855 s[b]
$\{[HC(pz)_3](CO)_2W[\eta^2{-}CH(PMePh_2)SMe]\}(BF_4)_2$, **X**-$2BF_4$	1951 s, 1853 s
$\{[HC(pz)_3](CO)_2W[\eta^2{-}CH(P(OMe)_3)SMe]\}(BF_4)_2$, **XI**-$2BF_4$	1962 s, 1848 s[b]
$\{[HC(pz)_3](CO)_2W[\eta^2{-}CH_2SMe]\}BF_4$, **XII**-$BF_4$	1938 s, 1814 s[b]
$\{[HC(pz)_3](CO)_2W[\eta^2{-}CH(SMe)SMe]\}BF_4$, **XIII**-$BF_4$	1938 s, 1827 vs[b]
$\{[HC(pz)_3](CO)_2W[\eta^2{-}CH(S{-}t{-}Bu)SMe]\}BF_4$, **XIV**-$BF_4$	1937 s, 1828 s
$\{[HC(pz)_3](CO)_2W[\eta^2{-}CH(SPh)SMe]\}BF_4$, **XV**-$BF_4$	1955 s, 1830 vs[b]

[a] Nujol Mull; ν_{CS} 1178 cm^{-1}.

[b] In $MeNO_2$.

Table 2. ^{1}H NMR Data for the Complexes in CD_3CN Solvent at Room Temperature[a]

complex	HC(pz)$_3$	H3 of pz[b]	H5 of pz[b]	H4 of pz[b]	other
II-PF_6	8.89	8.28 (br)	8.02 (br)	6.58 (br)	2.79 (SMe)
III-[c] $2BF_4$	9.57	8.64 (m)	8.25 (d)	6.58 (m)	13.15 (WCH)[d], 2.57 (SMe)
IV-BF_4	9.09	8.05 (d), 8.42 (d), 8.39 (d) 8.33 (d), 8.26 (d), 7.39 (d)		6.76 (t)[e] 6.64 (t)[e] 6.42 (t)[e]	2.73 (SMe), 1.36 (PMe_3)[f]
V-BF_4	9.30	8.51, 8.45, 8.37 (d), 8.30, 7.33 (d)		6.71 6.62 6.35	2.73 (SMe), 0.62 (Me)[g], 1.9-1.6 (m, P-CH_2)
VI-BF_4	9.11	8.52 (d), 8.42 (d), 8.39 (d), 8.33 (d), 8.27 (d), 7.44 (d)		6.74 (t)[e] 6.63 (t)[e] 6.44 (t)[e]	5.11 (P-H)[h], 2.74 (SMe), 1.79 (m, PCH_2), 0.93 (Me)[i], 0.83 (Me)[i]
VII-BF_4	9.03	8.37 (d), 8.33 (d), 8.20 (d), 7.83 (d), 7.71 (d)		6.60 (t)[e] 6.45 (t)[e] 6.38 (t)[e]	7.4-7.1 (m, Ph), 2.73 (SMe), 1.72 (d, J_{PH} = 10.2, PMe), 1.69 (d, J_{PH} = 9.8, PMe)

VIII- $2BF_4$	9.40	8.61 (d), 8.54 (d), 8.41 (d), 8.37 (d), 8.33 (d), 7.47 (d)	6.84 (t)[e] 6.71 (t)[e] 6.56 (t)[e]	4.51 (OMe), 2.43 (SMe), 1.48 (d, J_{PH} = 9.9, PMe)
IX- $2BF_4$	9.78	8.65	6.81 (t)[e]	8.1-7.7 (m)[j], 5.85 (W-CH), 2.27 (SMe)

---

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

[b] The hydrogen coupling constants for the pyrazolyl ligand are 0-3 Hz.

[c] In CD_3NO_2.

[d] J_{WH} = 19.3.

[e] Due to overlapping d of d.

[f] J_{PH} = 9.3.

[g] dt, J = 7.6, J_{PH} = 15.2.

[h] dt, J_{PH} = 335.8, J_{HH} = 5.5.

[i] dt, J_{PH} = 17.1, J_{HH} = 7.6.

[j] H5 of pz and Ph.

Table 2. (continued)

complex	$\underline{H}C(pz)_3$	H3 of pz[b]	H5 of pz[b]	H4 of pz[b]	other
X-$2BF_4$	9.16	8.40		6.64	7.85 (m)[j], 5.08 (W-CH), 2.43 (PMe)[k], 1.83 (SMe)
XI-$2BF_4$	9.11	8.36 (d)	8.31 (d)	6.62 (t)[e] 6.58, (t)[e]	4.39 (WCH)[l], 4.11 (POMe)[m], 1.85 (SMe)
XII-BF_4	9.46	8.42 (d)	8.17	6.54 (t)[e]	4.09[n], 3.59[n] (WCH$_2$); 2.46 (SMe)
XIII-BF_4					
(A)	9.01	8.36 (d)	8.28 (d)	6.55 (t)[e]	5.05 (WCH), 2.50 (CSMe), 2.37 (WSMe)
(B)	9.11	not resolved	8.32 (d)	6.57 (t)[e]	5.56 (WCH), 2.61 (CSMe), 1.78 (WSMe)
XIV-BF_4					
(A)	8.96	8.44	8.27 (d)	6.54 (t)[e]	4.52 (WCH), 2.37 (WSMe), 1.40 (S-*t*-Bu)
(B)	9.06	8.36	8.32 (d)	6.57 (t)[e]	5.35 (WCH), 1.88 (WSMe), 1.48 (S-*t*-Bu)

XV-BF_4						
(**A**)	8.94	8.41		8.28 (d)	6.56 (t)[e]	7.4-7.2 (m, Ph), 5.14 (WCH), 2.44 (WSMe)
(**B**)	9.05	8.39		8.33 (d)	6.59 (t)[e]	7.6-7.4 (m, Ph), 5.79 (WCH), 1.87 (WSMe)

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[k] d, J_{PH} = 12.9.

[l] d, J_{PH} = 2.6.

[m] d, J_{PH} = 11.1.

[n] d, J = 7.4.

Table 3. $^{13}C\{H\}$ NMR Data for the Complexes in CD_3NO_2 at Room Temperature[a]

complex	CO	$H\underline{C}(pz)_3$	C3 of pz	C5 of pz	C4 of pz	other
II-PF_6	223.0	68.5	149.9 149.4	138.9	110.5	276.0 (W≡C), 26.5 (SMe)
III-2BF_4	210.2	78.2	149.4(br)	136.4 135.9 135.8	110.1 109.7 108.9	223.3 (W=C), 26.1 (SMe)
IV[b]-BF_4	222.6	77.3	148.9 142.3	137.1 130.9	110.6 109.8 108.1	217.2 (ketenyl C), 209.8 (ketenyl CO), 23.4 (SMe), 11.4 (d, J_{PC} = 53, PMe_3)
VIII-2BF_4	229.1	78.4	151.1 150.0 148.5	138.5 137.1 136.5	111.6 110.9 109.8	241.9 ($MeO\underline{C}\equiv$), 205.3 ($MeS\underline{C}\equiv$), 69.4 (OMe), 18.2 (SMe), 10.4 (d, J_{PC} = 56, PMe_3)
IX[c]-2BF_4	241.7[d] 216.7	78.0	152.4 143.9	137.1 136.6	110.9 109.5 108.8	40.4 (d, J_{PC} = 67, W-C), 25.2 (SMe)
X[e]-2BF_4	239.3[f] 216.5	78.1	151.5	137.1	111.0	43.0 (d, J_{PC} = 58, W-C), 23.9 (SMe), 9.4 (PMe)[g]

XI-2BF$_4$	236.2 219.7	78.3	151.3	136.5 136.2 134.4	110.6 109.6 108.8	69.1 (d, J_{PC} = 38, W-C), 54.5 (d, J_{PC} = 20, POMe), 24.9 (SMe)
XIII-BF$_4$						
(**A**)	231.3 228.7	78.1	149.8	135.9	110.3	66.1 (W-C); 24.9, 21.5 (SMe)
(**B**)	233.4 220.7	78.3	150.8	136.2	110.5	71.2 (W-C); 26.5, 23.7 (SMe)

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

[b] In $(CD_3)_2CO$.

[c] PPh$_3$: 135.4 (d, J_{PC} = 9), 131.6 (d, J_{PC} = 13), 122.7, 121.5.

[d] J_{PC} = 8.

[e] PPh$_2$: 136.5, 136.2, 134.0 (d, J_{PC} = 8), 133.5 (d, J_{PC} = 8), 131.5 (t, J_{PC} = 13), 125.0, 123.8, 122.7, 121.5.

[f] d, J_{PC} = 5.

[g] d, J_{PC} = 62.

tried (hexanes, Et_2O, THF, CH_2Cl_2, acetone, MeCN, $MeNO_2$, DMSO) and could not be purified.

{[HC(pz)$_3$](CO)$_2$W≡C-SMe}PF$_6$, **II**-PF$_6$

A CH_2Cl_2 (25 mL) suspension of **I** (0.304 g, 0.610 mmol) and $[Me_3O]PF_6$ (0.126 g, 0.611 mmol) was stirred at room temperature for 2 h, giving a brown solution. This solution was filtered and hexanes (40 mL) were added to precipitate the orange product (0.305 g, 76%). Anal. Calcd for $C_{14}H_{13}F_6N_6O_2PSW$: C, 25.55; H, 1.99; N, 12.77; S, 4.87. Found: C, 25.49; H, 2.29; N, 12.65; S, 4.82. MS (FAB): m/e 513 (parent cation, M^+), 457 (M^+-2CO). Molar conductivity ($MeNO_2$): $\Lambda_M = 89.5\ \Omega^{-1}\ cm^2\ mol^{-1}$ at 10^{-3} M (1:1 electrolyte).[16] The analogous tetrafluoroborate salt (**II**-BF_4) was synthesized from a CH_2Cl_2 (100 mL) suspension of **I** (2.12 g, 4.26 mmol) and $[Me_3O]BF_4$ (0.630 g, 4.26 mmol). After 15 h, the brown solution was filtered, and hexanes were added to the filtrate thus precipitating the orange product powder (2.33 g, 91%). The IR and ^1H NMR spectra of **II**-BF_4 and **II**-PF_6 are identical.

{[HC(pz)$_3$](CO)$_2$W[η^2-CH(SMe)]}(BF$_4$)$_2$, **III**-2BF$_4$

A solution of **II**-BF_4 (0.100 g, 0.167 mmol) in $MeNO_2$ (10 mL) was treated with $HBF_4 \cdot Et_2O$ (27.0 µL, 0.183 mmol). The solution turns from orange to purple in *ca*. 5 min. The complex **III**-2BF_4 was not isolated (it tended to be a sticky oily solid, which was difficult to handle), but used *in situ* for further reactions.

$\{[HC(pz)_3](CO)(PMe_3)\overline{W[C(O)C}SMe]\}BF_4$, **IV**-BF$_4$

A solution of **II**-BF$_4$ (0.200 g, 0.334 mmol) in CH_2Cl_2 (15 mL) was treated with PMe_3 (36.0 μL, 0.353 mmol), which caused the solution to turn from orange to red. The solution was stirred for 30 min and then Et_2O (100 mL) was added to precipitate the pale red powder product (0.212 g, 94%). Anal. Calcd for $C_{17}H_{22}BF_4N_6O_2PSW$: C, 30.20; H, 3.28. Found: C, 29.77; H, 3.49. MS (FAB): m/e 589 (parent cation, M^+), 561 (M^+-CO), 513 (M^+-PMe_3). Molar conductivity ($MeNO_2$): Λ_M= 95.0 Ω^{-1} cm^2 mol^{-1} at 10^{-3} M (1:1 electrolyte).[16]

$\{[HC(pz)_3](CO)(PR_3)\overline{W[C(O)C}SMe]\}BF_4$, PR_3 = PEt_3, **V**-BF$_4$; PR_3 = PEt_2H, **VI**-BF$_4$; PR_3 = PMe_2Ph, **VII**-BF$_4$

Using a procedure similar to the one above, the ketenyl complexes **V**-BF$_4$, **VI**-BF$_4$ and **VII**-BF$_4$ were isolated in 61-68% yield. These complexes were characterized by their IR (Table 1) and ^{1}H NMR (Table 2) spectra.

$\{[HC(pz)_3](CO)(PMe_3)W(\eta^2\text{-}MeOC{\equiv}CSMe)\}(BF_4)_2$, **VIII**-2BF$_4$

A solution of **IV**-BF$_4$ (0.058 g, 0.086 mmol) in CH_2Cl_2 (20 mL) was treated with $[Me_3O]BF_4$ (0.013 g, 0.088 mmol). The mixture was stirred at room temperature for 18 h. The product precipitated from solution as an sticky solid. The solvent was removed *in vacuo*, and the residue was washed with

CH_2Cl_2 (2 x 5 mL). Yield: 0.032 g (48%). MS (FAB): m/e 623 (parent dication + F^-). Even after repeated recrystallizations from acetone/Et_2O the product contained small amounts of impurities; therefore, a good elemental analysis could not be obtained.

{[HC(pz)$_3$](CO)$_2$W[η^2-CH(PPh_3)SMe]}(BF_4)$_2$, **IX**-2BF_4

A solution of **III**-2BF_4 (0.254 mmol) in $MeNO_2$ (20 mL) was treated with PPh_3 (0.0666 g, 0.254 mmol). The solution was stirred at room temperature for 1 h. The solvent was then removed *in vacuo*, and the residue extracted with CH_2Cl_2 (10 mL). Filtration, followed by addition of hexanes (80 mL) to the CH_2Cl_2 solution, precipitated the product as a pale red powder (0.167 g, 70%). Anal. Calcd for $C_{32}H_{29}B_2F_8N_6O_2P$-$SW{\cdot}CH_2Cl_2$: C, 38.29; H, 3.02; N, 8.12. Found: C, 38.67; H, 3.44; N, 8.49. MS (FAB): m/e 863 (parent dication + BF_4^-), 795 (parent dication + F^-). Molar conductivity ($MeNO_2$): $\Lambda_M = 164\ \Omega^{-1}\ cm^2\ mol^{-1}$ at 10^{-3} M (2:1 electrolyte).[16]

{[HC(pz)$_3$](CO)$_2$W[η^2-CH($PMePh_2$)SMe]}(BF_4)$_2$, **X**-2BF_4

Using the same procedure as above, **III**-2BF_4 (0.208 mmol) in $MeNO_2$ (20 mL), when treated with PPh_2Me (39 µL, 0.21 mmol), yielded **X**-2BF_4 (red powder, 0.0878 g, 48%). Anal. Calcd for $C_{27}H_{27}B_2F_8N_6O_2PSW$: C, 36.42; H, 3.06; N, 9.44. Found: C, 36.38; H, 3.56; N, 9.15. MS (FAB): m/e 801 (parent dication + BF_4^-), 733 (parent dication + F^-).

Molar conductivity ($MeNO_2$): $\Lambda_M = 163\ \Omega^{-1}\ cm^2\ mol^{-1}$ at 10^{-3} M (2:1 electrolyte).[16]

$\{[HC(pz)_3](CO)_2W[\eta^2\text{-}CH(P(OMe)_3)SMe]\}(BF_4)_2$, **XI**-$2BF_4$

A solution of **III**-$2BF_4$ (0.21 mmol) in $MeNO_2$ (15 mL) was treated with $P(OMe)_3$ (25 µL, 0.21 mmol). The solution was stirred at room temperature for 1 h. The solvent was then removed *in vacuo*, and the residue extracted with CH_2Cl_2 (10 mL). Filtration, followed by addition of hexanes (75 mL) to the CH_2Cl_2 solution, precipitated the product as a red powder (0.094 g, 55%). This product was characterized by its IR, ^1H NMR and $^{13}C\{H\}$ NMR spectra.

$\{[HC(pz)_3](CO)_2W[\eta^2\text{-}CH_2SMe]\}BF_4$, **XII**-$BF_4$

Treatment of a solution of **III**-$2BF_4$ (0.338 mmol) in $MeNO_2$ (15 mL) with a solution of $NaBH_4$ (0.0250 g, 0.676 mmol) in H_2O (1 mL) gave an orange-brown solution after 1 h. The solvent was removed *in vacuo*, and the residue extracted with CH_2Cl_2 (20 mL). Filtration of the CH_2Cl_2 extract through Celite, followed by addition of hexanes (100 mL), precipitated the product as an orange powder (0.106 g, 52%). Anal. Calcd for $C_{14}H_{15}BF_4N_6O_2SW$: C, 27.93; H, 2.51; N, 13.96. Found: C, 27.78; H, 2.77; N, 13.97. MS (FAB): m/e 515 (parent cation). Molar conductivity ($MeNO_2$): $\Lambda_M = 79\ \Omega^{-1}\ cm^2\ mol^{-1}$ at 10^{-3} M (1:1 electrolyte).[16]

$\{[HC(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)SMe]\}BF_4$, **XIII**-$BF_4$

A solution of **III**-$2BF_4$ (0.502 mmol) in $MeNO_2$ (20 mL) was treated with NaSMe (0.0704 g, 1.00 mmol). The mixture was stirred at room temperature for 1 h. The solvent was then removed *in vacuo*, and the residue extracted with CH_2Cl_2 (20 mL). Filtration of the CH_2Cl_2 extract through Celite was followed by addition of hexanes (100 mL). This precipitated the product as an orange powder (0.199 g, 61%). MS (FAB): m/e 561 (parent cation, M^+), 533 (M^+-CO). Molar conductivity ($MeNO_2$): $\Lambda_M = 80\ \Omega^{-1}\ cm^2\ mol^{-1}$ at 10^{-3} M (1:1 electrolyte).[16]

$\{[HC(pz)_3](CO)_2W[\eta^2\text{-}CH(S\text{-}t\text{-}Bu)SMe]\}BF_4$, **XIV**-$BF_4$

Using the procedure above, **III**-$2BF_4$ (0.167 mmol) in $MeNO_2$ (10 mL) when treated with Na(S-*t*-Bu) (0.0375 g, 0.334 mmol) yielded **XIV**-BF_4 (orange powder, 0.062 g, 54%). MS (FAB): m/e 603 (parent cation, M^+), 575 (M^+-CO), 547 (M^+-2CO).

$\{[HC(pz)_3](CO)_2W[\eta^2\text{-}CH(SPh)SMe]\}BF_4$, **XV**-$BF_4$

In a similar preparation, **III**-$2BF_4$ (0.169 mmol) in $MeNO_2$ (10 mL) when treated with NaSPh (0.0447 g, 0.338 mmol) yielded **XV**-BF_4 (orange powder, 0.050 g, 41%). MS (FAB): m/e 623 (parent cation, M^+), 595 (M^+-CO), 567 (M^+-2CO).

RESULTS AND DISCUSSION

Preparation of $[HC(pz)_3](CO)_2W(CS)$, **I**

Refluxing a solution of $HC(pz)_3$ and $Bu_4N[IW(CO)_4(CS)]$[15] in acetone produces a gold precipitate, which is formulated as $[HC(pz)_3](CO)_2W(CS)$ (**I**). Its insolubility in a range of solvents precluded purification and characterization by NMR. The mass spectrum was also not very informative, showing only peaks due to $HC(pz)_3$. The IR spectrum (Nujol mull) shows two CO bands (1885s, 1794s cm^{-1}) and one terminal CS band (1178s cm^{-1}), which are similar to those reported for $Bu_4N\{[HB(pz)_3](CO)_2W(CS)\}$ (ν_{CO} 1884s, 1787s cm^{-1}; ν_{CS} 1149s cm^{-1}) and $Bu_4N[Cp(CO)_2W(CS)]$ (ν_{CO} 1890s, 1804vs cm^{-1}; ν_{CS} not reported).[17] It is interesting to note that based on the CO band energies, $HC(pz)_3$ is a more basic ligand than Cp^-. Because of the similarity of its preparation and its IR spectrum to $Bu_4N\{[HB(pz)_3](CO)_2W(CS)\}$, the gold powder is formulated as $[HC(pz)_3](CO)_2W(CS)$ (**I**).

