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Reactions of the Thiocarbyne [HB(pz)$_3$](CO)$_2$W(≡CSMe) and Thiocarbene [HB(pz)$_3$](CO)$_2$W[η^2-CH(SMe)]$^+$ Complexes with Phosphines

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Reaction of the carbyne complex [HB(pz)$_3$](CO)$_2$W(≡CSMe) (1) with PEt$_3$ gives the η^2-ketenyl derivative [HB(pz)$_3$](CO)(PEt$_3$)$\overline{\mathrm{W(C(O)C}}$SMe) (2) which upon methylation with MeOSO$_2$F at the ketenyl oxygen atom yields the unusual acetylene complex [HB(pz)$_3$](CO)(PEt$_3$)W(MeOC≡CSMe)$^+$ (5). The title thiocarbene complex [HB(pz)$_3$](CO)$_2$W[η^2-CH(SMe)]$^+$ (6) is prepared by protonation of the carbyne carbon in [HB(pz)$_3$](CO)$_2$W(≡CSMe) with CF$_3$SO$_3$H and other strong acids. Reactions of 6 with phosphorus donors, L (PPh$_3$, PEt$_3$, PPh$_2$H, P(OMe)$_3$), give the carbene adducts [HB(pz)$_3$](CO)$_2$W[η^2-CH(SMe)(L)]$^+$ (9–12). The phosphonium proton in [HB(pz)$_3$](CO)$_2$W[η^2-CH(SMe)(PPh$_2$H)]$^+$ is removed by NEt$_3$ to give [HB(pz)$_3$](CO)$_2$W[η^2-CH(SMe)(PPh$_2$)] (13) whose structure was established by an X-ray diffraction study.

Introduction

In recent years, the preparations and reactions of thiocarbene[1] and thiocarbyne[2] complexes have been studied extensively in this laboratory. One of those studies led to the synthesis of the thiocarbyne complex [HB(pz)$_3$](CO)$_2$W(≡CSMe) (1),[3] where HB(pz)$_3^-$ is the hydrotris(1-pyrazolylborato) ligand. Aside from a communication[4] describing the reaction of 1 with strong acids to give the η^2-thiocarbene complex {[HB(pz)$_3$](CO)$_2$W[η^2-CH(SMe)]}CF$_3$SO$_3$ (6), there are no other reports of reactions of 1. Only three other thiocarbyne compounds [HB(3,5-Me$_2$C$_3$HN$_2$)$_3$](CO)$_2$Mo(≡CSR) (R = Me, Ph, 4-C$_6$H$_4$NO$_2$)[5] and one other η^2-thiocarbene complex {(PPh$_3$)$_2$[CN(4-C$_6$H$_4$CH$_3$)](Cl)Os[η^2-C(SMe)(4-C$_6$H$_4$CH$_3$)]}ClO$_4$[6] have been reported, and very little is known about their reactivities. In this paper we describe studies of 1 and 6 which demonstrate that they are highly reactive toward certain nucleophiles and electrophiles.

Table I. IR Data for the Complexes in CH$_2$Cl$_2$ Solvent

complex	IR ν(CO), cm^{-1}
[HB(pz)$_3$](CO)$_2$W(≡CSMe) (1)	1980 s, 1888 s
[HB(pz)$_3$](CO)(PEt$_3$)$\overline{\mathrm{W(C(O)C}}$SMe) (2)	1881 s, 1665 m^a
(η^5-C$_5$H$_5$)(CO)(PPh$_2$Me)$\overline{\mathrm{W(C(O)C}}$S–DNP) (3)	1917 s, 1679 m^a
(η^5-C$_5$H$_5$)(CO)(PPh$_3$)$\overline{\mathrm{W(C(O)C}}$S–DNP) (4)	1925 s, 1671 m^a
{[HB(pz)$_3$](CO)(PEt$_3$)W(η^2-MeOC≡CSMe)}FSO$_3$ (5)	1959 s
{[HB(pz)$_3$](CO)$_2$W[η^2-CH(SMe)]}CF$_3$SO$_3$ (6)	2067 m, 1996s
[HB(pz)$_3$](CO)$_3$WCl (7)	2033 s, 1947 vs, 1904 s
[HB(pz)$_3$](CO)$_3$WI (8)	2021 s, 1942 vs, 1904 s
{[HB(pz)$_3$](CO)$_2$W[η^2-CH(SMe)(PPh$_3$)]}CF$_3$SO$_3$ (9)	1950 s, 1837 s
{[HB(pz)$_3$](CO)$_2$W[η^2-CH(SMe)(PEt$_3$)]}CF$_3$SO$_3$ (10)	1943 s, 1820 s
{[HB(pz)$_3$](CO)$_2$W[η^2-CH(SMe)(P(OMe)$_3$)]}CF$_3$SO$_3$ (11)	1955 s, 1826 s
{[HB(pz)$_3$](CO)$_2$W[η^2-CH(SMe)(PPh$_2$H)}CF$_3$SO$_3$ (12)	1946 s, 1831 s
[HB(pz)$_3$](CO)$_2$W[η^2-CH(SMe)(PPh$_2$)] (13)	1935 s, 1809 s

^{a} ν(CO) of ketenyl CO.