Synthesis of $[HC(pz)_3](CO)_2W{\equiv}C\text{-}SMe^+$, **II**

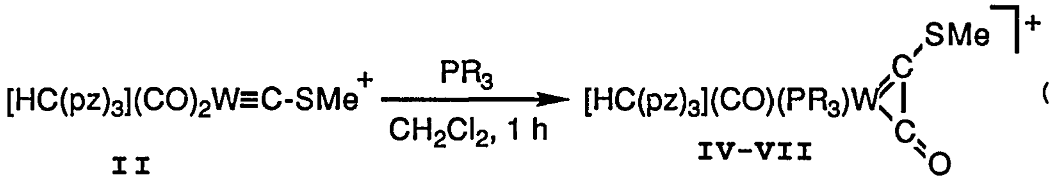
The sulfur atom in electron-rich tungsten thiocarbonyl comlexes is known to act as a nucleophile toward a variety of electrophiles.[17,18] When a suspension of the thiocarbonyl **I** in CH_2Cl_2 is treated with Me_3O^+ it gives the S-alkylated product **II** (eq 4). Consistent with the complex's formulation as a thiocarbyne is the lack of a ν_{CS} absorption and the

$$\underset{\textbf{I}}{[HC(pz)_3](CO)_2W(CS)} \xrightarrow[CH_2Cl_2,\ 18\ h]{Me_3O^+} \underset{\textbf{II}}{[HC(pz)_3](CO)_2W{\equiv}C\text{-}SMe^{+}} \tag{4}$$

presence of two ν_{CO} absorptions (Table 1). Its ^{13}C NMR spectrum (Table 3) exhibits a resonance at δ 276.0 ppm which is assigned to the carbyne carbon. This is similar to those of other tungsten thiocarbyne complexes: $[HB(pz)_3](CO)_2W{\equiv}C\text{-}SMe$ (δ 264.4 ppm)[3] and $Cp(CO)_2W{\equiv}C\text{-}S[2,4\text{-}C_6H_3(NO_2)_2]$ (δ 261.7 ppm).[3] Complex **II** was further characterized by its FAB mass spectrum which showed the parent cation (M^+, m/e 513) and M^+-2CO (m/e 457). In addition, its molar conductivity in $MeNO_2$ ($\Lambda_M = 89.5\ \Omega^{-1}cm^2\ mol^{-1}$) is consistent with a 1:1 electrolyte.[16]

Reactions of $[HC(pz)_3](CO)_2W{\equiv}C\text{-}SMe$, **II**, with Phosphorus Donors

Terminal carbyne ligands in cationic transition-metal complexes are reported to undergo attack by phosphines (e.g., eq 3) at the carbyne carbon.[19] However, in an electron-rich complex such as $[HB(pz)_3](CO)_2W{\equiv}C\text{-}SMe$, where the carbyne ligand is not susceptible to nucleophilic attack, PEt_3 causes carbonylation of the carbyne to give the η^2-ketenyl compound (eq 1).[5] Similarly, we observed that the thiocarbyne **II** reacts with a variety of phosphines to give the η^2-ketenyl complexes $[HC(pz)_3](CO)(PR_3)\overline{W[C(O)C}SMe]^+$ (eq 5). The characteristic ν_{CO} of the ketenyl CO was observed (Table 1) between 1685 and 1660 cm^{-1}.[4b,20] The chemical shifts in the ^1H NMR (Table 2) and ^{13}C NMR (Table 3) spectra were assigned by comparison with assignments for the complex $[HB(pz)_3](CO)(PEt_3)\overline{W[C(O)C}SMe]$.[5]



(5)

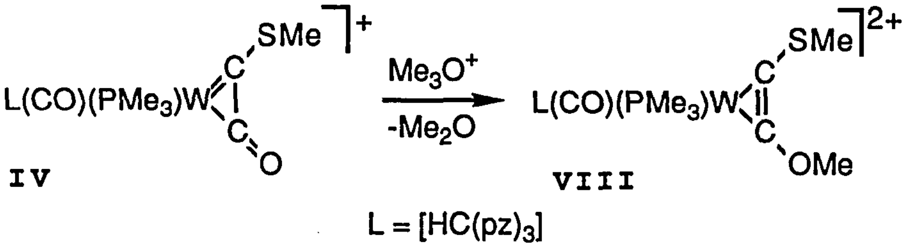
$PR_3 = PMe_3$ (**IV**), PEt_3 (**V**), PEt_2H (**VI**), PMe_2Ph (**VII**)

In addition to complexes **IV-VII**, a ketenyl complex is also observed by solution IR (ν_{CO} 1915, 1685 cm^{-1}) when the thiocarbyne **II** is reacted with 1 equivalent of $P(OMe)_3$ for 8 h at room temperature. In contrast, an equilibrium between **II** and the ketenyl complex is observed when **II** is treated with 1 equivalent of $P(O\text{-}i\text{-}Pr)_3$ or PPh_2Me at 25°C in CH_2Cl_2 (IR for the ketenyl complexes, ν_{CO} 1911, 1680 and 1905, 1682 cm^{-1}, respectively). Using five equivalents of the phosphite or phosphine shifts the equilibrium almost completely toward the ketenyl complex. By isolating the product and then redissolving it in CD_2Cl_2 in the absence of excess phosphorus ligand, it is observed by ^1H NMR that the equilibrium shifts back toward the thiocarbyne **II** (~ 90%) within 2-3 h. The phosphine donors PCy_3, PPh_3, $P(OPh)_3$ and dppe do not react with **II** even when present in a 10-fold excess. Thus the tendency of **II** to undergo reaction (5) decreases with the P-donor ligand in the order: $PMe_3 > PEt_2H > PEt_3 \sim PMe_2Ph > P(OMe)_3 > P(O\text{-}i\text{-}Pr)_3 \sim PPh_2Me \gg PCy_3 \sim PPh_3 \sim P(OPh)_3$. This trend suggests that the formation of the ketenyl complex is influenced both by the electronic and steric properties of the phosphorus nucleophile. Although $P(OPh)_3$ has a smaller cone angle(128°)[21] than PPh_2Me(136°),[21] it is not basic enough to form the ketenyl complex. Tricyclohexylphosphine (PCy_3) is more basic than any of the phosphines which do form the ketenyl complex; however, its large cone angle (170°)[21] inhibits formation of the ketenyl complex.

Kreissl and coworkers report[4a,b] the reaction of $Cp(CO)_2M{\equiv}CR$ (M = Mo, W; R = Me, tolyl) with 1 equivalent of PMe_3 produces η^2-ketenyl compounds. Addition of another equivalent of PMe_3 to the η^2-ketenyl compound or addition of 2 equivalents of PMe_3 directly to the carbyne gives η^1-ketenyl compounds. All of the ketenyl complexes formed from the thiocarbyne **II** exist only as the η^2-form even in the presence of a large excess of the phosphorus donor. This is attributed to the crowded environment around the metal caused by the bulky $HC(pz)_3$ ligand, which apparently prohibits the second phosphorus ligand access to tungsten. No reaction was observed between the thiocarbyne and SMe^-, CN^-, I^- or NH_2Me at room temperature or in refluxing CH_2Cl_2.

Reaction of $[HC(pz)_3](CO)(PMe_3)\overline{W[C(O)C}SMe]^+$ with $[Me_3O]BF_4$

Kreissl *et al.*[22] reported the methylation and addition of XCl_3 (X = B, Al or In) to the ketenyl CO in $Cp(CO)(PMe_3)$-$\overline{W[C(O)C}R]$ (R = Me, 4-$C_6H_4CH_3$) to give $Cp(CO)(PMe_3)W(RC{\equiv}COMe)^+$ and $Cp(CO)(PMe_3)W(RC{\equiv}COXCl_3)$. A similar carbyne to alkyne transformation was observed in the methylation reaction of $[HB(pz)_3](CO)(PEt_3)\overline{W[C(O)C}SMe]$ to give $[HB(pz)_3](CO)(PEt_3)$-$W(MeOC{\equiv}CSMe)^+$.[5] Likewise, the ketenyl complex **IV** reacts with Me_3O^+ to produce the violet complex $[HC(pz)_3](CO)(PMe_3)$-$W(MeOC{\equiv}CSMe)^{2+}$, **VIII** (eq 6). The IR, ^1H NMR and ^{13}C NMR data

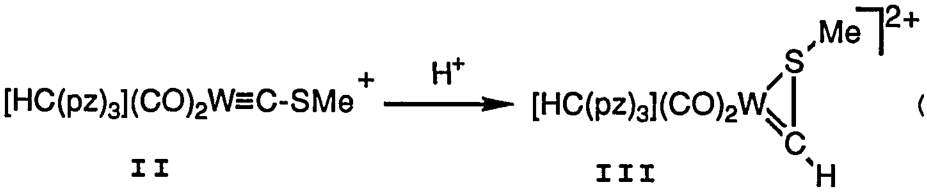


(6)

for **VIII** are similar to those for the related complexes $[HB(pz)_3](CO)(PEt_3)W(MeOC{\equiv}CSMe)^+$,[5] and $Cp(CO)(PMe_3)$-$W(MeOC{\equiv}CMe)^+$.[22] The lowfield positions of the alkyne carbon atoms (δ 241.9, 205.3 ppm) in the ^{13}C NMR spectrum of **VIII** are comparable with shifts reported for $[HB(pz)_3](CO)(PEt_3)W$-$(MeOC{\equiv}CSMe)^+$ (δ 231.1, 198.0 ppm),[5] $Cp(CO)(PMe_3)W(MeOC{\equiv}CMe)^+$ (δ 227.1, 197.7 ppm)[22] and $(CO)(\eta^2\text{-}S_2CNEt_2)_2W(HC{\equiv}CH)$ (δ 206.6, 207.1 ppm),[23] where the acetylene moiety is proposed to be a four-electron donor. The highest mass +1 ion in the FAB mass spectrum of **VIII** occurs at m/e 623 and corresponds to the parent dication + F^-, and it has the correct isotope pattern. In our experience in using FAB for dications, we never see the parent dication at $M^{2+}/2$; instead +1 ions with m/e values equal to the parent dication plus one anion (i.e., for BF_4^- salts the anion is either BF_4^- or F^-) are observed.

Preparation of $\{[HC(pz_3)](CO)_2W[\eta^2\text{-}CH(SMe)]\}^{2+}$, **III**

Whereas the carbyne carbon in electron-rich complexes is not susceptible to nucleophilic attack, it can be protonated. Protonation (eq 2) of the carbyne carbon in $[HB(pz)_3](CO)_2W{\equiv}C\text{-}SMe$ leads to the C- and S-coordinated thiocarbene complex $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]^+$, whose structure was established by an X-ray diffraction study.[8] Similarly, the addition of an equimolar amount of $HBF_4{\bullet}Et_2O$ to a $MeNO_2$ solution of the thiocarbyne **II** produces an immediate color change from orange to violet concomitant with the production of the thiocarbene $[HC(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]^{2+}$ (eq 7). The thiocarbene **III** was characterized by

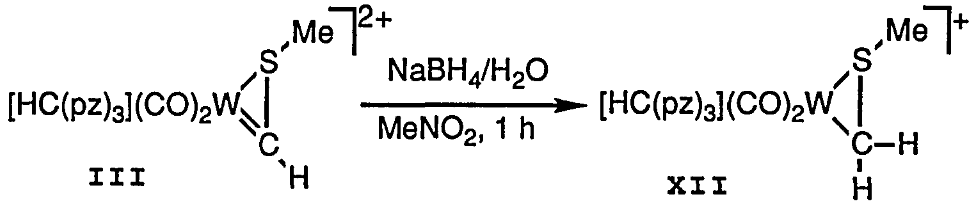


(7)

comparison of its IR, ^1H NMR and ^{13}C NMR spectra to the related complex $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]^+$.[5] The IR bands of **III** (ν_{CO} 2079s, 2010s cm^{-1}) are shifted to higher energy as compared with **II** (ν_{CO} 1991s, 1906s cm^{-1}) reflecting the increasing positive charge on the metal. The ^1H NMR of **III** exhibits a new resonance at δ 13.15 ppm, indicating that the proton is attached to the carbene carbon and not the metal, analogous to the carbene hydrogen in $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]^+$ (δ 12.78 ppm).[5] The ^{13}C NMR shows the characteristic downfield shift for the carbene carbon (δ 223.3 ppm), which is similar to the shifts reported for other thiocarbenes, $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]^+$(δ 227.8 ppm),[8] $[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)SMe]^+$(δ 230.5 ppm)[24] and $Cp(CO)_2W[\eta^2\text{-}C(4\text{-}C_6H_4Me)SMe]^+$ (δ 233.1 ppm).[25] Because attempts to precipitate **III** resulted in a sticky oily solid, it was not isolated and its subsequent reactions were performed *in situ*.

Reaction of $[HC(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]^{2+}$, **III**, with $NaBH_4$

The carbene carbon atom in transition-metal carbene complexes is frequently the site of attack by nucleophiles.[26] Similarly the thiocarbene **III**, when treated with $NaBH_4$, forms the hydride adduct **XII** in 48% yield (eq 8). No other carbonyl containing products are observed by IR during the reaction. The low yield is due to decomposition during the reaction and work-up. Upon addition of the hydride, the carbonyl bands in the IR shift to lower energy (ν_{CO} 2079s, 2010s cm^{-1} to 1938s, 1814s cm^{-1}), which is consistent with decreasing the positive charge on the metal. The ^1H NMR spectrum exhibits two doublets at δ 4.09 and 3.59 ppm, J = 7.4 Hz, which are assigned to the methylene protons (CH_2).

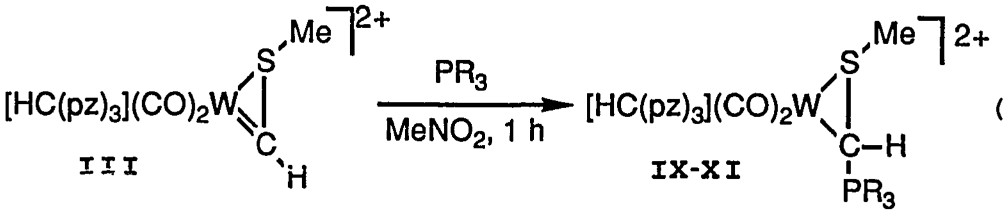


(8)

Nonequivalence of the two methylene protons is also observed in the analogous complexes $Cp(CO)_2W[\eta^2-CH_2SMe]$[27] (δ 2.64, 2.05 ppm; $J = 6.0$ Hz) and $(CO)_4Mn[\eta^2-CH_2SMe]$ (δ 2.35, 1.85; $J = 5.5$ Hz)[27] at 25°C.

Reactions of $[HC(pz)_3](CO)_2W[CH(SMe)]^{2+}$ with Phosphorus Donors

Phosphorus donors are among the nucleophiles which attack the carbene carbon in transition metal carbene complexes. Examples include the reactions of $Cp(CO)_2Fe-[CH(SMe)]^+$,[1d] and $[HB(pz)_3](CO)_2W[\eta^2-CH(SMe)]^+$,[9] with phosphines and phosphites to give the adducts $Cp(CO)_2Fe[CH(L)SMe]^+$ (L = PPh_2Me, PPh_3, PPh_2Cl, PPh_2H, $P(OPh)_3$) and $[HB(pz)_3](CO)_2W[\eta^2-CH(L)SMe]^+$ (L = PPh_3, PEt_3, $P(OMe)_3$, PPh_2H). Similarly, $[HC(pz)_3](CO)_2W[\eta^2-CH(SMe)]^{2+}$ reacts at room temperature with phosphorus donors to give the adducts $[HC(pz)_3](CO)_2W[\eta^2-CH(L)SMe]^{2+}$ (eq 9). The ^1H NMR



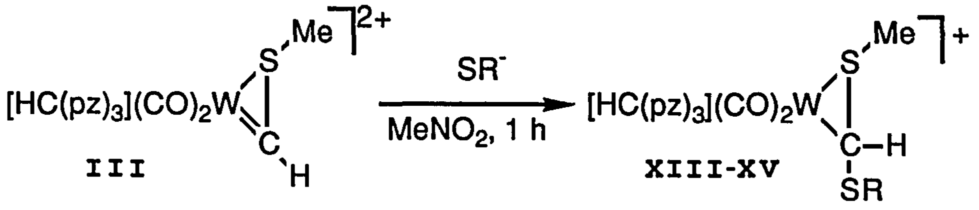
(9)

$PR_3 = PPh_3$ (**IX**), PPh_2Me (**X**), $P(OMe)_3$ (**XI**)

resonance of the methine hydrogen in **IX** and **X** occurs as a singlet. The absence of coupling to the phosphorus atom may be due to a Karplus-like dependence of $^2J_{PH}$ on the angle between the hydrogen and phosphorus atoms;[28] the coupling constant $^2J_{PH}$ ranges from 0 to 26 Hz depending on the angle between them. In contrast to the phosphine adducts, the methine hydrogen in the $P(OMe)_3$ adduct **XI** does occur as a doublet (J_{PH} = 2.6 Hz) due to coupling with the phosphorus atom. In the ^{13}C NMR spectrum of **IX, X** and **XI,** the methine carbon is coupled to the phosphorus atom giving a doublet. A carbene adduct was also observed by IR and ^1H NMR to form when a $MeNO_2$ solution of **III** was treated with PCl_3 at room temperature; however, attempts to isolate the adduct resulted in its decomposition.

Reactions of the Thiocarbene, **III**, with Thiolates, SR^-

Complex **III** reacts readily with thiolates (SR^-) at room temperature to give the corresponding adducts **XIII-XV** (eq 10). The low yields (40-65%) are due to decomposition during the reaction and workup. No other carbonyl-containing complexes were observed by IR during the reaction. The



(10)

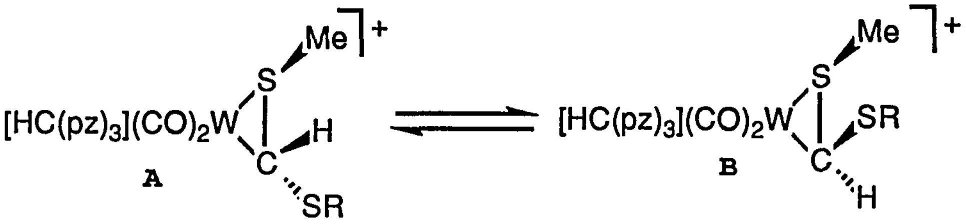
R = Me (**XIII**), *t*-Bu (**XIV**), Ph (**XV**)

products were characterized by comparison of their IR, ^1H NMR and ^{13}C NMR spectra to those of the analogous complexes $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SR)SMe]$.[9]

The ^1H and ^{13}C NMR spectra of **XIII** and the ^1H NMR spectra of **XIV** and **XV** show two sets of resonances, suggesting the presence of two isomers, designated **A** and **B**. In contrast, the IR spectra of **XIII**, **XIV** and **XV** show only one set of CO bands. However, the bands are very broad, suggesting the possible presence of two isomers. The relative ratio of the major isomer **A** to the minor isomer **B** for **XIII** is 8:1 at 25°C and was obtained by integration of the methine (CH) protons. This ratio was not observed to change with time at 25°C. The relative ratio **A:B** for **XIV** is initially 2:1 at 25°C. After 4 h, the ratio changes to 6:1. The equilibrium was not observed due to some decomposition of the complex. However, the change in the isomer ratio is not the result of the decomposition of one isomer since the signal intensity decreases only slightly during the isomerization process. Similarly, the relative ratio **A:B** for **XV** was also observed to change from 1:12 to 5:1 after 9 days at 25°C.

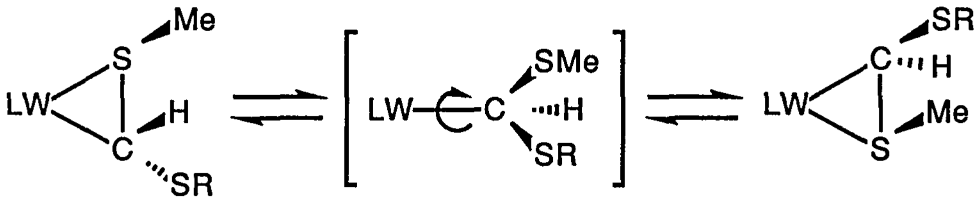
Attempts to grow single crystals of **XIII**, **XIV** or **XV** were unsuccessful. In all three compounds, the thermodynamically favored isomer is **A**. Presumably the structure of **A** is the same as that of $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(PPh_2)SMe]$, which was determined by X-ray analysis.[5] The structure shows that the Me group on the sulfur coordinated to tungsten is oriented above the WCS ring toward the pyrazolyl groups. Whereas, the PPh_2 group is positioned below the WCS ring toward the carbonyls and away from the bulky pyrazolyl groups. Based on this structure, there are 3 possible sets of isomers for **XIII-XV.** One set of isomers would result if attack of the nucleophile at the carbene carbon atom of **III** occurs from above and below the WCS ring (eq 11). In reactions of phosphorus donors with the thiocarbene **III** (eq 9) only one isomer is formed. If **A** and **B** are the isomers shown in eq 11, the lack of isomers in **IX-XI** may be due to the larger size of the phosphorus ligand, causing it to attack the carbene carbon only from the side opposite the bulky HC(pz)3 group. In support of isomers **A** and **B** (eq 11) is the lack of isomers in the hydride adduct **XII** which does not have a stereogenic ring carbon atom.

As noted above, the isomers of **XIV** and **XV** interconvert; one might consider three possible mechanisms for this isomerization. One, involving dissociation of SR^- to give **III** which can re-add SR^- on the same or opposite side, is



(11)

unlikely. This conclusion is based on the observation (by ^1H NMR) that there is no exchange of the SPh^- group in **XV** with excess added Na^+SMe^- in 0.5 mL of CD_2Cl_2 over a period of 36 h at 25°C; also, no other reactions are observed. An alternate isomerization process involves dissociation of the coordinated SMe to give a 16-electron species in which the W-C bond freely rotates (eq 12).

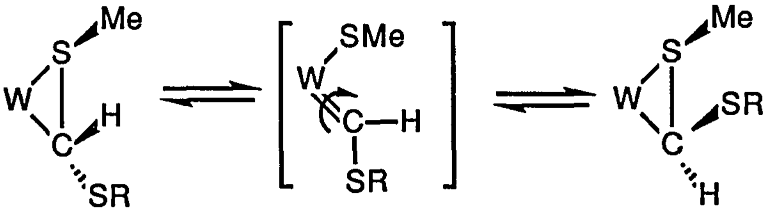


(12)

A **B**

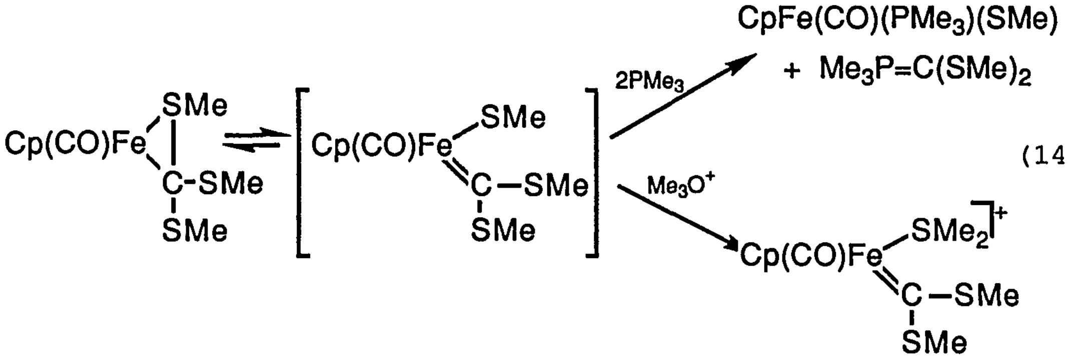
$L = [HC(pz)_3](CO)_2$

Another possible isomerization process involves cleavage of the C-S bond in the η^2-CH(SR)SMe 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 (eq 13). A related iron analog Cp(CO)Fe[η^2-C(SMe)$_2$SMe], which is not a carbene



(13)

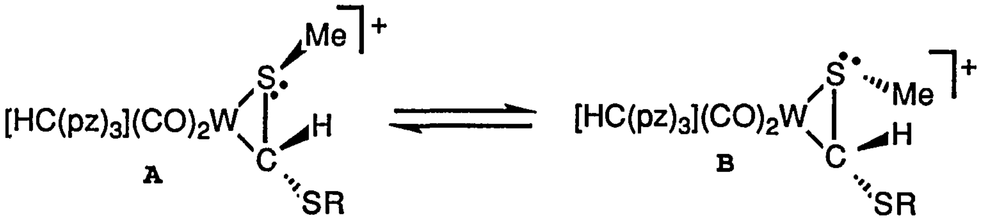
itself, appears to convert to and react as a carbene (eq 14).[29] Presumably, the presence of two thiolate groups on the ring carbon in the iron complex helps to stabilize the carbene form. Fast rotation around the iron-carbene bond gives one resonance in the ^{1}H NMR spectrum at 25°C for the two SMe groups not bound to iron. In complex **XV**, the isomerization process was observed to be slow (*vide supra*).



(14)

Possibly the hydrogen atom on the ring carbon destabilizes the carbene form, thus causing the rate of C-S bond cleavage to be slower than in the iron complex.

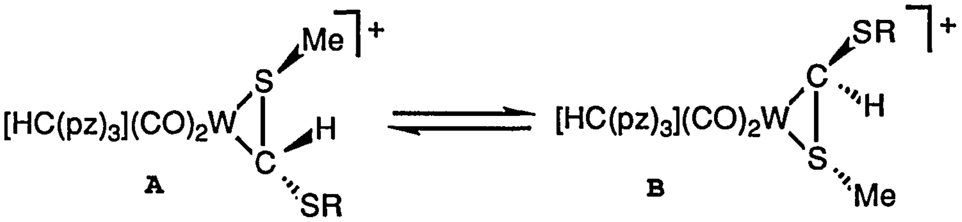
A different set of isomers for **XIII**, **XIV** and **XV** could result from the stereogenic center at the coordinated sulfur atom (eq 15). A mechanism for this isomerization is



(15)

inversion at the coordinated sulfur. Inversion at pyramidal sulfur has been observed in (2,5-dihydrothiophene)W(CO)$_5$ and [PhCH(Me)SMe]W(CO)$_5$ (T_C = -49 and -76.5°C, respectively).[30] If the isomers of **XIII-XV** result from inversion at sulfur, one would expect that similar isomers would be seen for the hydride adduct **XII**, for which only one isomer is observed in the ^{1}H NMR spectrum at 25°C. Similarly, only one isomer is observed in the ^{1}H NMR spectrum at 25°C for the analogous complexes $[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)_2SMe]$[24] and $Cp(CO)_2M[\eta^2\text{-}CH_2(SMe)]$ (M = Mo, W),[27] where there are equivalent groups on the ring carbon.

A third set of isomers could be derived by changing the configurations at both the ring carbon and sulfur atoms (eq 16). Rotation of the whole η^2-CH(SR)SMe unit around an



(16)

axis from the tungsten to the center of the η^2-C—S bond would interconvert isomers **A** and **B**. A similar three-membered MCS ring rotation was proposed by Ward and coworkers for a series of zirconium complexes $Cp_2ClZr[\eta^2\text{-}CH(R)SR']$[31] which show one set of resonances in the ^1H NMR spectrum at room temperature and two sets at -80°C. As in the case of sulfur inversion, if rotation of the η^2-CH(SR)SMe unit is occurring in **XIII-XV**, one might also expect to see two isomers for the hydride adduct **XII**, for which only one isomer is observed (*vide supra*).

Of the three possible sets of **A**, **B** isomers, it seems that isomers of the type in eq 11 are most likely, but there are no data that unequivocally eliminate the isomers in eqs 15 and 16.

The thiocarbene **III** reacts with a number of amines, NEt_3, 4-$NC_5H_4(N(Me)_2)$, 4-NC_5H_4Me, NEt_2H and NH_2CMe_3, in $MeNO_2$ at 25°C. The IR spectra of the reaction solutions show two ν_{CO} bands similar in position to those observed for the PR_3, SR^- and H^- adducts. However, attempts to isolate the products only gave free $HC(pz)_3$ ligand and free amine.

Conclusions

The reactivity of the pyrazolylmethane thiocarbyne $[HC(pz)_3](CO)_2W{\equiv}C\text{-}SMe^+$ (**II**) resembles that of the electron-rich carbynes like $[HB(pz)_3](CO)_2W{\equiv}C\text{-}SMe$ rather than that of the cationic Fischer carbynes. Comparison of the IR spectra of $[HC(pz)_3](CO)_2W{\equiv}C\text{-}SMe^+$ and $[HB(pz)_3](CO)_2W{\equiv}C\text{-}SMe$ (ν_{CO} 1991, 1906 cm^{-1} and 1980, 1888 cm^{-1}, respectively) with $CpFe(CO)_3^+$ [32] and $CpMn(CO)_3$ [33] (ν_{CO} 2120, 2068 cm^{-1} and 2025, 1938 cm^{-1}, respectively) indicates that $HC(pz)_3$ is nearly as strong an electron-donor as $HB(pz)_3^-$, and that there is only a small difference in the charge on the metal in the two carbyne complexes. This difference is observed in the rates of reactions of the carbynes with phosphorus donors. Under the same conditions, the $HC(pz)_3$ complex reacts approximately 10 times faster with PEt_3 than $[HB(pz)_3](CO)_2W{\equiv}C\text{-}SMe$. In addition, $[HC(pz)_3](CO)_2W{\equiv}C\text{-}SMe^+$ reacts with less basic phosphorus donors (i.e., phosphites) which do not react with $[HB(pz)_3](CO)_2W{\equiv}C\text{-}SMe$. This trend can be attributed to the slightly more electrophilic tungsten atom in

$[HC(pz)_3](CO)_2W{\equiv}C\text{-}SMe^+$, which makes it more susceptible to nucleophilic attack. Both the $HC(pz)_3$ and the $HB(pz)_3^-$ carbynes can be protonated at the carbyne carbon to give the η^2-thiocarbenes, which react similarly with nucleophiles forming the carbene adducts. However, the $HC(pz)_3$ complexes are less stable than their $HB(pz)_3^-$ analogs. The pyrazolylmethane complexes tend to decompose in solution, giving free $HC(pz)_3$ ligand and uncharacterized insoluble metal products. However, in general, the $HC(pz)_3$ and $HB(pz)_3^-$ systems possess very similar reactivity.

ACKNOWLEDGMENT

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SECTION III. SYNTHESIS AND REACTIONS OF THE η^2-DITHIOCARBENE $[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)SMe]^+$

ABSTRACT

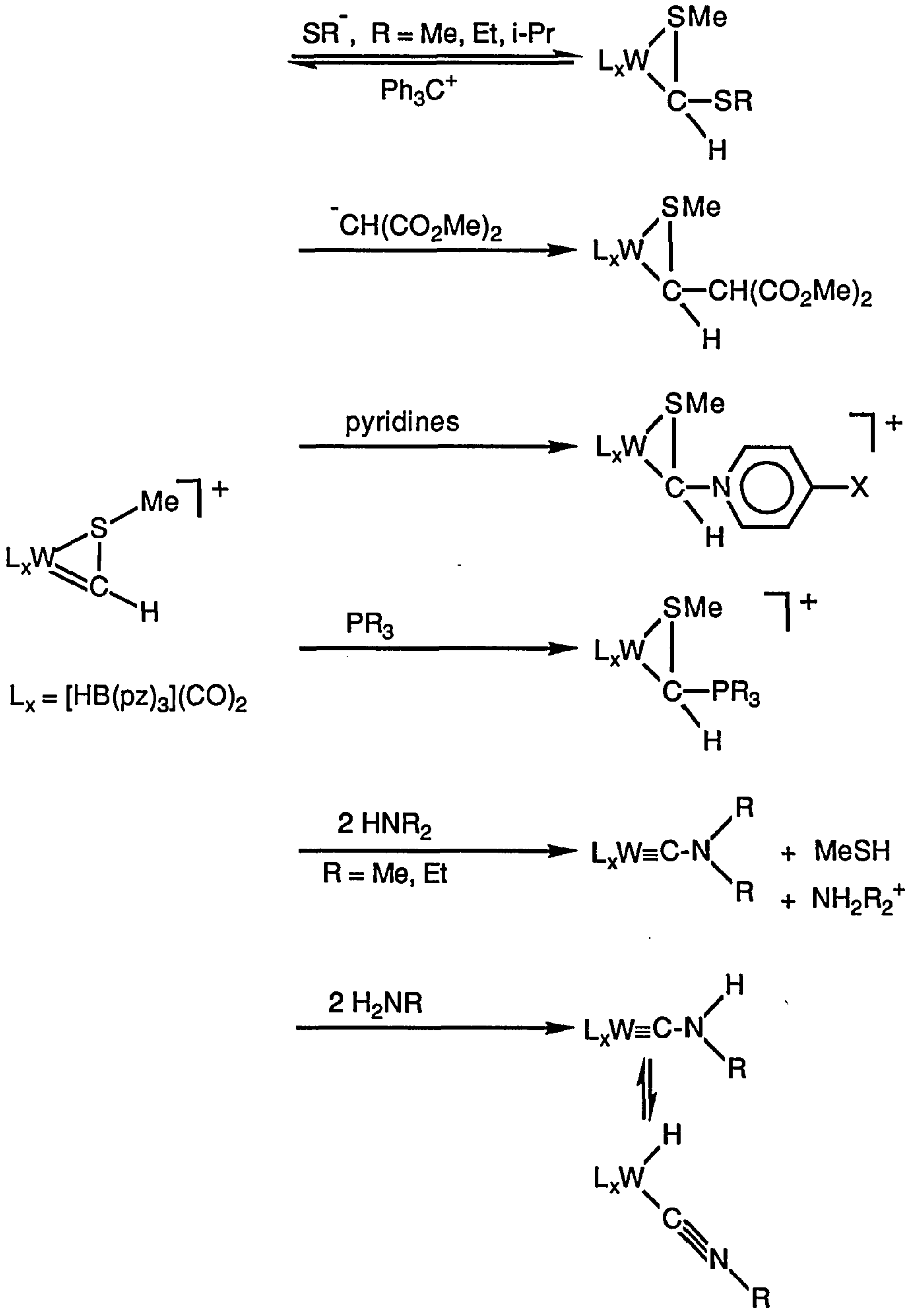
The SMe^+ electrophile adds to the carbyne carbon of $[HB(pz)_3](CO)_2W{\equiv}C{-}SMe$, **I**, to give $[HB(pz)_3](CO)_2W[\eta^2{-}C(SMe)SMe]^+$, **II**, the first example of an η^2-dithiocarbene bonded to the metal through both the carbene carbon and one of the sulfur atoms. Sodium naphthalenide, LiPh and $LiPPh_2$ act as reducing agents when reacted with **II** forming a mixture of **I** and $[HB(pz)_3](CO)_2W[\eta^2{-}C(SMe)_2SMe]$, **VII**. Reactions of **II** with nucleophiles (Nuc) give the air-stable adducts $[HB(pz)_3](CO)_2W[\eta^2{-}C(SMe)(Nuc)SMe]$ (Nuc = SR^-, H^-, CH_3^- and PMe_3). The dithiocarbene **II** also reacts with $CpMo(CO)_3^-$ or $Mn(CO)_5^-$ to give **I** and $CpMo(CO)_3SMe$ or $[Mn(CO)_4SMe]_2$, respectively. Treatment of **II** with excess $^-CH(CO_2Me)_2$ produces the air-stable complex $[HB(pz)_3](CO)_2\overline{W[C(S}Me)=C(CO_2Me)_2]$ (**VI**, 15%) and **VII** (45%).

INTRODUCTION

Only a few η^2-thiocarbene complexes, $\{(PPh_3)_2[CN(4\text{-}C_6H_4Me)](Cl)Os[\eta^2\text{-}C(4\text{-}C_6H_4Me)SMe]\}ClO_4$,[1] $\{[HB(pz)_3](CO)_2W\text{-}[\eta^2\text{-}CH(SMe)]\}SO_3CF_3$[2] and $\{Cp(CO)_2W[\eta^2\text{-}C(4\text{-}C_6H_4Me)SMe]\}BF_4$,[3] in which the carbene ligand is coordinated to the metal via both the carbene carbon and sulfur atoms, have been reported in the literature. The thiocarbene complex $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]^+$ reacts with a variety of nucleophiles to give a range of products (Scheme 1).[4,5] In those reactions where the carbene adduct $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(L)SMe]$ is formed, both the carbon and sulfur atoms remain coordinated to tungsten and the C-S bond remains intact.

In this paper, we describe the synthesis and characterization of the first η^2-dithiocarbene complex $[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)SMe]^+$ and its reactions with a variety of nucleophiles.

Scheme 1


SR⁻, R = Me, Et, i-Pr
Ph₃C⁺
⁻CH(CO₂Me)₂
pyridines
PR₃
2 HNR₂
R = Me, Et
2 H₂NR
Lₓ = [HB(pz)₃](CO)₂
+ MeSH
+ NH₂R₂⁺

EXPERIMENTAL

General Procedures

All reactions, chromatography, distillations and recrystallizations were carried out under an atmosphere of prepurified N_2, using standard inert atmosphere and Schlenk techniques[6,7] unless stated otherwise. Tetrahydrofuran (THF) and Et_2O were distilled from Na/benzophenone. Hexanes and CH_2Cl_2 were distilled from CaH_2. Reactions were carried out at room temperature unless stated otherwise. Neutral products were recrystallized by dissolving them in CH_2Cl_2 (1-2 mL), then adding hexanes (5-10 mL) and slowly cooling the solution to low temperature (-20 to -78°C).

Infrared spectra (Table 1) were obtained using a Perkin Elmer 681 spectrophotometer, and spectra were referenced to the 1601.0 cm^{-1} band of polystyrene. The ^{1}H (Table 2) and $^{13}C\{H\}$ NMR (Table 3) data were recorded on a Nicolet-NT-300 MHz spectrometer using the deuterated solvent as the internal reference. Electron impact mass spectra (EIMS) were obtained on a Finnigan 4000 instrument. Fast atom bombardment (FAB, CH_2Cl_2/3-nitrobenzyl alcohol matrix) mass spectra were obtained using a Kratos MS-50 spectrometer. Elemental microanalyses were performed by Galbraith Laboratories Inc., Knoxville, TN.

The compounds $[HB(pz)_3](CO)_2W{\equiv}C{-}SMe$,[8] **I**, $[Me_2SSMe]SO_3CF_3$,[9] NaSR[4] (R = Me, Et, *t*-Bu, Ph, 4-C_6H_4Me),

$NaCH(CO_2Me)_2$[10] and $LiCuMe_2$[11] were prepared by using previously described procedures. All other chemicals were used as received from commercial sources.

Synthesis of $\{[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)SMe]\}SO_3CF_3$, **II**-$SO_3CF_3$

To a solution of the thiocarbyne compound **I** (0.113 g, 0.221 mmol) in CH_2Cl_2 (10 mL), was added $[Me_2SSMe]SO_3CF_3$ (0.0570 g, 0.221 mmol). The color changed from orange to purple immediately. Diethyl ether (100 mL) was layered on top of the solution, and the solution was allowed to stand for 12 h to give air-stable, purple, microcrystals of **II**-SO_3CF_3 (0.143 g, 91%). Anal. Calcd for $C_{15}H_{16}BF_3N_6O_5S_3W$: C, 25.44; H, 2.28; N, 11.87. Found: C, 25.05; H, 2.36; N, 11.94. FAB: m/e 559 (parent cation, M^+), 503 (M^+-2CO).

Reaction of **II** with $NaBH_4$

To a solution of **II**-SO_3CF_3 (0.116 g, 0.164 mmol) in CH_2Cl_2 (5 mL), was added a solution of $NaBH_4$ (0.0187 g, 0.492 mmol) in H_2O (0.5 mL). The solution turned brown after 0.5 h and the solvent was removed *in vacuo*. The residue was extracted with CH_2Cl_2 (10 mL) and chromatographed on silica gel (Merck, grade 60, 2 x 25 cm). A single orange band was eluted with a 1:2 mixture of hexanes/CH_2Cl_2. The eluate was evaporated to dryness yielding an air-stable, yellow-orange powder $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)SMe]$ (**III**, 0.0712 g, 78%). This compound, which was prepared previously by another method,[4] was identified by comparing its IR and ^1H NMR spectra with those reported in the literature.