Results and Discussion

Reaction of [HB(pz)$_3$](CO)$_2$W(≡CSMe) with PEt$_3$. Terminal carbyne ligands in cationic transition-metal complexes are frequently observed to undergo attack at the carbyne carbon by a variety of nucleophiles.[7] Phosphines are among the nucleophiles which react in this manner.[8] However, in electron-rich complexes, e.g., (η^5-C$_5$H$_5$)(CO)$_2$W(≡CMe) and (Ph$_2$PCH$_2$CH$_2$PPh$_2$)(CO)$_2$W(≡CCH$_2$Ph)$^+$, where the carbyne ligand is not susceptible to nucleophilic attack, the PMe$_3$,[9a] CN$^-$,[9b] and $^-$S$_2$CNMe$_2$[9c] nucleophiles cause carbonylation of the car-

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

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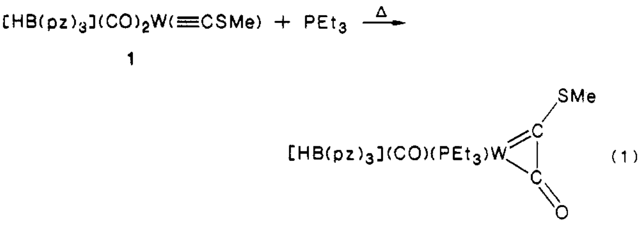
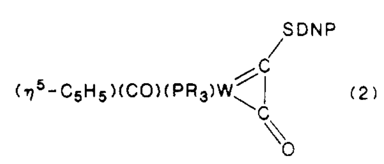
byne to give the unusual η^1- or η^2-ketenyl compounds, whose bonding has been recently discussed.[9d] Similarly, we observe that the thiocarbyne complex $[HB(pz)_3](CO)_2W(\equiv CSMe)$ (**1**) reacts with PEt_3 at 40 °C to give the air-stable η^2-ketenyl complex $[HB(pz)_3](CO)(PEt_3)W(C(O)CSMe)$ (**2**) in 61% yield according to eq 1. The re-



2

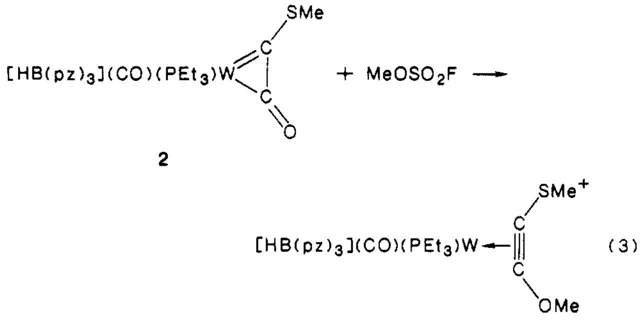
action of $(\eta^5\text{-}C_5H_5)(CO)_2W(\equiv CS\text{–}DNP)$, where DNP is 2,4-dinitrophenyl, with PPh_3 and PPh_2Me at room temperature gives the corresponding η^2-ketenyl compounds (eq 2). The reaction of $[HB(pz)_3](CO)_2W(\equiv CSMe)$ with PEt_3



3, PPh_2Me
4, PPh_3

takes place under more forcing conditions than the $(\eta^5\text{-}C_5H_5)(CO)_2W(\equiv CS\text{–}DNP)$ reactions probably because of the greater electron donor ability and steric hindrance of the $HB(pz)_3^-$ ligand. The characteristic $\nu(CO)$ of the ketenyl CO was observed (Table I) between 1660 and 1680 cm^{-1}.[9] The ^{13}C NMR spectrum of **2** was assigned (Table III) by comparison with assignments for the related complexes $(\eta^5\text{-}C_5H_5)(CO)(PMe_3)W(C(O)CR)$, reported by Kreissl;[9a] in particular, the relationship $J_{P\text{-ketenylC}} > J_{P\text{-ketenylCO}}$[9a] was used to assign the two carbon atoms bonded to the W atom in the ketenyl ligand. No reaction was observed between **1** and the nitrogen donors: NH_2Me (25 °C, 1 h, CH_2Cl_2), NH_2Et (40 °C, 13 h, CH_2Cl_2), and $LiNEt_2$ (50 °C, 19 h, THF). Sulfur atom sources (elemental sulfur and ethylene sulfide) did not react (25 °C, 20 h, CH_2Cl_2), while $3\text{-}ClC_6H_4CO_3H$ only gave decomposition; there was no evidence for the formation of W—C(=X)SMe or W≡CS(=X)Me (X = O or S) products in these reactions. The reaction of **1** with Cl_2 did not give CO-containing products, as detected by IR.

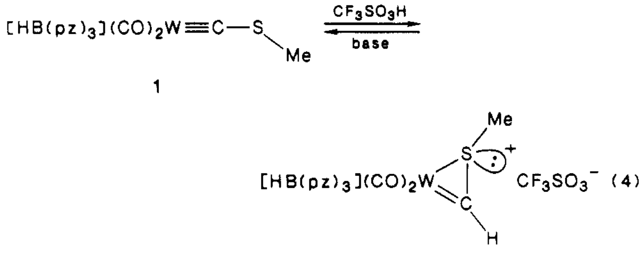
Reaction of $[HB(pz)_3](CO)(PEt_3)W(C(O)CSMe)$ with $MeOSO_2F$. Kreissl et al.[10] reported the methylation and addition of XCl_3 (X = B, Al, or In) to the ketenyl CO in $(\eta^5\text{-}C_5H_5)(CO)(PMe_3)W(C(O)CR)$ (R = Me, $4\text{-}C_6H_4CH_3$) to give $(\eta^5\text{-}C_5H_5)(CO)(PMe_3)W(RC\equiv COMe)^+$ and $(\eta^5\text{-}C_5H_5)(CO)(PMe_3)W(RC\equiv COXCl_3)$. A related conversion of a carbyne to an alkyne complex was observed in the coupling reaction of $Cl(PMe_3)_4W(\equiv CH)$ and CO in the presence of $AlCl_3$ to give $(CO)(PMe_3)_3(Cl)W(HC\equiv COAlCl_3)$.[11] We find that $[HB(pz)_3](CO)(PEt_3)W(C(O)CSMe)$ reacts similarly with $MeOSO_2F$ at room temperature (eq 3), producing the air-stable violet complex