Reaction of **II** with $LiCuMe_2$

To a suspension of **II**-SO_3CF_3 (0.314 g, 0.443 mmol) in THF (10 mL) was added an Et_2O/Me_2S solution (5 mL/5 mL) of $LiCuMe_2$ (0.576 mmol). After 20 min, the solution turned black. It was then filtered through a pad of alumina (6 cm). Washing the alumina with THF (50 mL) gave an orange-red solution, which was evaporated to dryness. The residue was extracted with CH_2Cl_2 (5 mL) and chromatographed on alumina (Fisher, Grade 1, 2 x 30 cm). The column was eluted with a 1:4 mixture (100 mL), a 2:3 mixture (100 mL) and then a 3:2 mixture of CH_2Cl_2/hexanes to remove the single orange band. The eluate was concentrated to 10 mL and hexanes (50 mL) were added. This solution was then evaporated to dryness yielding an air-stable, orange powder $[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)(Me)SMe]$ (**IV**, 0.158 g, 62%). Anal. Calcd for $C_{15}H_{19}BN_6O_2S_2W$: C, 31.38; H, 3.34; N, 14.64. Found: C, 31.44; H, 3.42; N, 14.53. EIMS (16 or 70 eV): m/e 574 (M^+), 518 (M^+-2CO).

Reaction of **II** with PMe_3

To a solution of **II**-SO_3CF_3 (0.110 g, 0.155 mmol) in CH_2Cl_2 (10 mL), was added PMe_3 (16 μL, 0.16 mmol). After 0.5 h, Et_2O (100 mL) was layered on top of the solution.

This solution was allowed to stand for 12 h to give an air-stable red powder $\{[HB(pz)_3](CO)_2W[\eta^2\text{-}C(PMe_3)(SMe)SMe]\}SO_3CF_3$ (**V**-SO_3CF_3, 0.091 g, 74%). Anal. Calcd for $C_{18}H_{25}BF_3N_6O_5PS_3W$: C, 27.57; H, 3.21; N, 10.72. Found: C, 27.68; H, 3.20; N, 10.55. FAB-MS: m/e 635 (parent cation, M^+), 559 (M^+-PMe_3), 503 (M^+-PMe_3-2CO).

Reaction of **II** with $NaCH(CO_2Me)_2$

A CH_2Cl_2 mixture (15 mL) containing **II**-SO_3CF_3 (0.205 g, 0.289 mmol) and $NaCH(CO_2Me)_2$ (0.233 g, 1.48 mmol) was refluxed 18 h. The solution was chromatographed on neutral alumina (Fisher, Grade 1, 2 x 40 cm). Elution with a 1:4 mixture of THF/hexanes removed a pink band of $[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)_2SMe]$ (**VII**, 0.084 g, 48%), which was synthesized independently (*vide infra*). A yellow band was then eluted with a 3:2 mixture of THF/hexanes. Evaporating the eluate to dryness yielded an air stable yellow powder $[HB(pz)_3](CO)_2\overline{W[C(S}Me)=C(CO_2Me)_2]$ (**VI**, 0.028 g, 15%). Anal. Calcd for $C_{18}H_{19}BN_6O_6SW$: C, 33.67; H, 2.98; N, 13.09. Found: C, 33.41; H, 2.93; N, 12.81. EIMS (70 eV): m/e 642 (M^+), 614 (M^+-CO), 586 (M^+-2CO), 558 (M^+-3CO), 543 (M^+-2CO-COMe), 515 (M^+-2CO-2COMe).

Reaction of **II** with SMe^-

A CH_2Cl_2 mixture (10 mL) containing **II**-SO_3CF_3 (0.381 g, 0.538 mmol) and NaSMe (0.0754 g, 1.08 mmol) was allowed to stir for 3 h. The orange solution was chromatographed on neutral alumina (Fisher, Grade 1, 2 x 40 cm). The thiocarbyne complex **I** was removed by eluting with a 1:4 mixture of CH_2Cl_2/hexanes; yield 10%. An orange band containing the product was then eluted with 1:4 THF/hexanes. The eluate was evaporated to dryness, yielding an air-stable, red powder $[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)_2SMe]$ (**VII**, 0.198 g, 61%). Anal. Calcd for $C_{15}H_{19}BN_6O_2S_3W$: C, 29.72; H, 3.16; S, 15.87. Found: C, 29.34; H, 3.10; S, 15.92. EIMS (70 eV): m/e 606 (M^+), 550 (M^+-2CO), 503 (M^+-2CO-SMe).

Reaction of **II** with SEt^-

A CH_2Cl_2 mixture (10 mL) containing **II**-SO_3CF_3 (0.122 g, 0.172 mmol) and NaSEt (0.029 g, 0.34 mmol) was allowed to stir for 3 h. The resulting orange solution was concentrated to 5 mL and chromatographed on neutral alumina (Fisher, Grade 1, 2 x 30 cm). The thiocarbyne complex **I** was removed by eluting with a 1:4 mixture of CH_2Cl_2/hexanes; yield 30%. An orange band was then eluted with CH_2Cl_2. The eluate was concentrated to 10 mL and hexanes (50 mL) were added. This solution was then evaporated to dryness, yielding an air-stable orange powder $[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)(SEt)SMe]$ (**VIII**, 0.0482 g, 45%). Complex **VIII** is a mixture of three isomers (see Discussion). Anal. Calcd for $C_{16}H_{21}BN_6O_2S_3W \cdot CH_2Cl_2$: C, 28.95; H, 3.29; S, 13.64. Found:

C, 28.90; H, 3.66; S, 13.95. EIMS (70 eV): m/e 620 (M^+), 564 (M^+-2CO), 461 (M^+-2CO-2SMe).

Reaction of **II** with SPh^-

A CH_2Cl_2 mixture (10 mL) containing **II**-SO_3CF_3 (0.152 g, 0.215 mmol) and NaSPh (0.0568 g, 0.430 mmol) was allowed to stir for 2 h. The resulting orange solution was chromatographed on neutral alumina (5-6% H_2O, 2 x 20 cm). An orange band was eluted with CH_2Cl_2. The eluate was concentrated to 10 mL and hexanes (50 mL) were added. This solution was then evaporated to dryness yielding an air-stable, orange powder $[HB(pz)_3](CO)_2W[\eta^2$-C(SMe)(SPh)SMe] (**IX**, 0.0981 g, 68%). Complex **IX** is a mixture of two isomers (see Discussion). Anal. Calcd for $C_{20}H_{21}BN_6O_2S_3W$: C, 35.95; H, 3.17; N, 12.58. Found: C, 36.40; H, 3.58; N, 12.18. EIMS (70 eV): m/e 612 (M^+-2CO).

Reaction of **II** with (4-C_6H_4Me)S^-

In a procedure similar to the one above, **II**-SO_3CF_3 (0.280 g, 0.395 mmol) was reacted in CH_2Cl_2 (10 mL) with NaS(4-C_6H_4Me) (0.166 g, 0.793 mmol) to give after chromatography an air-stable orange powder $[HB(pz)_3](CO)_2W[\eta^2$-C(SMe)(S-4-C_6H_4Me)SMe] (**X**, 0.204 g, 74%). Complex **X** is a mixture of two isomers (see Discussion). Anal. Calcd for $C_{21}H_{23}BN_6O_2S_3W$: C, 36.97; H, 3.40; S, 14.10.

Found: C, 36.50; H, 3.26; S, 14.27. EIMS (16 or 70 eV): m/e 626 (M^+-2CO).

Table 1. IR Data for the Complexes in CH_2Cl_2 Solvent

complex	IR ν(CO), cm^{-1}
$[HB(pz)_3](CO)_2W{\equiv}C\text{-}SMe$, **I**	1973 s, 1885 s
$\{[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)SMe]\}(SO_3CF_3)$, **II**-$SO_3CF_3$	2047 m, 1965 s
$[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)SMe]$, **III**	1930 s, 1804 s
$[HB(pz)_3](CO)_2W[\eta^2\text{-}C(Me)(SMe)SMe]$, **IV**	1921 s, 1800 s
$\{[HB(pz)_3](CO)_2W[\eta^2\text{-}C(PMe_3)(SMe)SMe]\}(SO_3CF_3)$, **V**-$SO_3CF_3$	1948 s, 1835 s
$[HB(pz)_3](CO)_2W[C(SMe){=}C(CO_2Me)_2]$, **VI**	1962 s, 1854 s, 1710 m, 1689 m
$[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)_2SMe]$, **VII**	1929 s, 1818 s
$[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)(SEt)SMe]$, **VIII**	1927 s, 1806 s
$[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)(SPh)SMe]$, **IX**	1928 s, 1808 s
$[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)(4\text{-}SC_6H_4\text{-}Me)SMe]$, **X**	1931 s, 1815 s

VIII[f,i]	8.8 (br), 8.1 (br)	7.79	6.29	2.68, 2.65, 2.42, 2.35, 2.34, 2.24 (SMe); 2.87 (m, SCH_2); 1.58, 1.32, 0.85 (Me)[j]
IX[d]	8.10 (br), 7.77 (m),	7.67	6.23 (br)	7.5-7.1 (m, SPh); 2.86, 1.37 (SMe, A); 2.71, 1.95 (SMe, B)
X[d,k]	8.15 (br)	7.65 (m)	6.23 (br)	2.85, 1.40 (SMe, A); 2.36, 2.29 (ArMe; A, B); 2.68, 1.40 (SMe, B)

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

[b] The coupling constants in the pyrazolyl rings range from 0-3 Hz.

[c] Due to overlapping d of d.

[d] Two isomers; see Discussion.

[e] J_{WH} = 3.5.

[f] CD_3NO_2 solvent.

[g] d, J_{PH} = 12.7 Hz.

[h] J_{WH} = 2.2.

[i] Three isomers; see Discussion.

[j] t, J = 7.4.

[k] Arene resonances 7.34 (d, J = 8.2), 7.19 (d, J = 7.9), 7.04 (d, J = 7.9).

Table 3. ^{13}C{H} NMR Data for the Complexes in CD$_2$Cl$_2$ Solvent at Room Temperature[a]

complex	CO	C3 of pz	C5 of pz	C4 of pz	other
I[b]	224.7	144.9	135.2	105.7	264.4 (W≡C), 17.4 (SMe)
II-[c]	216.3	148.3	139.9	109.5	230.5 (W=C), 29.1 (WSMe),
SO$_3$CF$_3$	215.3	146.3	139.3	108.9	26.5 (CSMe)
		146.2	139.1	108.7	
IV	247.5	147.7	135.6	106.3	59.2 (WC); 25.9, 25.6 (SMe);
	222.3	144.7	135.3	105.8	18.6 (Me)
		143.3	135.1	105.5	
V-SO$_3$CF$_3$	244.3	149.6	140.1	108.8	66.6 (WC); 26.3,25.4 (SMe);
	221.8	149.2	139.2	108.5	14.4 (d, J_{PC} = 51, PMe$_3$)
		147.0	137.7	108.4	
VI	228.2	144.2	135.7	106.3	201.2 (W-$\underline{\text{C}}$=C); 128.4 (W-C=$\underline{\text{C}}$);
	225.2				168.4, 163.1 ($\underline{\text{C}}$O$_2$Me); 52.1,
					51.9 (OMe); 27.9 (WSMe)
VII	247.0	145.4 (br)	135.8	106.2	60.6 (WC, J_{WC} = 38);
	223.0[d]			106.1	28.1 (WSMe); 25.6, 23.0
					(CSMe)

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

[b] $CDCl_3$ solvent.

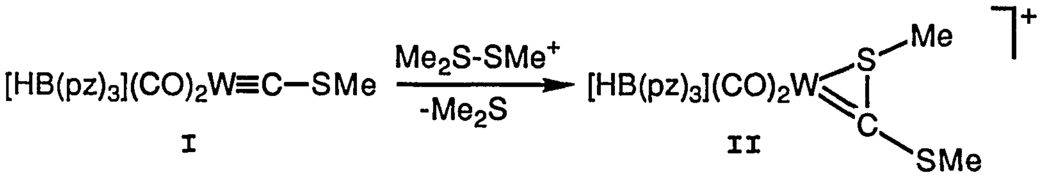
[c] CD_3NO_2 solvent.

[d] $J_{WC} = 179$.

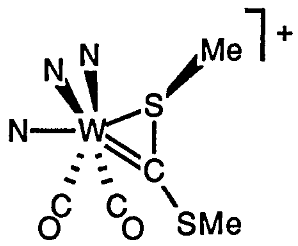
RESULTS AND DISCUSSION

Synthesis of $[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)SMe]^+$, **II**

The thiocarbyne complex **I** reacts readily at room temperature with the electrophile $[Me_2SSMe]SO_3CF_3$ to give the air-stable dithiocarbene complex **II** in 90-95% yield (eq 1). A similar electrophilic addition of SMe^+ to a carbyne carbon to produce the carbene $Cp(CO)_2W[\eta^2\text{-}C(4\text{-}C_6H_4Me)SMe]^+$ was reported by Kreissl and Keller.[3] The purple solid **II**-SO_3CF_3 was characterized by its elemental analysis, FAB MS, IR (Table 1), ^1H NMR (Table 2) and $^{13}C\{H\}$ NMR (Table 3) spectra. Chemical shifts were assigned by comparison with the spectra of the thiocarbene complex $[HB(pz)_3](CO)_2W[\eta^2\text{-}C(H)SMe]^+$.[2] The $^{13}C\{H\}$ NMR spectrum shows the characteristic downfield shift of carbenes at δ 230.5 ppm, which compares with the carbene chemical shifts in $[HB(pz)_3](CO)_2W[\eta^2\text{-}C(H)SMe]^+$ (δ 228.0 ppm)[2] and $Cp(CO)_2W[\eta^2\text{-}C(4\text{-}C_6H_4Me)SMe]^+$ (δ 233.1 ppm).[3] Presumably the structure of **II** is the same as that of $[HB(pz)_3](CO)_2W[\eta^2\text{-}C(H)SMe]^+$, which was determined by X-ray analysis.[2] The structure shows that the Me group on the coordinated sulfur is oriented above the WCS ring toward the pyrazolyl groups and away from the carbonyls.



(1)



II

The ^{1}H NMR spectrum of **II** in CD_2Cl_2 shows only one set of resonances both at room temperature and at -85°C. If pyramidal inversion were occurring at the coordinated sulfur, one might expect to see two sets of resonances at lower temperature for the two isomers. Inversion isomers were observed in (2,5-dihydrothiophene)W(CO)$_5$, [PhCH(Me)SMe]W-(CO)$_5$[12] (T_c = -49 and -76.5°C, respectively) and (CO)$_4$Mo($PhCH_2SCH_2CH_2SCH_2Ph$)[13] (T_c = 33°C). Thus, it appears that **II** either still inverts at sulfur at -85°C or only one isomer is present.

Reactions of **II** with NaNp and Bases

The thiocarbene complex [HB(pz)$_3$](CO)$_2$W[η^2-C(H)SMe]$^+$ is reported to yield a mixture of **I** (10-20%) and [HB(pz)$_3$](CO)$_2$-W[η^2-C(H)(SMe)SMe] (5-40%) when treated with a variety of bases or sodium naphthalenide (NaNp).[4] Similarly when [HB(pz)$_3$](CO)$_2$W[η^2-C(SMe)SMe]$^+$, **II**, is treated with one equivalent of NaNp in THF at room temperature, the thiocarbyne **I** and the MeS$^-$ carbene adduct [HB(pz)$_3$](CO)$_2$W[η^2-C(SMe)$_2$SMe] (**VII**) are produced in an ~1:1 ratio (overall yield ~80%). A possible mechanism for this is shown in eqs 2 and 3. Under the same reaction conditions, LiPh, $LiPPh_2$ and NaSePh also appear to act as reducing agents, giving **I**

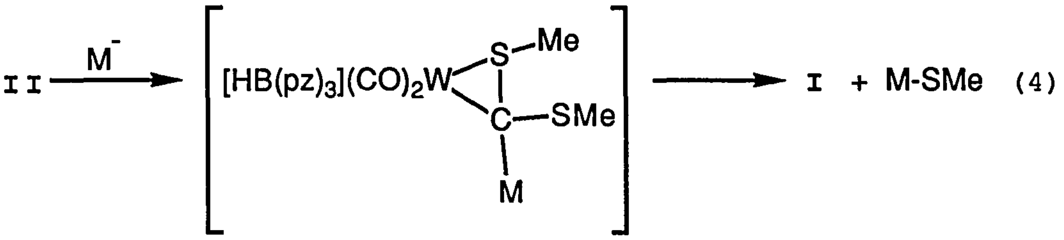
$$\mathbf{II} \xrightarrow{e^-} [HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)SMe]^\bullet \longrightarrow \mathbf{I} + SMe\,\bullet \qquad (2)$$

$$\bullet SMe \xrightarrow{e^-} {}^-SMe \xrightarrow{\mathbf{II}} \underset{\mathbf{VII}}{[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)_2SMe]} \qquad (3)$$

(70%, 40% and 80%, respectively) and **VII** (5%, 40% and 5%, respectively). In all of these reactions some insoluble brown decomposition material is also seen. The dithiocarbene **II** does not react with 4-picoline at 40°C or NEt_2H at 25°C; however, at 66°C **II** decomposes in the presence of NEt_2H.

Reactions of **II** with $NaMoCp(CO)_3$ and $NaMn(CO)_5$

When treated with $NaMoCp(CO)_3$ in THF at room temperature, the dithiocarbene **II** quantitatively forms the thiocarbyne **I** and $CpMo(CO)_3SMe$[14] (identified by its IR and ^1H NMR spectra) in ~10 min. Similarly, when **II** is treated with $NaMn(CO)_5$ under the same conditions, **I** and $[Mn(CO)_4SMe]_2$[15] (identified by its IR and ^1H NMR spectra) are formed quantitatively. It is likely that $Mn(CO)_5SMe$ is the initial product of the reaction, since it has been reported[16] to dimerize in 0.10 h, at room temperature, to $[Mn(CO)_4SMe]_2$. It is unlikely that these two reactions go by electron transfer since no $[CpMo(CO)_3]_2$ or $Mn_2(CO)_{10}$ is produced. A possible mechanism is initial adduct formation by the metal anion (M^-) and then elimination of M-SMe (eq 4). An

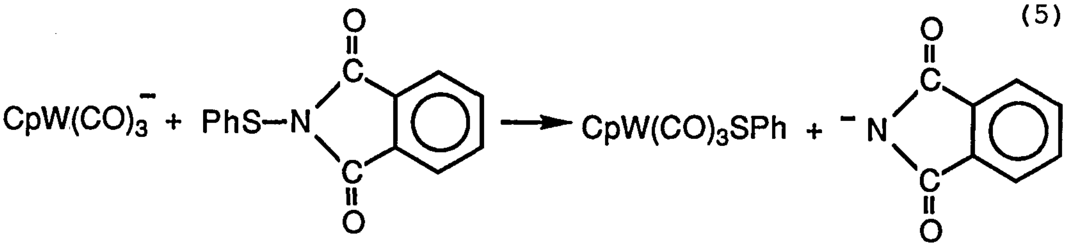


(4)

$M^- = CpMo(CO)_3^-, Mn(CO)_5^-$

alternative mechanism would be direct attack of the metal anion on the sulfur atom. This in not unreasonable considering that the dithiocarbene **II** is synthesized by adding SMe^+ to the carbyne carbon. Thus, like $[Me_2SSMe]^+$, the carbene can also be considered a sulfenylium ion (SMe^+) source for stronger nucleophiles. A similar attack by a metal anion on a sulfur atom was reported by Treichel *et al.*[17] (eq 5). Also, attack by $(Et_2N)_3P$ on the sulfur atom in disulfides has been observed.[18]

(5)

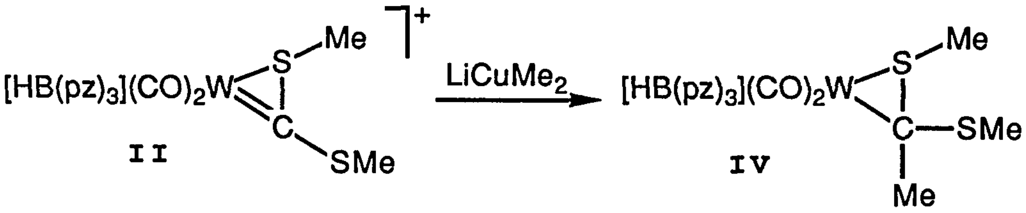


Reactions of **II** with H, C and P Nucleophiles

The carbene carbon atom in transition-metal carbene complexes is frequently the site of attack by a variety of nucleophiles.[19] When treated with a solution of $NaBH_4$ in

H_2O, **II** forms the air-stable hydride adduct $[HB(pz)_3](CO)_2$-$W[\eta^2$-$CH(SMe)SMe]$ (**III**) quantitatively. This known compound was identified by comparing its IR and ^1H NMR with those reported in the literature.[4] Complex **III** exists as two isomers in solution (*vide infra*).

The dithiocarbene **II** also reacts with $LiCuMe_2$ to form the Me^- adduct, $[HB(pz)_3](CO)_2W[\eta^2$-$C(SMe)(Me)SMe]$ (**IV**), in 62% yield (eq 6). Some decomposition occurs in this reaction but no other products are identified. The $^{13}C\{H\}$ NMR

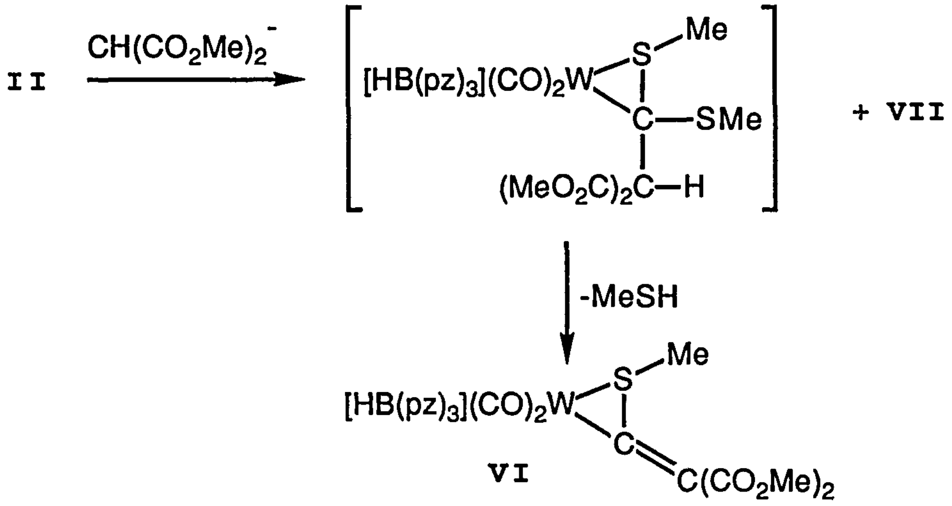


(6)

spectrum of **IV** exhibits the methine carbon at δ 59.2 ppm, which is similar to the methine carbon shifts reported for $[HB(pz)_3](CO)_2W[\eta^2$-$CH(SMe)SMe]$ (δ 61.8 ppm)[4] and $Cp(CO)Fe[\eta^2$-$C(SMe)_2SMe]$ (δ 70.8 ppm).[20]

Trimethylphosphine (PMe_3) adds to the carbene carbon in **II** to produce quantitatively the air-stable adduct $[HB(pz)_3](CO)_2W[\eta^2$-$C(SMe)(PMe_3)SMe]^+$, **V**. Complex **V** was characterized by its elemental analysis, FAB MS, IR (Table 1), ^1H NMR (Table 2) and ^{13}C NMR (Table 3) spectra. Chemical shifts were assigned by comparison with the spectra of the thiocarbene adduct $\{[HC(pz)_3](CO)_2W[\eta^2$-$CH(PMe_3)SMe]\}(BF_4)_2$[21] Unlike **III**, complexes **IV** and **V** show only one set of resonances in their ^1H NMR spectra (Table 2) at 25°C, indicating the presence of a single isomer (*vide infra*).

When **II** is treated with an excess of $NaCH(CO_2Me)_2$, two products, $[HB(pz)_3](CO)_2\overline{W[C(S}Me)=C(CO_2Me)_2]$ (**VI**, 15%) and $[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)_2SMe]$ (**VII**, 45%), are isolated (eq 7). The reaction is slow (18 h) and insoluble decomposition material is also formed. Complex **VI** is a yellow, air-stable solid which was characterized by its elemental analysis, MS, IR (Table 1), ^1H NMR (Table 2) and ^{13}C NMR (Table 3) spectra. The $^{13}C\{H\}$ chemical shift for the α-carbon of the vinyl group occurs at δ 201.2 ppm. This is similar to what is seen for the α-carbons in $Cp(CO)_3W\text{-}CH=C(CN)_2$ (δ 206.7 ppm),[22] $(CO)_5Mn\text{-}CH=C(CN)_2$ (δ 208.0 ppm)[22] and $[N(PPh_3)_2][(CO)_4Fe\text{-}CH=C(CN)_2]$ (δ 228.2 ppm).[23] The $^{13}C\{H\}$ chemical shift for the β-carbon in **VI** occurs at 128.4 ppm, which is similar to the β-carbon shifts reported for $(CO)_5Mn\text{-}CH=C(CN)_2$ (δ 101.3 ppm),[22] $Cp(CO)_3W\text{-}C(CN)=C(CN)_2$ (δ 107 ppm)[22] and $[N(PPh_3)_2][(CO)_4Fe\text{-}CH=C(CO_2Me)(Me)]$ (the β-carbon resonance is in the region of the PPh_3 resonances, δ 125-134 ppm).[23] The mechanism (eq 7) for the formation of **VI** may involve initial addition of $^-CH(CO_2Me)$ to the carbene carbon followed by the rapid elimination of HSMe, which could be promoted by the excess $^-CH(CO_2Me)_2$.

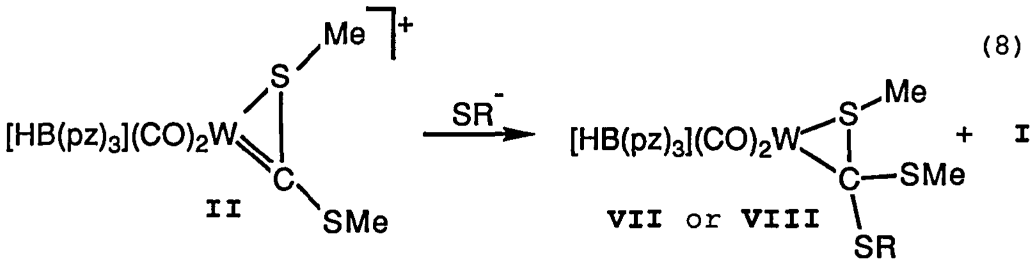


(7)

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

The thiocarbene $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]^+$ is reported[4] to react with RS^- to give the adducts $[HB(pz)_3]$-$(CO)_2W[\eta^2\text{-}C(H)(SR)SMe]$ (R = Me, Et, *i*-Pr). Likewise, **II** reacts with RS^- (R = Me, Et), giving the corresponding air-stable carbene adduct and **I** (eq 8). However, treating **II** with *t*-BuS^- does not yield a *t*-BuS^- adduct but only a mixture of **I** and the MeS^- adduct, **VII**, in a 9:1 ratio.

Formation of the thiocarbyne complex **I** in these reactions suggests the presence of a competing pathway, that of electron transfer as seen in the reactions of **II** with NaNp (eqs 2, 3), LiPh, $LiPPh_2$ and NaSePh. The amount of electron transfer apparently increases from approximately 10% for MeS^- to 30% for EtS^-. In the reaction involving *t*-BuS^-, electron transfer appears to become the exclusive pathway and no adduct formation is seen. This trend in RS^- reactivity is



(8)

R = Me; **VII**:**I** (9:1)

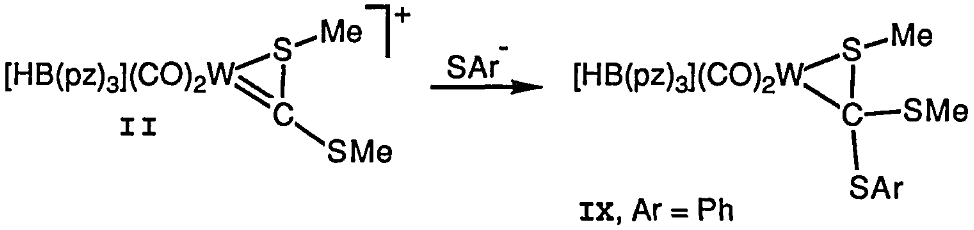
R = Et; **VIII**:**I** (3:2)

likely due to the increase in size of RS$^-$ which slows the rate of adduct formation.

The ^{1}H NMR spectrum of **VII** in d$_8$-THF shows only one set of resonances at room temperature and at -95°C. However, the ^{1}H NMR spectrum of **VIII** shows three sets of resonances at room temperature, indicating the presence of three isomers. A 5:7:8 ratio was obtained by integration of the SCH$_2$C$\underline{H}_3$ protons. In contrast, the IR spectrum of **VIII** shows only one set of CO bands. However, the bands are very broad, suggesting the possible presence of isomers. Probable structures for the isomers will be discussed in a later section.

The dithiocarbene **II** reacts quantitatively with ArS$^-$ to give only the air-stable carbene adducts (eq 9). The ^{1}H NMR spectra (Table 2) of **IX** and **X** at room temperature show two sets of peaks, indicating the presence of two isomers, designated **A** and **B**. The relative ratio of the major isomer **A** to the minor isomer **B** in CD$_2$Cl$_2$ at 25°C was observed by ^{1}H

NMR to be 3:2 and 3:1 for **IX** and **X**, respectively. These ratios were the same in different solvents (C_6D_6, CD_2Cl_2, CD_3NO_2) and did not change with time (48 h).



II

(9)

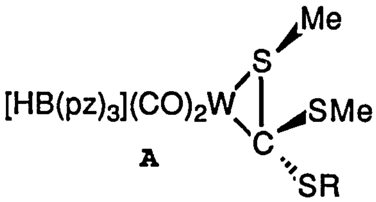
IX, Ar = Ph

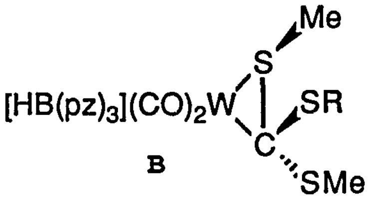
X, Ar = 4-C_6H_4Me

Attempts to grow single crystals of **VIII**, **IX** or **X** were unsuccessful. Presumably the structure of **A** is the same as that of $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(PPh_2)SMe]$, which was determined by X-ray analysis.[5] In this structure the Me group on the sulfur coordinated to tungsten is oriented above the WCS ring toward the pyrazolyl groups; whereas, the PPh_2 group is positioned below the WCS ring toward the carbonyls and away from the bulky pyrazolyl groups. Based on this structure, there are 3 possible sets of isomers for **IX** and **X**:

(a) Two isomers would result if attack of the nucleophile at the carbene carbon atom of **II** occurred from above and below the WCS ring (eq 10). If the two isomers were of the type (**A** and **B**) in eq 10, the MeS^- adduct **VII** would not be expected to occur as two isomers; indeed only one isomer is observed (*vide supra*). Similarly, only one isomer is observed in the ^1H NMR spectra of $Cp(CO)_2M[\eta^2\text{-}$

$CH_2(SMe)]$ (M = Mo, W)[24] and $\{[HC(pz)_3](CO)_2W[\eta^2$-$CH_2(SMe)]\}BF_4$,[21] complexes which also contain identical

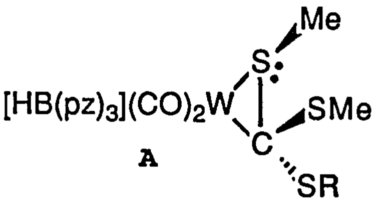

A

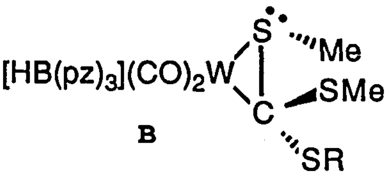

B

(10)

groups on the ring carbon atom. In the reactions of $Li[CuMe_2]$ (eq 6) and PMe_3 with the dithiocarbene **II**, only one isomer is formed. If **A** and **B** are the isomers shown in eq 10, the lack of isomers in **V** and **VI** may be due to the larger size of the nucleophile, causing it to attack the carbene carbon only from the side opposite the bulky $HB(pz)_3^-$ group. The phosphide complex $[HB(pz)_3](CO)_2W[\eta^2$-$CH(PPh_2)SMe]$ (*vide supra*) also exists only as one isomer presumably as a result of stereoselective attack by the bulky Ph_2P^- nucleophile.

(b) A set of inversion isomers are possible due to the stereogenic center at the coordinated sulfur atom (eq 11).

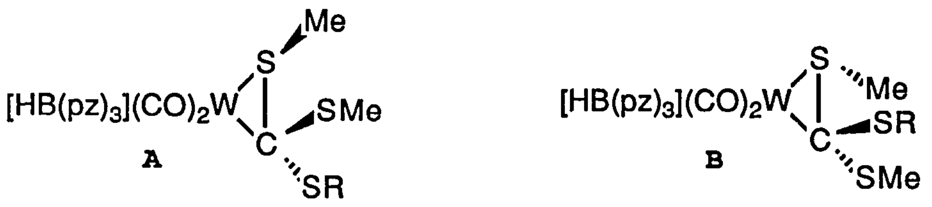

A


B

(11)

If the isomers of **IX** and **X** result from inversion at sulfur, one would expect that similar inversion isomers would be seen for the MeS^- adduct **VI**, for which only one isomer is observed (*vide supra*). Hence, these sulfur inversion isomers seem less likely.

(c) A third set of isomers could result from changing the configuration at both the ring carbon and sulfur atoms (eq 12). As in the case of sulfur inversion ((b) above),



A **B** (12)

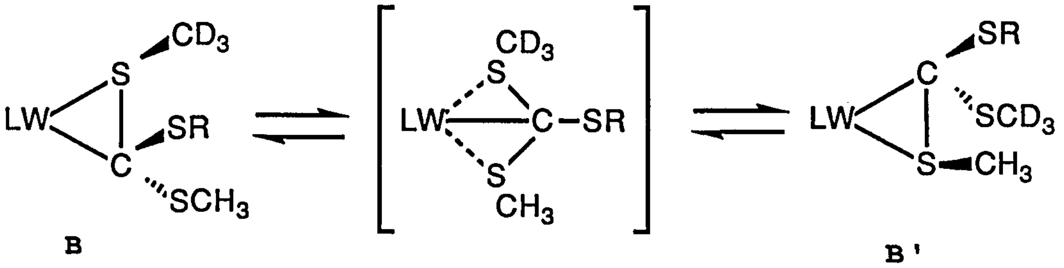
if the isomers are of the type (**A** and **B**) in eq 12, one would also expect to see two isomers for the MeS$^-$ adduct **VII**, which is not observed (*vide supra*).

Of the three possible sets of **A**, **B** isomers, it seems that isomers of the type in eq 10 are most likely, but there are no results that unequivocally eliminate the isomers in eqs 11 and 12.

The isomers (**A**, **B**) were not observed by ^{1}H NMR to interconvert with time or in various solvents (*vide supra*). However, an analogous series of complexes $[HC(pz)_3](CO)_2W$-$[\eta^2\text{-CH(SR)SMe}]^{+}$,[21] has been observed by ^{1}H NMR to exist as two interconverting isomers. Thus, it is possible that the isomer ratios (**A:B**) observed for complexes **IX** and **X** are equilibrium ratios. There are several possible mechanisms for the interconversion of isomers **A** and **B**; these have been discussed in some detail for the complexes $[HC(pz)_3](CO)_2W[\eta^2-CH(SR)SMe]^+$,[21].

The deuterated thiocarbene $[HB(pz)_3](CO)_2W[\eta^2-C(SCH_3)SCD_3]^+$ was synthesized from $[HB(pz)_3](CO)_2W{\equiv}C{-}SCD_3$[25] and Me_2SSMe^+ using a procedure analogous to that used for **II**. No exchange between SCH_3 and SCD_3 groups was observed by ^1H NMR after 72 h at 25°C in CD_2Cl_2. Reactions of the deuterated thiocarbene with RS^- (R = Me, SPh) give products in which the SCD_3 group is in both positions (i.e., uncoordinated and coordinated to tungsten). The exchange process reaches equilibrium by the time the reaction and work-up are complete (~3 h). A possible mechanism for this scrambling is a concerted process in which attack of the SCH_3 group on the tungsten is associated with dissociation of SCD_3 from the metal (eq 13). A complex, $\{Cp(CO)_2W[\eta^3-C(SMe)_2(4-C_6H_4Me)]\}(BF_4)_2$, similar to the proposed intermediate has been reported by Kreissl and Keller.[3] The exchange process would produce the enantiomer. A non-concerted dissociation

(13)

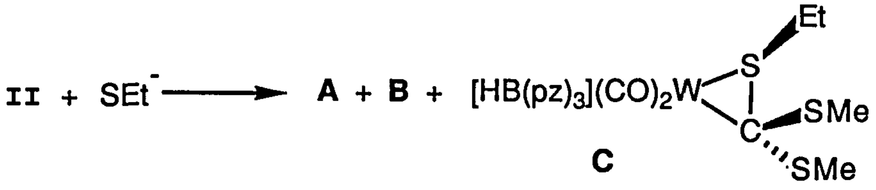


B **B'**

L = $[HB(pz)_3](CO)_2$

of the coordinated SCD_3 group to give a 16-electron intermediate which could then coordinate SCD_3 or SCH_3 is also a possible mechanism. However, this mechanism seems less likely since $[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)_2SMe]$ (**VII**) does not react with excess PMe_3 (25°C, 48 h) and $[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)(S\text{-}4\text{-}C_6H_4Me)SMe]$ (**X**) does not react with excess MeS^- (25°C, 48 h), as might be expected of an unsaturated intermediate.

Eq 13 suggests a probable structure for the third isomer (**C**) observed when EtS^- is reacted with **II** (eqs 8, 14). Isomers **A** and **B** would be of the type in eq 10. Isomer **C**



C

(14)

presumably results from interchange of the coordinated SMe group with the uncoordinated SEt group. This scrambling process was verified independently by synthesizing the dithiocarbene $[HB(pz)_3](CO)_2\overline{W[\eta^2\text{-}C(SMe)S}Et]^+$, 27 and then treating it with MeS^-. This reaction produces the same three isomers in the same ratio as the reaction of **II** with EtS^-. No interchange of the coordinated SMe group with the uncoordinated SAr group in **IX** or **X** is observed. This may be due to the lower nucleophilicity of the SAr group compared to the SMe group.

Conclusions

The reactivity of the dithiocarbene $[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)SMe]^+$ (**II**) with nucleophiles is very similar to that reported [4,5] for the thiocarbene $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]^+$ (Scheme 1). Both readily add nucleophiles to the carbene carbon to form air-stable adducts. The lower frequencies of the ν(CO) absorptions in **II** as compared to $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]^+$ (ν_{CO} 2047m, 1965s cm^{-1} vs. 2067m, 1996s cm^{-1},[2] respectively) indicate that the dithiocarbene **II** may be less electrophilic than $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]^+$. This probably accounts for the lack of reaction of **II** with amines, whereas $[HB(pz)_3](CO)_2W\text{-}[\eta^2\text{-}CH(SMe)]^+$ reacts with amines to give aminocarbyne complexes (Scheme 1).