5

$\{[HB(pz)_3](CO)(PEt_3)W(MeOC\equiv CSMe)\}FSO_3$ with the unusual $MeOC\equiv CSMe$ acetylene ligand. To our knowledge, this acetylene has not previously been prepared as either the free molecule or the ligand. IR, ^1H NMR, and ^{13}C NMR data for **5** are similar to those for the related complex $(\eta^5\text{-}C_5H_5)(CO)(PMe_3)W(MeOC\equiv CMe)^+$.[10] The low-field positions of the alkyne carbon atoms (δ 231.13, 198.02) in the ^{13}C NMR spectrum of complex **5** are similar to those in $(\eta^5\text{-}C_5H_5)(CO)(PMe_3)W(MeOC\equiv CMe)^+$ (δ 227.1, 197.7),[10] $(\eta^5\text{-}C_5H_5)(PMe_3)_2W(MeOC\equiv CMe)$ (δ 227.9, 200.5),[12] and $(CO)(\eta^2\text{-}S_2CNEt_2)_2W(HC\equiv CH)$ (δ 206.6, 207.1),[13] where the acetylene moiety is believed to be a four-electron donor. The violet compound **5** exhibits a low-energy absorption in the visible spectrum (λ_{max} = 560 nm). This absorption is probably a d–d transition as was proposed for the cationic alkyne complexes $(\eta^5\text{-}C_5H_5)(PMe_3)(CO)W[MeOC\equiv C(4\text{-}C_6H_4CH_3)]^+$ (λ_{max} = 465 nm)[12] and $(\eta^5\text{-}C_5H_5)(PMe_3)_2W[MeOC\equiv C(4\text{-}C_6H_4CH_3)]^+$ (λ_{max} = 562 nm).[12] Both electronic spectroscopy and electrochemical measurements have been used as convenient probes of the dπ interactions in the acetylene complexes.[14] Compound **5** exhibits a reversible reduction wave ($E_{1/2}$) at –1.16 V and a reversible oxidation wave ($E_{1/2}$) at 1.00 V (vs. Ag/AgCl in 0.10 M $(n\text{-}Bu)_4NPF_6$, 200 mV/s scan rate, CH_3CN).

Preparation of $\{[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]\}CF_3SO_3$. In a communication,[4] we reported that protonation of $[HB(pz)_3](CO)_2W(\equiv CSMe)$ with CF_3SO_3H gives the violet air-stable complex $\{[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]\}CF_3SO_3$ (**6**) in which the carbene ligand is bonded to the metal through both the C and S atoms, as shown by an X-ray diffraction study (eq 4). Reaction 4 also



6

occurs with $HBF_4\cdot Et_2O$ and CF_3CO_2H but not with acetic

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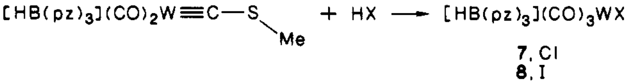
Table II. ^{1}H NMR Data for the Complexes in CD_2Cl_2 Solvent at Room Temperature[a]

complex	H3 of pz	H4 of pz	H5 of pz	CH	SMe	other
1[b]	7.91 (br)	6.23 (br)	7.65 (br)		2.69	
2[b]	8.29 (d, J = 1.45)	6.41 (t, J = 2.02)[c]	7.72 (d, J = 2.01)		2.80	1.74 (m, PCH_2)
	8.06 (d, J = 1.66)	6.29 (t, J = 2.09)	7.51 (d, J = 1.42)			0.64 (quintet, CH_3)[d]
	7.77 (d, J = 2.14)	6.04 (t, J = 2.08)	7.20 (d, J = 1.48)			
5[b]	8.00 (d, J = 2.15)	6.58 (t, J = 2.13)[c]	7.91 (d, J = 1.88)		1.94	4.45 (OMe)
	7.98 (d, J = 2.30)	6.45 (t, J = 2.18)	7.75 (d, J = 2.22)			1.82 (m, PCH_2)
	7.93 (d, J = 1.88)	6.21 (t, J = 2.21)	6.91 (d, J = 1.96)			0.66 (quintet, CH_3)[e]
6	8.07 (d, J = 2.21)	6.50 (t, J = 2.37)[c]	7.91 (d, J = 2.36)	12.78 (s, J_{WH} = 19.83)	2.37	
	7.94 (t, J = 2.90)[c]	6.47 (t, J = 2.35)	7.83 (d, J = 2.14)			
			7.81 (d, J = 2.07)			
7[b]	8.23 (d, J = 1.22)	6.30 (t, J = 1.10)[c]	7.70 (d, J = 0.98)			
8[b]	8.42 (d, J = 1.21)	6.30 (br)	7.68 (d, J = 1.38)			
9[b]	8.50 (d, J = 1.50)	6.52 (t, J = 1.05)[c]		5.67	1.93	7.70 (m, H5 of pz and Ph)
	8.04 (d, J = 1.52)	6.30 (t, J = 2.34)				
	7.93 (d, J = 1.73)	6.19 (t, J = 1.92)				
10	8.11 (br)	6.31 (br)	7.75 (br)	4.75	1.74	2.35 (m, PCH_2)
						1.40 (quintet, CH_3)[f]
11	8.15 (br)	6.31 (br)	7.75 (br)	4.99 (d, J_{PH} = 3.2)	1.81 (d, J_{PH} = 1.57)	4.23 (d, J_{PH} = 10.98, OMe)
12		6.29 (br)		5.45	1.89	8.05 (d, J_{PH} = 510.25, PH)
						8.08–7.30 (m, H3, H5 of pz and Ph)
13	8.09 (d, J = 1.73)	6.26 (t, J = 2.20)[c]	7.69 (d, J = 2.19)	4.65 (d, J_{PH} = 1.45)	1.47	7.74–7.30 (m, Ph)