ACKNOWLEDGMENT

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27. $\{[HB(pz)_3](CO)_2\overline{W[\eta^2\text{-}C(SMe)S}Et]\}SO_3CF_3$ was prepared from $[HB(pz)_3](CO)_2W{\equiv}CSEt$[8] and $[Me_2SSMe]SO_3CF_3$ in a procedure analogous to that used for **II**. ^1H NMR (CD_2Cl_2): 7.99 (d, J = 2.3), 7.93 (d, J = 2.3), 7.91 (d, J = 2.4), 7.88 (d, J = 2.4), 7.84 (d, J = 2.1), 7.75 (d, 2.1) H3 and H5; 6.48 (m) H4; 3.81 (q, J = 7.5) SCH_2; 2.42 (s) SMe; 1.55 (t, J = 7.5) Me.

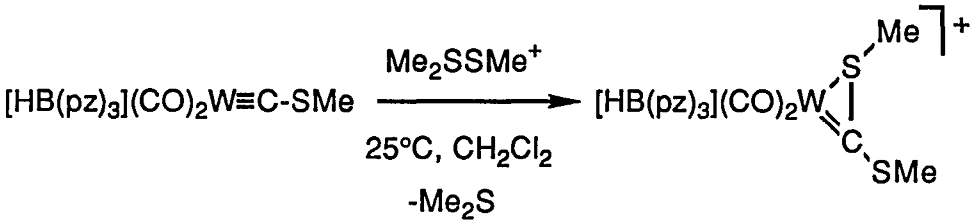
SECTION IV. THERMAL AND PHOTOLYTIC PROMOTION OF α-THIOLATE (RS^-) MIGRATION IN $[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SR)_2SR]$ TO GIVE CARBYNE COMPLEXES $[HB(pz)_3](RS)_2W\equiv C\text{-}SR$

ABSTRACT

Heating the complexes, [HB(pz)$_3$](CO)$_2$W[η^2-C(SMe)(SR)SMe] (**I**, R = Me; **III**, R = Et), above 60°C results in CO loss, C-S bond cleavage, and MeS or EtS migration to give the carbynes [HB(pz)$_3$](MeS)(RS)W≡C-SR' (**II**, R = R' = Me; **IV**, R = Me, Et, R' = Et, Me). In contrast, the analogous SAr complexes, [HB(pz)$_3$](CO)$_2$W[η^2-C(SMe)(SAr)SMe] (**V**, Ar = Ph; **VII**, Ar = 4-C_6H_4Me), eliminate the disulfide ArSSMe upon heating, producing the known carbyne [HB(pz)$_3$](CO)$_2$W≡C-SMe. However, photolysis of **V** and **VII** gives the carbynes [HB(pz)$_3$](MeS)-(ArS)W≡C-SMe (**VI**, Ar = Ph; **VIII**, Ar = 4-C_6H_4Me) in a reaction very similar to the thermal reactions of **I** and **III**. Similarly, photolysis of [HB(pz)$_3$](CO)$_2$W[η^2-C(SMe)(Me)SMe] (**IX**) yields [HB(pz)$_3$](MeS)$_2$W≡C-Me (**X**). Mechanisms of the reactions and structural features of the carbyne products are discussed.

INTRODUCTION

The carbyne carbon in electron-rich transition metal carbyne complexes is known to be susceptible to electrophilic attack.[1] Thus, treating the thiocarbyne $[HB(pz)_3](CO)_2W{\equiv}C$-SMe with $[Me_2SSMe]SO_3CF_3$ gives the η^2-dithiocarbene $\{[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)SMe]\}SO_3CF_3$ (eq 1).[2] This

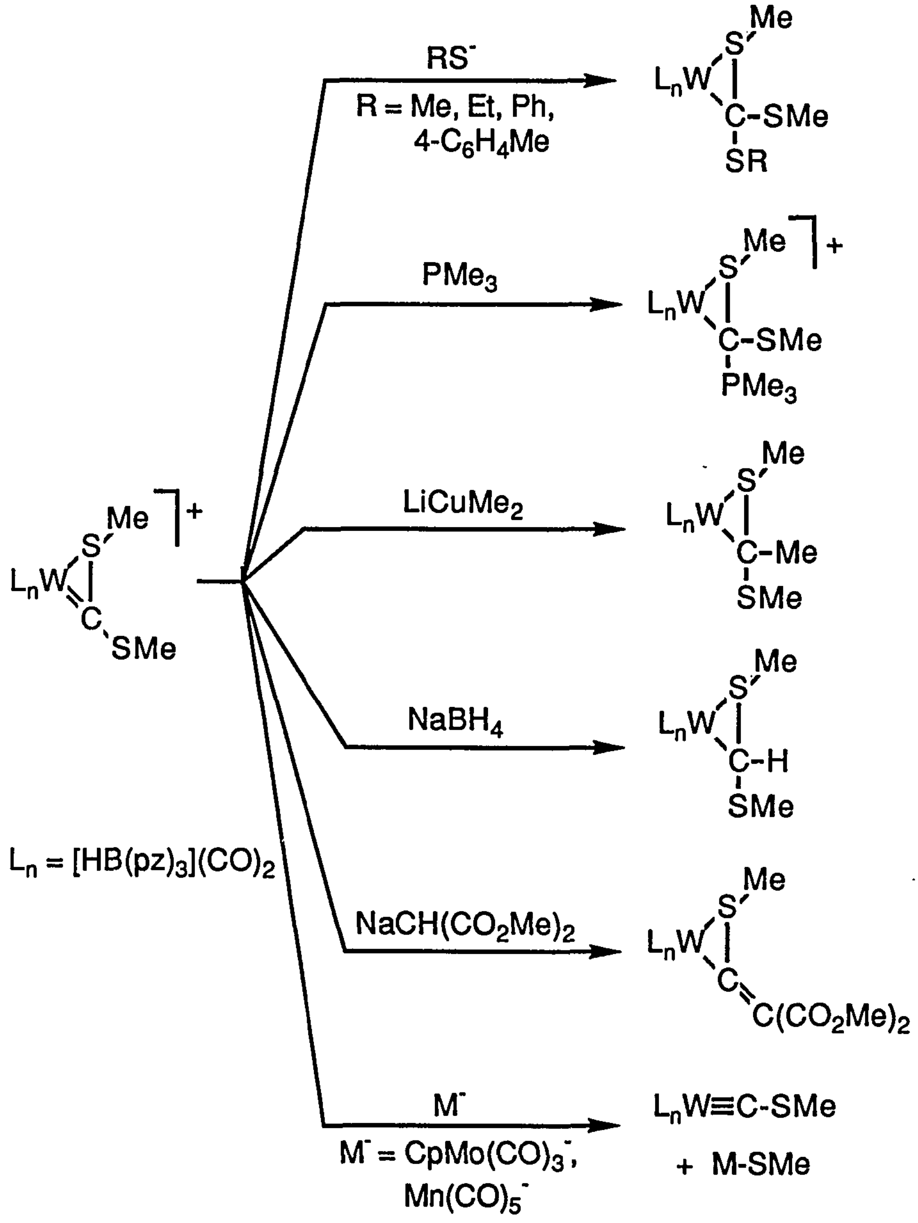


(1)

dithiocarbene reacts with a variety of nucleophiles to give a range of products (Scheme 1).[2] In those reactions where the dithiocarbene adduct $[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)(Nuc)SMe]$ is formed, both the carbon and sulfur atoms remain coordinated to tungsten and the C-S bond remains intact.

In this paper, we describe thermal and photolytic reactions of the complexes $[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)(Nuc)SMe]$ (Nuc = SMe, SEt, SPh, S-4-C_6H_4Me, Me),[2] which involve a novel migration of thiolate (RS) groups from the α-carbon to tungsten to generate a carbyne complex.

Scheme 1


RS⁻
R = Me, Et, Ph, 4-C6H4Me
PMe3
LiCuMe2
NaBH4
NaCH(CO2Me)2
M⁻
M⁻ = CpMo(CO)3⁻, Mn(CO)5⁻
LnW
S
Me
C
SMe
+
Ln = [HB(pz)3](CO)2
C-SMe
SR
PMe3
C-Me
C-H
C(CO2Me)2
LnW≡C-SMe
+ M-SMe

EXPERIMENTAL

General Procedures

All reactions, chromatography, distillations and recrystallizations were carried out under an atmosphere of prepurified N_2 using standard inert atmosphere and Schlenk techniques[3,4] unless stated otherwise. Tetrahydrofuran (THF) and Et_2O were distilled from Na/benzophenone. Hexanes and CH_2Cl_2 were distilled from CaH_2. 1,2-Dichloroethane was distilled from P_2O_5. Reactions were carried out at room temperature unless stated otherwise. Neutral products were recrystallized by dissolving them in a mixture of CH_2Cl_2 or Et_2O (1-2 mL) and hexanes (40-60 mL) and slowly cooling the solution to low temperature (-20 to -78°C) over 2-4 days.

The ^1H and $^{13}C\{H\}$ NMR data were recorded on a Nicolet-NT-300 MHz spectrometer using the deuterated solvent as the internal reference (CD_2Cl_2: δ 5.32 and 53.8 ppm, respectively). Electron impact mass spectra (EIMS) were obtained on a Finnigan 4000 instrument. Photochemical reactions were carried out under N_2 in a quartz tube, using a Canrad-Hanovia medium pressure, 450 Watt, quartz, mercury vapor lamp (40-48% UV, 40-43% visible, the balance is IR). Elemental microanalyses were performed by Galbraith Laboratories Inc., Knoxville, TN.

The compounds $[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)(Nuc)SMe]$ (Nuc = SMe, SEt, SPh, S-4-C_6H_4Me, Me) were prepared by using previously described procedures.[2] All other chemicals were used as received from commercial sources.

Thermal Reaction of $[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)_2SMe]$, **I**

A solution of $ClCH_2CH_2Cl$ (15 mL) containing **I** (0.137 g, 0.226 mmol) was refluxed for 8 h, giving a brown solution. The solution was concentrated to 5 mL. Hexanes (80 mL) were then layered on top, and the solution was allowed to stand at -20°C for 18 h. This afforded air-stable, brown crystals of $[HB(pz)_3](MeS)_2W{\equiv}C\text{-}SMe$ (**II**, 0.0845 g, 68%). Anal. Calcd for $C_{13}H_{19}BN_6S_3W$: C, 28.38; H, 3.48; S, 17.48. Found: C, 28.31; H, 3.47; S, 17.65. EIMS (70 eV): m/e 550 (M^+). ^1H NMR:[5] δ 3.42 (s, 6 H, J_{WH} = 4.2 Hz, WSMe), 2.84 (s, 3 H, CSMe), 8.11 (d, J = 2.1 Hz, 2 H, H3), 8.07 (d, J = 1.9 Hz, 1 H, H3), 7.83 (d, J = 2.4 Hz, 1 H, H5), 7.69 (d, J = 1.9 Hz, 2 H, H5), 6.35 (pseudo-t, J = 2.2 Hz, 1 H, H4), 6.25 (pseudo-t, J = 2.2 Hz, 2 H, H4). ^{13}C NMR:[5] δ 268.3 (W≡C), 27.0 (WSMe), 19.7 (CS<u>Me</u>), 146.3, 144.1 (C3), 136.0, 135.3 (C5), 106.2, 105.9 (C4).

Thermal Reaction of $[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)(SEt)SMe]$, **III**

Refluxing a solution of $ClCH_2CH_2Cl$ (20 mL) containing **III** (0.134 g, 0.216 mmol) for 18 h gave a brown solution. This solution was concentrated to 5 mL and chromatographed on neutral alumina (Grade 1, 1 x 10 cm). A brown band containing $[HB(pz)_3](MeS)(RS)W{\equiv}C\text{-}SR'$ (**IV**, R = Me, Et; R' =

Et, Me) was eluted with a 3:2 mixture of hexanes/CH_2Cl_2. A second green band sticks to the column. The eluate was evaporated to dryness, giving **IV** as an air-stable, brown powder (0.484 g, 40%). Complex **IV** is a mixture of two isomers (**A**, **B**; see Discussion). Anal. Calcd for $C_{14}H_{21}BN_6S_3W$: C, 29.80; H, 3.75; N, 14.89. Found: C, 30.00; H, 3.88; N, 14.91. EIMS (70 eV): m/e 564 (M^+). ^1H NMR: δ 4.05 (m, $WSCH_2$, **B**), 3.45 (s, WSMe, **B**), 3.37 (s, WSMe, **A**), 3.20 (q, J = 7.4 Hz, $CSCH_2$, **A**), 2.83 (s, CSMe, B), 1.51 (t, J = 7.4 Hz, Me, **A**), 1.40 (t, J = 7.6 Hz, Me, **B**), 8.14(m, H3, H5), 7.85 (d, J = 2.1 Hz, H3 or H5), 7.70(m, H3, H5), 6.36(m, H4), 6.26(m, H4).

Photolysis of $[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)(SPh)SMe]$, **V**

A THF (10 mL) solution of **V** (0.177 g, 0.265 mmol) was photolyzed for 6.5 h giving a brown solution. The solvent was removed *in vacuo*, and the residue dissolved in CH_2Cl_2 (5 mL). The CH_2Cl_2 solution was chromatographed on neutral alumina (5% H_2O, 2 x 15 cm) by eluting with CH_2Cl_2/hexanes (1:2). Removal of the solvent gave the brown powder product $[HB(pz)_3](PhS)(MeS)W{\equiv}C\text{-}SMe$ (**VI**, 0.119 g, 73%). Anal. Calcd for $C_{18}H_{21}BN_6S_3W$: C, 35.31; H, 3.46; N, 13.73. Found: C, 35.56; H, 3.58; N, 13.53. EIMS (70 eV): m/e 612 (M^+). ^1H NMR: δ 3.69 (s, 3 H, WSMe), 2.51 (s, 3 H, CSMe), 7.23 (m, 5 H, SPh), 8.09 (d, J = 2.0 Hz, 1 H, H3 or H5), 8.03 (d, J = 1.9 Hz, 1 H, H3 or H5), 7.84 (d, J = 1.4 Hz, 1 H, H3 or H5), 7.80 (d, J = 2.4 Hz, 1 H, H3 or H5), 7.73 (d, J = 1.8 Hz, 1 H, H3 or H5), 7.70 (d, J = 2.4 Hz, 1 H, H3 or H5), 6.27 (pseudo-t, J = 2.1, 2.3 Hz, 1 H, H4) 6.25 (pseudo-t, J = 2.4, 2.1 Hz, 1 H, H4), 6.22 (pseudo-t, J = 2.0, 2.2 Hz, 1 H, H4). ^{13}C NMR: δ 271.1 (W≡C), 150.1, 132.1, 128.0, 125.7 (WSPh), 29.1 (WSMe), 19.3 (CSMe), 151.5, 150.8, 150.5 (C3), 136.3, 135.7, 135.6 (C5), 106.7, 106.4, 106.2 (C4).

Photolysis of $[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)(S\text{-}4\text{-}C_6H_4Me)SMe]$, **VII**

Similar to the procedure directly above, photolysis of **VII** (0.143 g, 0.210 mmol) in THF for 3.5 h (10 mL) gave a brown solution. The solvent was removed *in vacuo* and the residue was dissolved in CH_2Cl_2 (5 mL); the CH_2Cl_2 solution was chromatographed on neutral alumina (5% H_2O, 2 x 15 cm). Elution with CH_2Cl_2/hexanes (2:3) gave a single brown band containing the product $[HB(pz)_3][(4\text{-}MeC_6H_4)S](MeS)W{\equiv}C\text{-}SMe$, **VIII.** A green band remained at the top of the column. Recrystallization gave brown microcrystals of **VIII** (0.0684 g, 52%). Anal. Calcd for $C_{19}H_{23}BN_6S_3W$: C, 36.44; H, 3.70; N, 13.42. Found: C, 36.75; H, 3.85; N, 13.05. EIMS (70 eV): m/e 626 (M^+). ^1H NMR: δ 3.65 (s, 3 H, WSMe), 2.51 (s, 3 H, CSMe), 2.36 (s, 3 H, ArMe), 7.13 (m, 4 H, SAr), 8.09 (d, J = 2.0 Hz, 1 H, H3 or H5), 8.01 (d, J = 1.9 Hz, 1 H, H3 or H5), 7.86 (d, J = 1.3 Hz, 1 H, H3 or H5), 7.80 (d, J = 2.2 Hz, 1 H, H3 or H5), 7.72 (d, J = 2.2 Hz, 1 H, H3 or H5), 7.70 (d, J = 2.2 Hz, 1 H, H3 or H5, 6.26 (m, 3 H, H4). ^{13}C NMR: δ

270.8 (W≡C), 145.5, 131.8, 130.1, 128.7 (WSAr), 28.8 (WSMe), 21.1 (Ar<u>Me</u>), 19.3 (CS<u>Me</u>), 147.1, 146.6, 144.7 (C3), 136.3, 135.7, 135.5 (C5), 106.7, 106.4, 106.2 (C4).

Photolysis of $[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)(Me)SMe]$, **IX**

A THF (20 mL) solution of **IX** (0.0966 g, 0.168 mmol) was photolyzed for 8 h giving a brown solution. The solvent was removed *in vacuo* and the residue was dissolved in CH_2Cl_2 (10 mL); the solution was filtered through neutral alumina (Grade 1, 5 cm). Addition of hexanes, followed by slow removal of the solvent *in vacuo* to dryness, gave the orange powder product $[HB(pz)_3](MeS)_2W{\equiv}C\text{-}Me$ (**X**, 0.0681 g, 78%). Anal. Calcd for $C_{13}H_{19}BN_6S_2W$: C, 30.14; H, 3.70; S, 12.38. Found: C, 30.18; H, 3.91; S, 12.14. EIMS (70 eV): m/e 518 (M^+), 471 (M^+-SMe). ^1H NMR: δ 4.38(s, J_{WH} = 9.3 Hz, 3 H, CMe), 3.37 (s, 6 H, WSMe), 8.08 (d, J = 1.6 Hz, 2 H, H3), 8.04 (d, J = 1.7 Hz, 1 H, H3), 7.82 (d, J = 2.1 Hz, 1 H, H5), 7.68 (d, J = 2.0 Hz, 2 H, H5), 6.34 (pseudo-t, J = 2.1 Hz, 1 H, H4), 6.24 (pseudo-t, J = 2.1 Hz, 2 H, H4). ^{13}C NMR: δ 303.9 (W≡C), 32.8 (C<u>Me</u>), 26.2 (WSMe), 146.8, 144.3 (C3), 136.1, 135.5 (C5), 106.5, 106.1 (C4).

Structure Determination of $[HB(pz)_3](MeS)_2W{\equiv}C\text{-}SMe$, **II**

A dark brown block-shaped crystal of **II** was mounted on a glass fiber in a random orientation. The cell constants were determined from a list of reflections found by an automated search routine. Pertinent data collection and reduction information is given in Table 1.

A total of 8867 reflections were collected in the ±h, +k, ±l hemisphere. The average intensity of three intensity standards, measured every hour of exposure time, increased about 7% over the entire data collection period. Therefore, a non-linear intensity correction was made based on the three standards. An empirical absorption correction was made, based on a series of psi-scans.

Structure Solution and Refinement

The position of the W atom was taken from a Patterson map, and all of the remaining non-hydrogen atoms were then found in a difference Fourier map. Full matrix least-squares refinement converged smoothly, and in the later stages included anisotropic thermal parameters for every atom. The final cycle of refinement included 217 variable parameters.

The X-ray data collection and structure solution were carried out at the Iowa State University Molecular Structure Laboratory. All calculations were performed on a Digital Equipment Corp. MicroVAX II computer using the CAD4-SDP package (Enraf-Nonius Structure Determination Package; Enraf-Nonius: Delft, Holland).