[a] Chemical shifts in δ and coupling constants in Hz. Signals are singlets unless indicated otherwise. [b] $CDCl_3$ solvent. [c] Due to overlapping d of d. [d] J_{HH} = 7.53; J_{PH} = 15.03. [e] J_{HH} = 7.76; J_{PH} = 15.77. [f] J_{HH} = 7.75; J_{PH} = 17.82.

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

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



$$[HB(pz)_3](CO)_2W\equiv C-S(Me) + HX \longrightarrow \underset{\mathbf{7},\ Cl \quad \mathbf{8},\ I}{[HB(pz)_3](CO)_3WX} \qquad (5)$$

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

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

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

Reactions of $[HB(pz)_3](CO)_2W[CH(SMe)]^+$ with Phosphorus Donors. The C(carbene) atom in transition-metal carbene complexes is frequently the site of

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[15] Kim, H. P.; Angelici, R. J., *Organometallics*, following paper in this issue.

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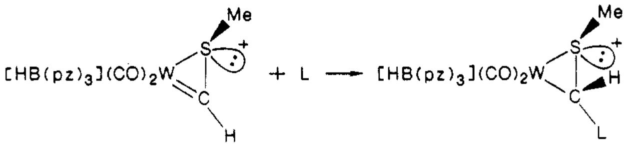
Table III. ^{13}C NMR Data for the Complexes in CD_2Cl_2 Solvent at Room Temperature[a]

complex	CO	C3 of pz	C4 of pz	C5 of pz	CH	SMe	Other
1[b]	224.7	144.9	105.7	135.2		17.4	264.4 (WCS)
2	229.75	145.67, 144.72, 142.21	107.54, 106.67	135.96, 135.10, 134.67		16.18	209.16 (d, J_{PC} = 5.86, ketenyl C), 205.22 (ketenyl CO), 18.44 (d, J_{PC} = 27.34, PCH_2), 6.04 (CH_3)
5	221.20 (d, J_{PC} = 9.97)	145.93, 144.98, 142.55	107.45, 106.67	137.96, 136.83, 136.23		19.57	231.13 (WCO), 198.02 (WCS), 66.54 (OMe), 18.79 (d, J_{PC} = 27.34, PCH_2), 6.22 (CH_3)
6	212.98, 212.55	147.21, 146.31, 145.95	109.06, 108.48, 108.33	138.76, 138.51, 138.27	227.95	28.40	121.53 (quartet, J_{CF} = 320.81, CF_3SO_3)
9	244.83, 216.31	147.15, 143.51	106.50	136.05, 134.23	38.72 (d, J_{PC} = 54.69)	22.77	[133.06 (d, J_{PC} = 5.86), 129.42 (d, J_{PC} = 9.77), 122.27, 118.46, Ph]
10	245.12 (d, J_{PC} = 4.99), 218.26	147.94, 147.49, 144.53	107.39, 106.99, 106.41	136.56, 136.37	39.65 (d, J_{PC} = 50.18)	22.08	15.04 (d, J_{PC} = 49.07, PCH_2), 6.42 (d, J_{PC} = 4.37, CH_3)
13	239.89 (d, J_{PC} = 12.12), 220.55	146.06	106.28	135.81	58.21 (d, J_{PC} = 45.32)	22.25	[143.56 (d, J_{PC} = 19.91), 140.99 (d, J_{PC} = 14.50), 133.39, 133.11, 132.91, 132.66, 128.76, 128.29, 128.22, 128.13, Ph]

[a] Chemical shifts in δ and coupling constants in Hz. [b] $CDCl_3$ solvent.

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



6 **9–12** (6)

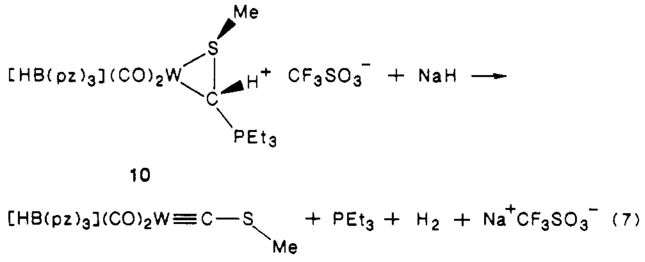
L = PPh_3 (**9**), PEt_3 (**10**), $P(OMe)_3$ (**11**), PPh_2H (**12**)

On the basis of the structure of deprotonated **12** discussed in the next section, the phosphine adducts **9–12** probably have the structure (eq 6) in which the phosphorus donor adds to the carbene carbon on the side opposite the Me on the S atom, which is also the side opposite the bulky $[HB(pz)_3]$ group. The three-membered ring in **6** might be strained; however, there is no evidence for phosphine displacement of the sulfur from the W to give products $[HB(pz)_3](CO)_2(L)W{=}CH(SMe)^+$ with an η^1-carbene ligand.

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

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

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



10

1

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

Reaction of $\{[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)(PPh_2H)]\}CF_3SO_3$ with NEt_3. The P–H proton in **12** is readily removed with NEt_3 in CH_2Cl_2 at room temperature to give $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)(PPh_2)]$ (**13**) (eq 8). The ^1H NMR resonances of the methine hydrogen (δ 4.65) and methyl hydrogens (δ 1.47) in **13** are upfield from those of the parent PPh_2H adduct **12** (δ 5.45, 1.89), as expected for the removal of a proton. In the ^{31}P NMR spectrum of **13**, a singlet (δ 10.52), without W satellite peaks, is observed, which establishes that the P atom is not bound

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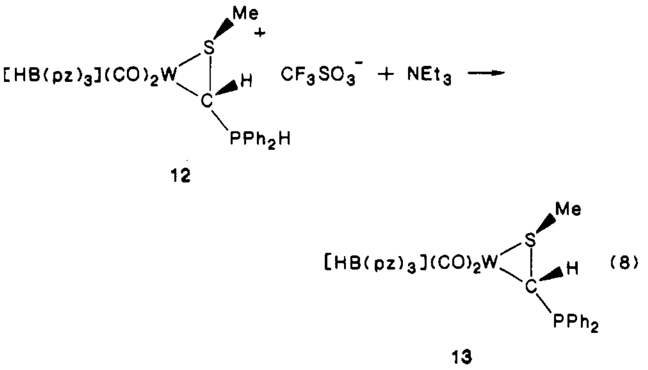

12

13

(8)

to the W; when phosphines are bound to a W atom, $^1J_{WP}$ is usually about 200–300 Hz.[31] These NMR results, together with the lower ν(CO) values, suggest that complex **13** contains a [CH(SMe)(PPh$_2$)] ligand which is bonded to the metal through both the C and S atoms, as is the η^2-CH(SMe) ligand in the starting complex **6**. ^{1}H NMR spectra (50, 80 °C) of **13** in CD$_3$NO$_2$ at elevated temperatures are the same as at room temperature; thus, no rearrangement to the form in which the [CH(SMe)(PPh$_2$)] ligand coordinates through the C and P atoms occurs. Several complexes with three-membered metal–C–P rings are known,[32] and rearrangement of primary and secondary phosphine carbene adducts to give complexes with metal–P bonds have been reported. Thus, the reaction of (CO)$_5$Cr[C(OMe)Ph] with PMe$_2$H gives the adduct (CO)$_5$Cr[C(OMe)Ph(PMe$_2$H)] which upon stirring in acetone rearranges to give the phosphine complex (CO)$_5$Cr[PMe$_2$[CH(Ph)(OMe)]].[33] Also the reaction of (CO)$_5$W[C(SMe)$_2$] with PPh$_2$H is believed to give initially the adduct, which rapidly rearranges to yield the final phosphine product (CO)$_5$W[PPh$_2$[CH(SMe)$_2$]].[1a,34] (η^5-C$_5$H$_5$)(CO)$_2$Fe[CH(SMe)(PPh$_2$H)]$^+$ also rearranges to give (η^5-C$_5$H$_5$)(CO)$_2$Fe[PPh$_2$(CH$_2$SMe)]$^+$ at 168 °C in the solid state.[1d]

Table IV. Final Atomic Parameters[a] for [HB(pz)$_3$](CO)$_2$W[η^2-CH(SMe)(PPh$_2$)] (13)