Table 1. Crystal and Data Collection Parameters for the X-ray Diffraction Study of $[HB(pz)_3](MeS)_2W{\equiv}C\text{-}SMe$

formula	$WS_3N_6C_{13}BH_{24}$
fw	550.19
space group	$P2_1/n$
a, Å	10.059(2)
b, Å	13.192(3)
c, Å	14.649(3)
β, deg	91.90(2)
V, $Å^3$	1943(1)
Z	4
d_{calcd}, g/cm^3	1.881
cryst size, mm	0.30 x 0.25 x 0.20
μ(MoKα), cm^{-1}	63.92
diffractometer	Enraf-Nonius CAD4
radiation (monochromated in incident beam)	MoKα
orientation reflections number, range (2θ)	25, 19° < 2θ < 35°
temperature, °C	23 ± 1
scan method	θ - 2θ
max 2θ, deg	55.0
R^a	0.0358
$R_w{}^b$	0.0452
quality of fit indicator^c	0.966
total unique reflections	4443

---

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

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

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

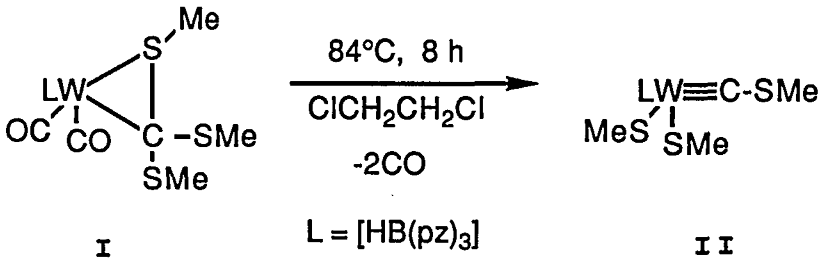
Table 1 (continued)

unique reflections observed ($F_o^2 > 3\sigma(F_o^2)$)	3091
no. of parameters refined	217
T_{min}/T_{max}	1.00/0.747
largest shift/esd, final cycle	<0.01
largest peak, e/Å^3	2.85, 0.76 Å from W

RESULTS AND DISCUSSION

Thermal Reactions of $[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)(Nuc)SMe]$

Upon heating above 65°C, $[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)_2SMe]$ (**I**) undergoes irreversible C-S bond cleavage, SMe migration to the tungsten and CO loss to form the 16-electron terminal thiocarbyne $[HB(pz)_3](MeS)_2W{\equiv}C\text{-}SMe$ (**II**, eq 2) in 68% isolated

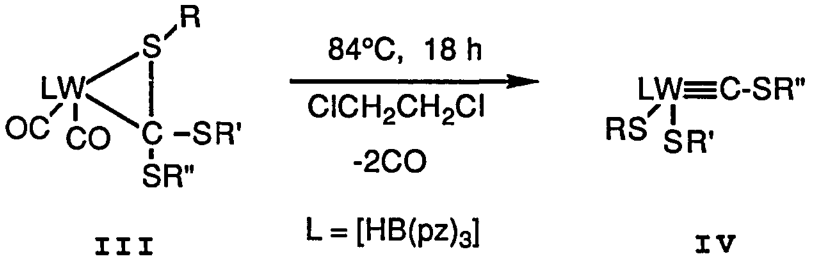


(2)

I **II**

yield. No other products are identified by ^1H NMR spectroscopy in the reaction mixture; however, a small amount (5-10%) of an uncharacterized insoluble green material is also formed. The $^{13}C\{H\}$ NMR spectrum of **II** shows the carbyne carbon resonance at δ 268.3 ppm, which is similar to the chemical shifts reported for the 18-electron thiocarbyne complexes $[HB(pz)_3](CO)_2W{\equiv}C\text{-}SMe$ and $Cp(CO)_2W{\equiv}C\text{-}S[2,4\text{-}C_6H_3(NO_2)_2]$ (δ 264.4 and 261.7 ppm, respectively).[6] Thus, the carbyne ^{13}C chemical shift is essentially unaffected by the change in the oxidation state of tungsten. This suggests that **II**, like the 18-electron complexes, is an electron-rich carbyne as compared to the electron-poor carbyne $(t\text{-}BuO)_3W{\equiv}C\text{-}S\text{-}t\text{-}Bu$, in which the carbyne ^{13}C shift occurs ~40 ppm further upfield at δ 222.7 ppm.[7] The structure of **II** was established by X-ray analysis and will be discussed later. Although **II** is a 16-electron complex, it does not react with PMe_3 (25°C, 72 h), and it does not react with CO (250 psi, 25 or 85°C) to form either an adduct or complex **I** by the reverse of eq 2.

Upon heating, $[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)(SEt)SMe]$ (**III**), which is a mixture of 3 isomers (**X**, **Y**, **Z**), also loses both CO ligands, and two thiolate groups migrate to tungsten forming **IV** (eq 3), which exists as two isomers, $[HB(pz)_3](MeS)_2W{\equiv}C\text{-}SEt$ (**A**) and $[HB(pz)_3](MeS)(EtS)W{\equiv}C\text{-}SMe$ (**B**). These isomers



(3)

III

X; R = R' = Me, R" = Et
Y; R = R" = Me, R' = Et
Z; R = Et, R' = R" = Me

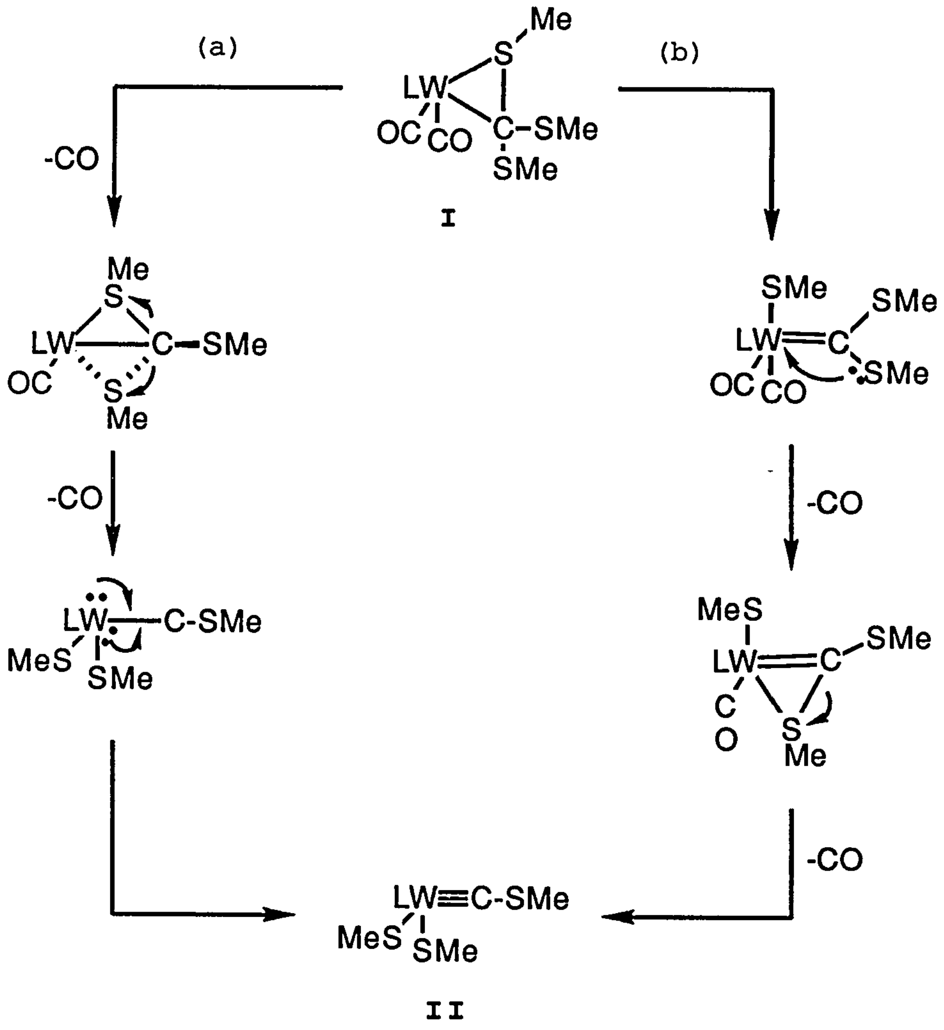
IV

A; R" = Et, R = R' = Me
B; R = R" = Me, R' = Et
A:**B** = 5:1

could not be separated by chromatography or recystallization. The resonances in the ^1H NMR spectrum of the mixture of isomers were assigned by comparison with those of **II**, in which the two MeS groups bound to tungsten occur further downfield than the MeS group bound to the carbyne carbon.

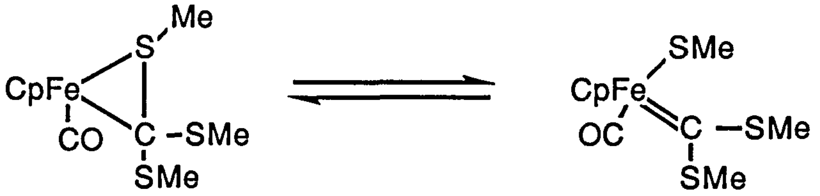
No intermediates are detected by ^1H NMR spectroscopy during the reactions (eq 2 and 3) of **I** and **III**. Two possible pathways for reaction (2) are shown in Scheme 2. In pathway (a), the first step involves CO loss and coordination of a

Scheme 2



L = [HB(pz)$_3$]

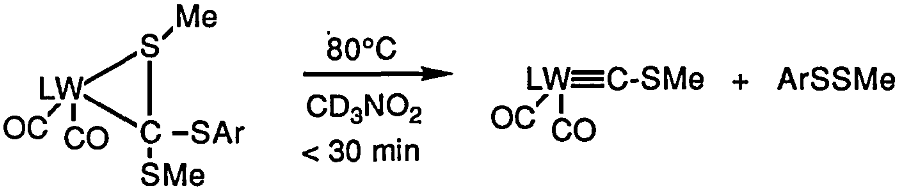
second SMe group to tungsten. The resulting intermediate with an η^3-$C(SMe)_3$ ligand is similar to the known complexes, $\{Cp(CO)_2\overline{W[C(S}Me)_2(4\text{-}C_6H_4Me)]\}(BF_4)_2$[8] and $I(CO)_3\overline{W[C(S}Me)_2\text{-}(Me)]$,[9] each with a carbon and two sulfur donors coordinated to tungsten. Subsequent cleavage of both C-S bonds in this intermediate with loss of a second CO gives the carbyne product **II.** In pathway (b), C-S bond cleavage occurs first, producing a W-SMe group and an η^1-carbene, in a process which is essentially the same as that (eq 4) for $Cp(CO)Fe[\eta^2\text{-}C(SMe)_2SMe]$ for which there is substantial evidence.[10] This



(4)

is followed by loss of CO and coordination of one of the carbene SMe groups to tungsten, thus forming an η^2-carbene. Similar η^2-carbenes, $\{[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)SMe]\}SO_3CF_3$,[2] $\{[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]\}SO_3CF_3$,[11] $\{Cp(CO)_2W[\eta^2\text{-}C(4\text{-}C_6H_4Me)SMe]\}BF_4$[8] and $\{(PPh_3)_2[CN(4\text{-}C_6H_4Me)](Cl)Os[\eta^2\text{-}C(4\text{-}C_6H_4Me)SMe]\}ClO_4$[12] have been reported in the literature. Additional CO loss and C-S bond cleavage give the carbyne product **II.** There are no results which exclude either pathway (a) or (b) as the mechanism of these reactions.

The SAr complexes $[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)(SAr)SMe]$[2] (**V**, Ar = Ph; **VII**, Ar = $4\text{-}C_6H_4Me$) do not lose CO upon heating but quantitatively eliminate the disulfides ArSSMe (identified by ^{1}H NMR and mass spectroscopy), and form the known thiocarbyne complex $[HB(pz)_3](CO)_2W{\equiv}C{-}SMe$[6] (eq 5). A


(5)

V, Ar = Ph

VII, Ar = 4-C_6H_4Me

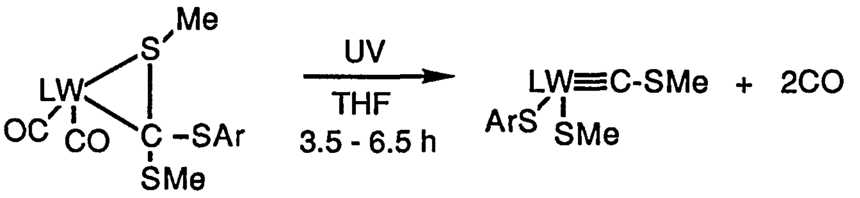
L = $[HB(pz)_3]$

mechanism involving thiolate radicals (ArS·) seems unlikely since no ArSSAr or MeSSMe is produced in the reaction. A more likely pathway is a concerted α-elimination of the disulfide. To our knowledge, no analogous α-eliminations of disulfides from organic thioketals ($R_2C(SR')_2$) to generate carbenes (R_2C:) have been reported.

One might ask why the alkylsulfide compounds (**I** and **III**) undergo RS migration (eq 2 and 3) while the arylsulfide derivatives (**V** and **VII**) eliminate disulfide (eq 5). If reactions (2) and (3) proceed by either mechanism (a) or (b) in Scheme 2, the SR group which is not coordinated to the tungsten must become coordinated at some point. Since the arylsulfide groups (SAr) are less nucleophilic and basic than the SMe and SEt groups, it seems that they will be less likely to coordinate to the metal and give products of the type in eqs 2 and 3. Apparently the elimination of the disulfide in the arylsulfide then is the favored reaction. The weaker nucleophilicity (or basicity) of the SAr groups is also seen in the lack of scrambling of the SMe and SAr groups in **V** or **VII** to give $[HB(pz)_3](CO)_2\overline{W[\eta^2-C(SMe)_2S}Ar]$; whereas, **III** does show scrambling of the SMe and SEt groups to give $[HB(pz)_3](CO)_2\overline{W[\eta^2-C(SMe)_2S}Et]$ in less than 3 h at 25°C.[2]

Photolytic Reactions of $[HB(pz)_3](CO)_2W[\eta^2-C(SMe)(Nuc)SMe]$

In contrast to their thermal reactions (eq 5), $[HB(pz)_3](CO)_2W[\eta^2-C(SMe)(SPh)SMe]$ (**V**) and $[HB(pz)_3](CO)_2W[\eta^2-C(SMe)(S-4(C_6H_4Me)SMe]$ (**VII**) under UV photolysis at room temperature lose two CO ligands, undergo C-S cleavage and migration of the SAr group from the carbon to the tungsten to form the thiocarbynes $[HB(pz)_3](ArS)(MeS)W{\equiv}C-SMe$ (**VI**, Ar = Ph, 73%; **VIII**, Ar = 4-C_6H_4Me, 52%) (eq 6). These



(6)

V, Ar = Ph

VII, Ar = 4-C_6H_4Me

L = $[HB(pz)_3]$

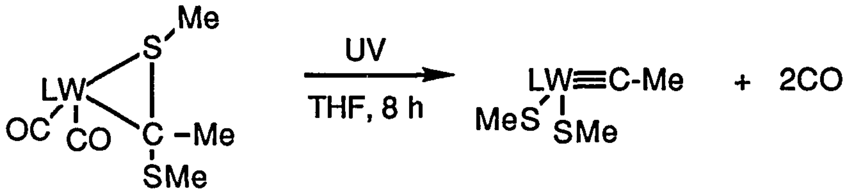
VI, Ar = Ph

VIII, Ar = 4-C_6H_4Me

reactions are similar to the thermolysis reactions (eq 2, 3) of **I** and **III**. As in those reactions, an uncharacterized insoluble green material (10-30%) is also formed. Complexes **VI** and **VIII** were characterized by their elemental analyses, MS, ^1H NMR and $^{13}C\{H\}$ NMR spectra. The ^1H NMR spectra of **VI** and **VIII** show two different SMe groups (δ 3.69 and 2.51 ppm; δ 3.65 and 2.51 ppm, respectively). As in complexes **II** and **IV**, the MeS group bound to tungsten occurs further downfield than the MeS group bound to carbon. Unlike complex **IV**, **VI** and **VIII** exist as only one isomer, the one in which an SMe and the SAr group are bound to tungsten. The $^{13}C\{H\}$ NMR spectra of **VI** and **VIII** show carbyne carbon resonances at δ 271.1 and 270.8 ppm, repectively, which are similar to that of $[HB(pz)_3](MeS)_2W{\equiv}C\text{-}SMe$ (**II**) at δ 268.3 ppm (*vide supra*).

While compounds **I** and **III** produce the carbyne complexes **II** and **IV**, respectively, upon heating (eq 2 and 3), these reactions also occur under photolysis; however, the yields (**II**, 34%; **IV**, 26%) are lower than those (**II**, 68%; **IV**, 40%) obtained from the thermolysis reactions. In addition, a larger amount (30-40%) of the uncharacterized green product is also obtained.

The methyl complex $[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)(Me)SMe]$ (**IX**)[2] upon photolysis also undergoes loss of two CO ligands and transfer of the two MeS groups to the tungsten to give the methyl carbyne complex **X** in 78% yield (eq 7). It was somewhat surprising that complex **IX** did not undergo any type of thermolysis reaction (85°C, CD_3NO_2, 2 h). The product of the photolytic reaction $[HB(pz)_3](MeS)_2W{\equiv}C\text{-}Me$ (**X**) was characterized by its elemental analysis, MS, ^1H NMR and



(7)

IX L = [HB(pz)$_3$] **X**

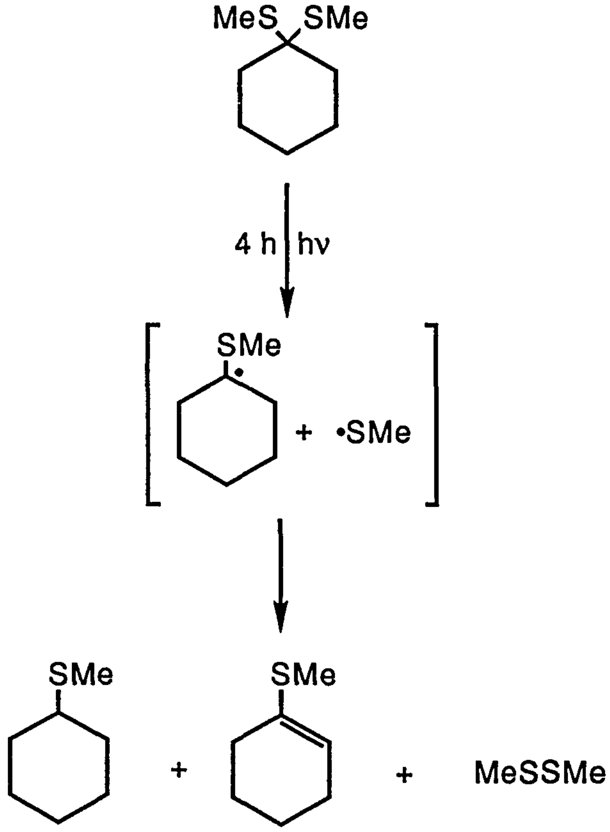
^{13}C{H} NMR spectra. In the ^{1}H NMR spectrum of **X**, the two SMe groups exhibit a single resonance at δ 3.37 ppm, which is similar to that (δ 3.42 ppm) observed for the two SMe groups bound to tungsten in [HB(pz)$_3$](MeS)$_2$W≡C-SMe (**II**) (*vide supra*). The resonance at δ 4.38 ppm (J_{WH} = 9.3 Hz) is assigned to the Me group bound to the carbyne carbon. This is much further downfield than the resonance observed for the carbyne Me group in the 18-electron complex [HB(pz)$_3$](CO)$_2$W≡C-Me (δ 2.43 ppm).[5] However, similar downfield Me resonances have been reported for the alkylidyne complexes (*t*-BuO)$_3$(py)W≡C-Me (δ 3.89 ppm, J_{WH} = 8.1 Hz) and (*t*-BuO)$_3$W≡C-Me (δ 3.56 ppm, J_{WH} = 7.13 Hz).[7] The carbyne ^{13}C{H} resonance in **X** occurs at δ 303.9 ppm, which compares with the shift reported for the 18-electron complex [HB(pz)$_3$](CO)$_2$W≡C-Me (δ 295.2 ppm).[5] Thus, as in the thiocarbynes (**II, IV, VI, VIII**), an increase in the oxidation state of tungsten changes the carbyne carbon chemical shift very little. This suggests that the carbyne carbon in **X** is more similar to the carbyne in the electron-rich [HB(pz)$_3$](CO)$_2$W≡C-Me than to the Schrock-type carbyne in

$(t\text{-}BuO)_3W{\equiv}C\text{-}Me$, in which the carbyne carbon shift occurs ~50 ppm further upfield at δ 254.3 ppm.[7]

Photolysis of the phosphine complexes $\{[HB(pz)_3](CO)_2W\text{-}[\eta^2\text{-}C(SMe)(PR_3)SMe]\}SO_3CF_3$ ($PR_3 = PMe_3$, PEt_2H)[2] at 25°C in THF for 3 h gives a mixture of products, one of which was identified by IR and ^1H NMR as the η^2-dithiocarbene $\{[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)SMe]\}SO_3CF_3$.[2] Under similar conditions, photolysis of the complex $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)SMe]$[2] also gives a mixture of uncharacterized products.