	x	y	z	U_{eq},[b] Å^2
W	913 (1)	2732 (1)	3737 (2)	39 (0)
S	−884 (7)	3828 (5)	5056 (11)	43 (3)
P	−2184 (8)	3256 (5)	1617 (11)	43 (3)
B	3329 (30)	1611 (25)	6351 (48)	42 (14)
C(1)	931 (25)	3644 (19)	2538 (36)	30 (7)
O(1)	876 (24)	4258 (16)	1854 (33)	64 (11)
C(2)	624 (24)	2355 (17)	1291 (36)	29 (6)
O(2)	475 (22)	2075 (18)	−325 (32)	77 (11)
C(3)	−1081 (26)	2882 (19)	3476 (37)	35 (7)
C(4)	−1017 (36)	3530 (27)	7162 (54)	70 (11)
N(1)	1129 (23)	1592 (18)	5257 (33)	51 (11)
N(11)	2214 (23)	1280 (16)	6264 (32)	42 (10)
C(11)	415 (29)	1125 (20)	5511 (46)	47 (14)
C(12)	983 (31)	510 (19)	6575 (48)	50 (14)
C(13)	2177 (28)	555 (22)	7028 (36)	45 (13)
N(2)	2718 (20)	1905 (17)	3104 (36)	42 (10)
N(21)	3614 (22)	1444 (16)	4349 (33)	41 (6)
C(21)	3377 (31)	1636 (24)	1591 (38)	50 (15)
C(22)	4569 (31)	1065 (27)	1850 (46)	59 (17)
C(23)	4641 (37)	996 (30)	3607 (47)	70 (19)
N(3)	2022 (23)	3180 (17)	6156 (29)	40 (10)
N(31)	2947 (23)	2592 (19)	7043 (33)	46 (11)
C(31)	1854 (35)	4006 (21)	7025 (49)	56 (15)
C(32)	2833 (36)	3878 (25)	8468 (45)	55 (17)
C(33)	3469 (29)	3034 (25)	8420 (42)	49 (15)
C(41)	−3701 (29)	3620 (19)	2528 (44)	46 (13)
C(42)	−4029 (33)	3031 (23)	3315 (59)	67 (17)
C(43)	−5178 (41)	3324 (32)	3992 (66)	88 (24)
C(44)	−6020 (27)	4204 (32)	3709 (64)	81 (20)
C(45)	−5715 (41)	4732 (26)	2875 (75)	91 (24)
C(46)	−4542 (33)	4396 (26)	2294 (56)	74 (17)
C(51)	−2266 (33)	2219 (27)	251 (41)	58 (16)
C(52)	−2855 (29)	2238 (29)	−1403 (38)	55 (17)
C(53)	−2971 (47)	1549 (36)	−2753 (70)	95 (14)
C(54)	−2433 (44)	654 (34)	−2158 (46)	86 (24)
C(55)	−1703 (48)	570 (23)	−532 (53)	83 (21)
C(56)	−1731 (39)	1381 (23)	633 (45)	70 (16)

[a] Estimated standard deviations are given in parentheses. Positional parameters ×10^4. [b] $U_{eq} = (^1/_3)\sum\sum \vec{\mathbf{a}}_i\cdot\vec{\mathbf{a}}_j U_{ij} a^*_i a^*_j \times 10^3$.

Table V. Selected Bond Distances (Å)[a] in [HB(pz)$_3$](CO)$_2$W[η^2-CH(SMe)(PPh$_2$)] (13) and [HB(pz)$_3$](CO)$_2$W[η^2-CH(SMe)]$^+$ (6)[4]

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

[a] Estimated standard deviations are given in parentheses.

To ensure that the ligand [CH(SMe)(PPh$_2$)] is bonded to the tungsten through both the C and S atoms and to establish the stereochemistry within the ligand, an X-ray structural determination of **13** was undertaken. The [HB(pz)$_3$](CO)$_2$W[CH(SMe)] portion of the molecule **13** retains the atomic connectivity of the carbene cation **6** as shown in Figure 1. Some structural changes, however, are noticeable. The W–S bond distance, 2.440 (9) Å is somewhat shorter than the 2.481 (6) Å found in **6**. The W—C(3) distance (2.22 (3) Å) is substantially longer than the W═C(carbene) distance (1.93 (2) Å) in **6** and is comparable to W—C(sp^3) bond distances found in W(≡CCMe$_3$)(═CHCMe$_3$)(CH$_2$CMe$_3$) (dmpe) (2.258 (9) Å)[35] and in [Cp$_2$W(CH$_3$)(CH$_2$CH$_2$-PMe$_2$Ph)]PF$_6$ (average 2.26 (3) Å).[36] The S–C(3) distance (1.80 (3) Å) is similar to single-bond S–C(sp^3) distances obtained in microwave studies of MeSH (1.819 Å)[37] and Me$_2$S (1.802 Å).[38] Also, S–C(3) is comparable to S–C(4) (1.82 (4) Å) but is longer than the S–C(3) distance (1.72 (2) Å) in **6**. Unfortunately, the large estimated standard deviations make more precise comparisons impossible. The single-bond C(3)–P distance (1.81 (3) Å) is similar to P–C(sp^3) distances (average 1.829 (3) Å) found in PPh$_2$CH$_2$CH$_2$PPh$_2$ (DPPE).[39] These changes in bond distances from molecules **6** to **13** involving C(3) can be easily rationalized by recognizing that the C(3) atom is approximately sp^2-hybridized in **6** and sp^3-hy-

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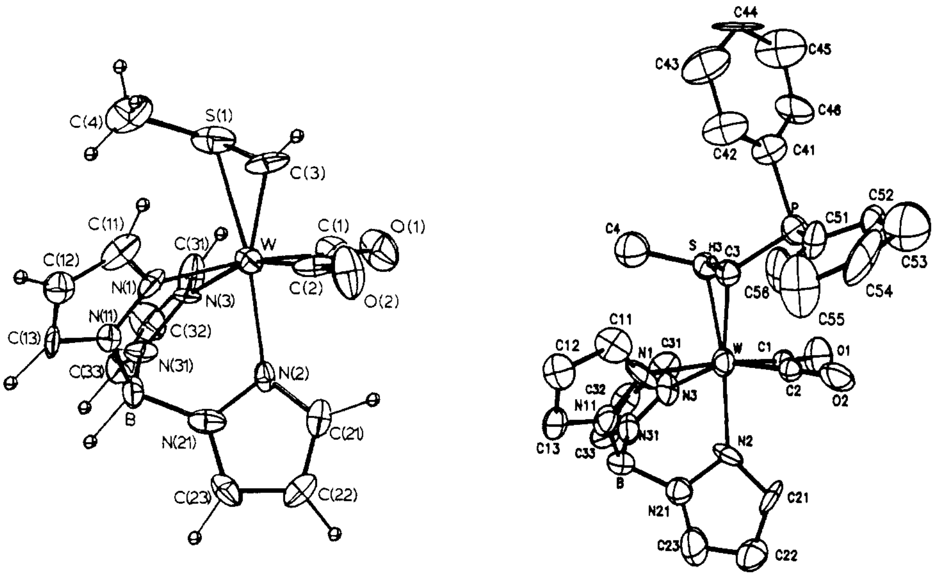

Figure 1. ORTEP plots of $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]^+$ (**6**;[4] left) and $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)(PPh_2)]$ (**13**; right).

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

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

[a] Estimated standard deviations are given in parentheses.

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

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

bridized in **13**. All of the bonds around C(3) in **13** are those expected for single-bond distances to an sp^3 C atom.

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

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

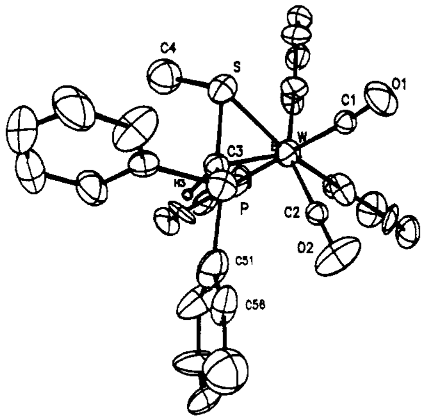

Figure 2. Perspective of $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)(PPh_2)]$ (**13**).

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[40] Least-squares plane of W-S-C(3): $-1.659x - 10.624y + 6.570z + 0.599 = 0$; W, 0.000; S, 0.000; C(3), 0.000; P, -1.436; C(4), 1.722.

Experimental Section

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

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

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

$[HB(pz)_3](CO)(PEt_3)W(C(O)CSMe)$ (2). A solution of 40 mL of CH_2Cl_2 containing PEt_3 (0.22 mL, 1.5 mmol) and the thiocarbyne compound 1 (0.39 g, 0.76 mmol) was refluxed for 22 h, yielding a dark red solution. The solution was evaporated to dryness under reduced pressure, and the residue was redissolved in a minimum amount of CH_2Cl_2. This CH_2Cl_2 solution was chromatographed on a 1 × 30 cm Florisil column. Unreacted starting material was eluted first with CH_2Cl_2. Then a dark red band on the top of the column was eluted with methanol. The methanol eluate was evaporated to give a solid, which was recrystallized from CH_2Cl_2/hexane at −20 °C, yielding air-stable, maroon needles of $[HB(pz)_3](CO)_2W(C(O)CSMe)$ (2; 0.29 g, 61%). Anal. Calcd for $C_{19}H_{28}BN_6O_2PSW$: C, 36.21; H, 4.48; N, 13.34. Found: C, 36.26; H, 4.66; N, 13.15. EIMS (18 eV): *m/e* 602 (M^+ − CO), 512 (M^+ − PEt_3), 484 (M^+ − PEt_3 − CO).

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

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

$\{[HB(pz)_3](CO)(PEt_3)W(MeOC{\equiv}CSMe)\}FSO_3$ (5). Into a 30-mL CH_2Cl_2 solution of 2 (0.20 g, 0.31 mmol) was added $MeOSO_2F$ (25 μL, 0.31 mmol). After the reaction mixture was stirred for 30 min, the solvent was removed under vacuum. The residue was washed with hexane (30 mL) three times. Air-stable, violet crystals of 5 were obtained by recrystallizing the solid from CH_2Cl_2/Et_2O at −20 °C (0.21 g, 93%). Anal. Calcd for $C_{20}H_{31}BFN_6O_5PS_2W$: C, 32.28; H, 4.20; N, 11.29. Found: C, 31.91; H, 4.13; N, 11.08. ^{31}P NMR ($CDCl_3$): δ 10.07 (J_{WP} = 305.17 Hz). MS (FAB): *m/e* 645 (parent cation), 602 (parent cation − CO − Me). Molar conductivity (CH_2Cl_2): $\Lambda_M = 56.40\ \Omega^{-1}\ cm^2\ mol^{-1}$ at 10^{-3} M (1:1 electrolyte).[42] UV–vis: λ_{max} 560 nm.

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

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

$[HB(pz)_3](CO)_3WI$ (8). Hydrogen iodide was bubbled through a 20-mL CH_2Cl_2 solution of the thiocarbyne complex 1 (0.19 g, 0.37 mmol) until the IR spectrum showed no CO bands corresponding to the starting thiocarbyne complex 1 (ca. 1 min). The solution was evaporated to dryness under reduced pressure, and the residue was redissolved in a minimum amount of CH_2Cl_2. This solution was chromatographed on a 1 × 30 cm column of Florisil. The yellow band was eluted with a 1:2 mixture of CH_2Cl_2/hexane, concentrated under vacuum, and diluted with hexane. Upon cooling to −20 °C, air-stable, rusty brown crystals of $[HB(pz)_3](CO)_3WI$ (8) resulted (0.22 mg, 10%). Anal. Calcd for $C_{12}H_{10}BIN_6O_3W$: C, 23.71; H, 1.66; N, 13.83. Found: C, 23.51; H, 1.78; N, 13.73. EIMS (20 eV): *m/e* 580 (M^+ − CO), 552 (M^+ − 2CO), 524 (M^+ − 3CO).