A possible mechanism for the photolytic reactions (eqs 6, 7) of **V**, **VII** and **IX** could involve UV-promoted CO loss, followed by coordination of a second SR group to tungsten. This is basically the same as path (a) in Scheme 2, one of the mechanisms proposed for the thermal reactions. Photolytic CO substitution is well known in transition metal carbonyl complexes.[13] King *et al.* have reported[14] UV photolytic CO substitution in $CpMo(CO)_2(\eta^3\text{-}C_3H_5)$ by $(Et_2N)PF_2$ to give $CpMo(CO)(\eta^3\text{-}C_3H_5)(PF_2NEt_2)$. Similarly, photolyzing $CpMo(CO)_2(NO)$ in the presence of PPh_3 produces $CpMo(CO)(NO)(PPh_3)$.[15]

Another possible mechanism could involve light-promoted homolytic C-S bond cleavage as the initial step. Kohrman and Berchtold have reported[16] the photolysis of a series of thioketal compounds which give products resulting from homolytic C-S bond cleavage. An example is shown in eq (8). Based on the precedent for photolytic CO substitution in



(8)

transition metal carbonyl complexes, the mechanism shown in path (a) of Scheme 2 seems more likely. However, there are no results that unequivocally eliminate a mechanism involving homolytic C-S bond cleavage.

Structure of $[HB(pz)_3](MeS)_2W{\equiv}C\text{-}SMe$ **(II)**

Crystals of **II** suitable for X-ray analysis were grown from CD_2Cl_2 by layering with hexanes at -20°C. The coordination geometry is pseudo-octahedral as shown in Figure

1. Selected bond distances and angles are given in Table 2. The W-C(1) bond distance (1.788(7) Å) is within experimental error of the metal-carbyne carbon distances reported for the electron-rich carbyne complexes Cp(PPh$_3$)(CO)W≡C-SPh (1.807(18) Å)[17] and [HB(3,5-Me$_2$-C$_3$HN$_2$)$_3$](CO)$_2$Mo≡C-S(4-C$_6$H$_4$NO$_2$) (1.801(4) Å).[18] It is interesting to note that these W-C distances are slightly longer than the W-C distance (1.759(6) Å)[19] found in the Schrock-type carbyne [(*t*-BuO)$_3$W≡C-Me]$_2$. The W-C-S angle (171.6(5)°) is within the range (170-180°)[20] typical for terminal carbynes. The C(1)-S(1) distance (1.700(7) Å) appears to be slightly longer than the C(sp)-S distance in MeS-C≡C-SMe (1.671(2) Å)[21] determined by electron diffraction in the gas phase; however, it is similar to the C(carbyne)-S distances in Cp(PPh$_3$)(CO)W≡C-SPh (1.716(10) Å)[17] and in [HB(3,5-Me$_2$-C$_3$HN$_2$)$_3$](CO)$_2$Mo≡C-S(4-C$_6$H$_4$NO$_2$) (1.712(4) Å).[18]

The S(1)-C(2) (1.81(1) Å), S(2)-C(3) (1.81(1) Å) and S(3)-C(4) (1.831(8) Å) distances compare well with S-C(sp^3) single-bond distances obtained in microwave studies of MeSH (1.819 Å),[22] Me$_2$S (1.802 Å)[23] and MeS-C≡C-SMe (1.806(2) Å).[21] The W-S(2) (2.338(2) Å) and W-S(3) (2.343(2) Å) distances are similar to the Mo-S distances in *trans*-[Mo(S-*n*-Bu)$_2$(dppe)$_2$] (2.361(1) Å),[24] Mo(S-*t*-Bu)$_2$(CN-*t*-Bu)$_2$(PhC≡CPh) (2.338(3) Å)[25] and *cis*-[Mo(S-*t*-Bu)$_2$(CN-*t*-Bu)$_4$] (2.374(3) Å).[26] Since all of these complexes are formally 16-electron species, the sulfur

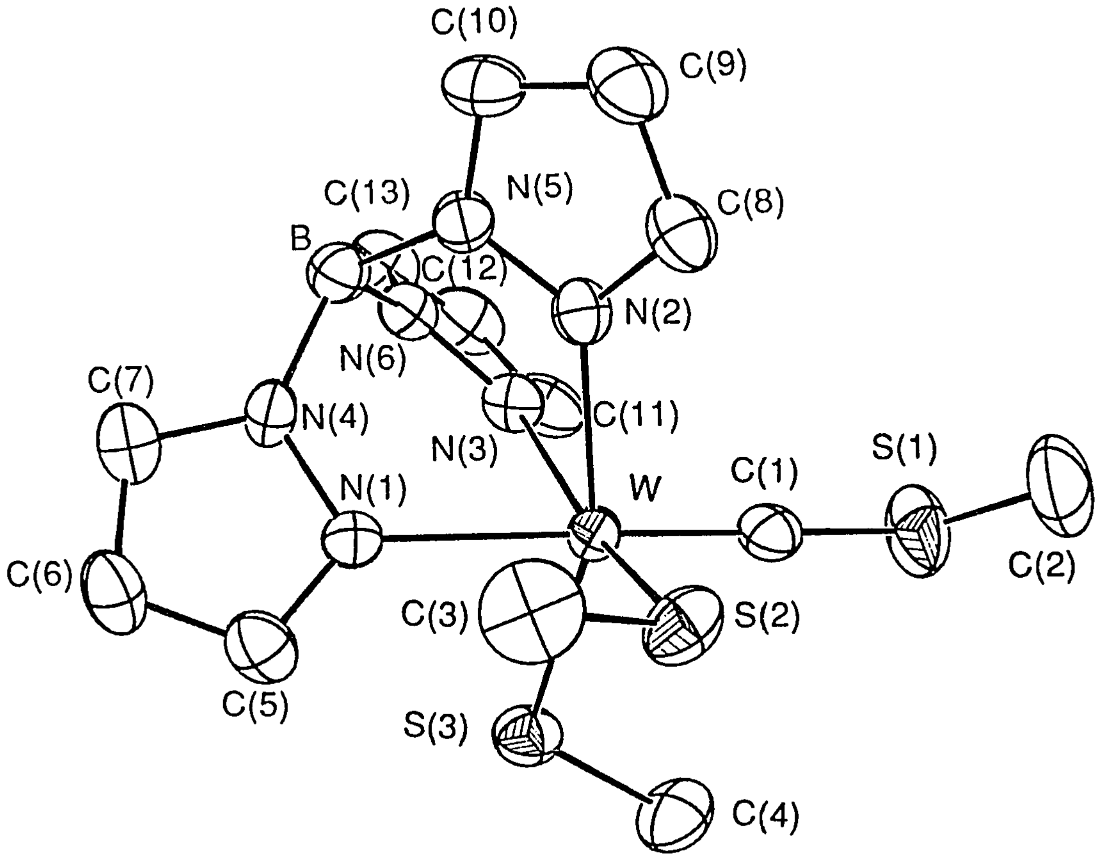


Figure 1. ORTEP plot of $[HB(pz)_3](MeS)_2W{\equiv}C\text{-}SMe$ (II)

Table 2. Selected Bond Distances (Å)[a] and Angles (deg)[a] in $[HB(pz)_3](MeS)_2W{\equiv}C\text{-}SMe$

W-C(1)	1.788(7)	W-C(1)-S(1)	171.6(5)	S(2)-W-N(2)	86.1(2)
C(1)-S(1)	1.700(7)	C(1)-S(1)-C(2)	103.2(5)	S(2)-W-N(3)	163.2(2)
S(1)-C(2)	1.82(1)	W-S(2)-C(3)	110.7(3)	S(2)-W-C(1)	90.6(2)
W-S(2)	2.338(2)	W-S(3)-C(4)	110.9(3)	S(3)-W-C(1)	95.3(2)
W-S(3)	2.343(2)	N(1)-W-N(2)	82.0(2)	S(3)-W-N(1)	80.4(1)
S(2)-C(3)	1.81(1)	N(1)-W-N(3)	81.1(2)	S(3)-W-N(2)	160.5(1)
S(3)-C(4)	1.831(8)	N(2)-W-N(3)	77.2(2)	S(3)-W-N(3)	91.8(1)
W-N(1)	2.288(5)	S(2)-W-S(3)	103.65(7)	N(2)-W-C(1)	101.4(2)
W-N(2)	2.222(5)	S(2)-W-N(1)	94.9(2)	N(3)-W-C(1)	94.5(3)
W-N(3)	2.196(6)				

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 3. Comparative Structural Data for Mo and W Thiolate Complexes

complex	no. of electrons	M-S (Å)	reference
$[\mathrm{HB(pz)_3}](\mathrm{MeS})_2\mathrm{W{\equiv}C{-}SMe}$	16	2.338(2) 2.343(2)	this work
trans-$[\mathrm{Mo}(\mathrm{S}\text{-}n\text{-}\mathrm{Bu})_2(\mathrm{dppe})_2]$	16	2.361(1)	24
$\mathrm{Mo}(\mathrm{S}\text{-}t\text{-}\mathrm{Bu})_2(\mathrm{CN}\text{-}t\text{-}\mathrm{Bu})_2(\mathrm{PhC{\equiv}CPh})$	16	2.338(3)	25
cis-$[\mathrm{Mo}(\mathrm{S}\text{-}t\text{-}\mathrm{Bu})_2(\mathrm{CN}\text{-}t\text{-}\mathrm{Bu})_4]$	16	2.374(3)	26
$\mathrm{CpMo(NO)(SPh)_2}$	16	2.345(1) 2.339(1)	27
$[\mathrm{Na(18\text{-}crown\text{-}6)}][\mathrm{W(CO)_5(SH)}]$	18	2.567(5)	28
$[\mathrm{NEt_4}][\mathrm{W_2(CO)_{10}}(\mu\text{-}\mathrm{SC_6Cl_5})]$	18	2.568(4)	29
$\mathrm{W_2(CO)_8}(\mu\text{-}\mathrm{S}\text{-}t\text{-}\mathrm{Bu})_2{}^a$	18	2.480(2)	30
$\mathrm{W_2(CO)_8}(\mu\text{-}\mathrm{SMe})_2{}^a$	18	2.47(1) 2.477(6)	31
$[\mathrm{NEt_4}]_2[\mathrm{W_2(CO)_8}(\mu\text{-}\mathrm{SPh})_2]$	18	2.582(2) 2.599(2)	32
$[\mathrm{NEt_4}]_2[\mathrm{Mo_2(CO)_8}(\mu\text{-}\mathrm{SCH_2CO_2Et})_2]$	18	2.586(1) 2.587(1)	33
$\mathrm{Mo_2(CO)_6}(\mu\text{-}\mathrm{SCH_2CO_2Et})_2(\mathrm{MeCN})_2{}^a$	18	2.455(2) 2.467(2)	33
$\{[\mathrm{HB(pz)_3}](\mathrm{CO})_2\mathrm{W}[\eta^2\text{-}\mathrm{CH(SMe)}]\}\mathrm{SO_3CF_3}$	18	2.481(6)	11

^{a} Contains a M-M bond.

atoms of the thiolate ligands could donate π-electron density to the metal, thus shortening the M-S distances. The M-S distances for a variety of molybdenum and tungsten 16- and 18-electron complexes are listed in Table 3. The M-S distances in the 16-electron compounds are 0.1-0.2 Å shorter than in the 18-electron compounds, thus indicating some degree of sulfur donation of π-electron density into vacant metal d-orbitals. Perhaps, it is the electron-donating ability of the RS groups in the carbyne complexes (**II**, **IV**, **VI**, **VIII** and **X**) reported in this paper which makes the carbyne ligands so similar in these formally 16-electron complexes and in the related 18-electron analogs, e.g., $[HB(pz)_3](CO)_2W{\equiv}C{-}SMe$, $[HB(pz)_3](CO)_2W{\equiv}C{-}Me$ and $[HB(3,5{-}Me_2{-}C_3HN_2)_3](CO)_2Mo{\equiv}C{-}S(4{-}C_6H_4NO_2)$.

Conclusion

Migration of an α-hydrogen from an alkylidene ligand to produce an alkylidyne has been reported in several reactions by Schrock and co-workers.[20] For example, when PMe_3 is added to $Cp(Cl)[(t{-}Bu)CH_2]Ta{=}CH(t{-}Bu)$, the carbyne complex $Cp(Cl)(Me_3P)_2Ta{\equiv}C(t{-}Bu)$ and neopentane are formed.[34]

In this paper, we have shown that a novel α-thiolate (RS) migration occurs when solutions of the complexes $[HB(pz)_3](CO)_2W[\eta^2{-}C(SMe)(SR)SMe]$ (R = Me, Et, Ph, $C_6H_4Me{-}4$) are heated or irradiated. The resulting carbyne complexes $[HB(pz)_3](MeS)(RS)W{\equiv}C{-}SMe$ contain carbyne ligands which are spectroscopically and crystallographically similar to those of related $L(CO)_2W{\equiv}C{-}X$ ($L = HB(pz)_3$ or Cp; X = SR, Me) derivatives despite the difference in oxidation state and formal electron count (16- vs 18-electrons) of the metal.

ACKNOWLEDGMENT

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SUPPLEMENTARY MATERIAL

Table 1. Final Atomic Position Parameters[a] for $[HB(pz)_3](MeS)_2W{\equiv}C\text{-}SMe$, **II**

atom	x	y	z	B(Å^2)
W	0.03513(2)	0.21521(2)	0.14936(2)	2.095(4)
S(1)	-0.2055(2)	0.3958(2)	0.1956(2)	5.00(5)
S(2)	0.0414(2)	0.2548(2)	-0.0060(1)	3.58(3)
S(3)	-0.1167(2)	0.0807(1)	0.1540(1)	3.17(3)
N(1)	0.1794(5)	0.0816(4)	0.1414(3)	2.65(9)
N(2)	0.2238(5)	0.3021(4)	0.1646(4)	2.46(9)
N(3)	0.0867(5)	0.1992(4)	0.2955(4)	2.45(9)
N(4)	0.2953(5)	0.0810(4)	0.1949(3)	2.47(9)
N(5)	0.3323(5)	0.2676(3)	0.2126(4)	2.5(1)
N(6)	0.2095(5)	0.1734(4)	0.3295(3)	2.42(9)
C(1)	-0.0856(6)	0.3125(5)	0.1657(5)	2.8(1)
C(2)	-0.178(1)	0.5039(6)	0.1210(6)	6.2(2)
C(3)	0.184(1)	0.1960(7)	-0.0572(7)	5.1(2)
C(4)	-0.2881(7)	0.1276(6)	0.1496(6)	4.4(2)
C(5)	0.1769(7)	-0.0031(5)	0.0944(4)	3.3(1)
C(6)	0.2927(7)	-0.0600(5)	0.1124(5)	3.7(1)
C(7)	0.3613(7)	-0.0040(5)	0.1782(5)	3.5(1)
C(8)	0.2563(7)	0.3923(5)	0.1328(5)	3.3(1)

C(9)	0.3866(7)	0.4184(5)	0.1593(5)	3.6(1)
C(10)	0.4309(6)	0.3355(5)	0.2118(5)	3.4(1)
C(11)	0.0082(8)	0.2042(5)	0.3663(5)	3.7(1)
C(12)	0.0811(8)	0.1807(6)	0.4477(5)	4.1(2)
C(13)	0.2067(7)	0.1639(5)	0.4203(4)	3.2(1)
B	0.3273(7)	0.1658(5)	0.2638(5)	2.7(1)

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

Table 2. Other Bond Distances for $[HB(pz)_3](MeS)_2W{\equiv}C\text{-}SMe^a$

N(1)-N(4)	1.382(6)
N(1)-C(5)	1.313(8)
N(2)-N(5)	1.357(7)
N(2)-C(8)	1.324(8)
N(3)-N(6)	1.359(7)
N(3)-C(11)	1.33(1)
N(4)-C(7)	1.330(8)
N(4)-B	1.534(9)
N(5)-C(10)	1.337(9)
N(5)-B	1.540(9)
N(6)-C(13)	1.338(9)
N(6)-B	1.55(1)
C(5)-C(6)	1.40(1)
C(6)-C(7)	1.38(1)
C(8)-C(9)	1.40(1)
C(9)-C(10)	1.40(1)
C(11)-C(12)	1.41(1)
C(12)-C(13)	1.36(1)

[a] Bond distances are in angstroms (Å). Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 3. Other Bond Angles for $[HB(pz)_3](MeS)_2W{\equiv}C\text{-}SMe$, **II**[a]

N(1)-W-C(1)	173.7(3)	N(3)-N(6)-C(13)	109.8(6)
W-N(1)-N(4)	120.0(4)	N(3)-N(6)-B	119.5(5)
W-N(1)-C(5)	132.9(4)	C(13)-N(6)-B	130.6(5)
N(4)-N(1)-C(5)	107.1(5)	N(1)-C(5)-C(6)	110.8(6)
W-N(2)-N(5)	123.3(4)	N(4)-C(7)-C(6)	109.8(6)
W-N(2)-C(8)	130.4(4)	N(2)-C(8)-C(9)	111.3(6)
N(5)-N(2)-C(8)	106.3(5)	C(8)-C(9)-C(10)	103.8(6)
W-N(3)-N(6)	124.3(4)	N(5)-C(10)-C(9)	107.7(6)
W-N(3)-C(11)	129.1(5)	C(5)-C(6)-C(7)	103.8(6)
N(6)-N(3)-C(11)	106.5(5)	N(3)-C(11)-C(12)	110.1(8)
N(1)-N(4)-C(7)	108.5(5)	C(11)-C(12)-C(13)	104.4(8)
N(1)-N(4)-B	121.5(5)	N(6)-C(13)-C(12)	109.2(6)
C(7)-N(4)-B	129.8(5)	N(4)-B-N(5)	108.9(5)
N(2)-N(5)-C(10)	110.8(5)	N(4)-B-N(6)	107.9(5)
N(2)-N(5)-B	120.4(5)	N(5)-B-N(6)	106.4(6)
C(10)-N(5)-B	128.6(5)		

[a] Angles given in degrees; Numbers in parentheses are estimated standard deviations in the least significant digits.

GENERAL SUMMARY

The research described in this dissertation shows that carbon monsulfide (CS) can act as a four-electron donating, side-on bridging thiocarbonyl ligand. Thus, CS can coordinate to metals in all of the bonding modes that are known for CO. Moreover, in carbonyl thiocarbonyl complexes, the CS group always prefers bridging positions.

It is also demonstrated that the electron-rich thiocarbonyl ligand in $[HC(pz)_3]W(CO)_2(CS)$ can be methylated to give the cationic thiocarbyne $\{[HC(pz)_3](CO)_2W{\equiv}C\text{-}SMe\}BF_4$. This cationic carbyne was observed to react similarly to electron-rich carbynes rather than the cationic Fischer-type carbynes. In addition, it is shown that the neutral thiocarbyne $[HB(pz)_3](CO)_2W{\equiv}C\text{-}SMe$ reacts with the electrophile MeS^+ to give the dithiocarbene $[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)SMe]^+$, in which the carbene carbon atom and one of the sulfur atoms is coordinated to tungsten, thus forming a W-C-S ring. Nucleophiles add to the carbene carbon forming the adducts $[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)(Nuc)SMe]$ in which the W-C-S ring remains intact.

Finally, this dissertation demonstrates that the complexes $[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)(SR)SMe]$ undergo novel photolytic and thermal reactions, which result in CO loss, C-S bond cleavage and α-thiolate (RS) migration to give the carbynes $[HB(pz)_3](MeS)(RS)W{\equiv}C\text{-}SMe$ (R = Me, Et, Ph, Tolyl).

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