$\{[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)(PPh_3)]\}CF_3SO_3$ (9). A CH_2Cl_2 (30-mL) solution containing $\{[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]\}CF_3SO_3$ (6; 0.19 g, 0.29 mmol) and PPh_3 (76 mg, 0.29 mmol) was allowed to stir for 15 min. The brownish solution was then evaporated to dryness, and the resulting residue was washed with hexane. Crystallization of this residue from CH_2Cl_2/Et_2O at −20 °C afforded air-stable, brown crystals of 9 (0.24 g, 90%). Anal. Calcd for $C_{32}H_{29}BF_3N_6O_5PS_2W\cdot(CH_2Cl_2)_{0.3}$: C, 40.85; H, 3.14; N, 8.85. Found: C, 40.80; H, 3.52; N, 8.93. ^{31}P NMR ($CDCl_3$): δ 38.68 (J_{WP} = 10.49 Hz). MS (FAB): *m/e* 775 (parent cation), 719 (parent cation − 2CO). Molar conductivity (CH_2Cl_2): $\Lambda_M = 41.08\ \Omega^{-1}\ cm^2\ mol^{-1}$ at 10^{-3} M (1:1 electrolyte).[42]

$\{[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)(PEt_3)]\}CF_3SO_3$ (10). This complex was prepared by a route analogous to that used for 9. After the reaction mixture of 6 (0.19 g, 0.29 mmol) and PEt_3 (64 μL, 0.44 mmol) in 30 mL of CH_2Cl_2 was stirred for 1 h, the solvent was removed under vacuum. The resulting solid was washed with hexane and ether and then recrystallized from CH_2Cl_2/Et_2O at

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

(42) (a) (*n*-Bu)$_4$NBF$_4$, molar Conductivity (CH_2Cl_2): $\Lambda_M = 28.69\ \Omega^{-1}\ cm^2\ mol^{-1}$ at 10^{-3} M. (b) Muetterties, E. L.; Alegrant, C. W. *J. Am. Chem. Soc.* **1972**, *94*, 6386.

−20 °C to give air-stable, brown crystals of **10** (0.21 g, 92%). Anal. Calcd for $C_{20}H_{29}BF_3N_6O_5PS_2W\cdot(CH_2Cl_2)_{0.3}$: C, 30.26; H, 3.70; N, 10.43. Found: C, 29.99; H, 3.91; N, 10.39. MS (FAB): *m/e* 631 (parent cation), 575 (parent cation − 2CO), 560 (parent cation − 2CO − Me). The presence of CH_2Cl_2 in crystals of **9** and **10** was also established by their ^{1}H NMR spectra.

Reaction of $\{[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)(PEt_3)]\}CF_3SO_3$ (10) with NaH. A 5-mL CH_2Cl_2 solution containing **10** (16 mg, 0.02 mmol) and dry NaH (1 mg, 0.04 mmol) was allowed to stir for 24 h. $[HB(pz)_3](CO)_2W(\equiv CSMe)$ (**1**), in about 90% yield, was identified by the IR spectrum of the reaction mixture. A small amount of $[HB(pz)_3](CO)(PEt_3)\overline{W(C(O)C}SMe)$ (**2**) was also obtained from the further reaction of **1** and the liberated PEt_3.

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

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

$[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)(PPh_2)]$ (13). A CH_2Cl_2 solution (10 mL) of **12** (0.11 g, 0.13 mmol) was treated with NEt_3 (18 μL, 0.13 mmol). After the solution was allowed to stir for 30 min, a reddish-yellow solution was obtained. It was diluted with 30 mL of hexane; slow evaporation under reduced pressure furnished a white precipitate ($Et_3NH^+CF_3SO_3^-$). After the salt was removed by filtration through Celite, the solution was evaporated to dryness. The resulting solid was recrystallized from CH_2Cl_2/hexane at −20 °C to give air-stable, orange crystals of **13** (82 mg, 90%). Microscopic crystals were found which were suitable for X-ray analysis. Anal. Calcd for $C_{25}H_{24}BN_6O_2PSW$: C, 43.00; H, 3.46; N, 12.04. Found: C, 42.92; H, 3.66; N, 11.79. ^{31}P NMR ($CDCl_3$): δ 10.52. EIMS (20 eV): *m/e* 698 (M^+), 642 (M^+ − 2CO), 513 (M^+ − PPh_2), 457 (M^+ − 2CO − PPh_2).

Crystal Data and Data Collection. $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)(PPh_2)]$ (**13**): mol wt, 698.20 g/mol; triclinic $P\bar{1}$; a = 11.548 (14) Å, b = 16.148 (7) Å, c = 7.682 (5) Å, α = 101.67 (6)°, β = 99.06 (7)°, γ = 70.49 (5)°, V = 1316.1 (18) Å^3, Z = 2, ρ_{calcd} = 1.761 g/cm^3, μ = 48.09 cm^{-1} (Mo Kα, λ = 0.71069 Å, monochromated by a graphite crystal).

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

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

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

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

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Registry No. **1**, 77827-54-4; **2**, 104875-70-9; **3**, 104875-71-0; **4**, 104875-72-1; **5**, 104875-74-3; **6**, 104875-76-5; **7**, 104875-77-6; **8**, 104875-78-7; **9**, 104875-80-1; **10**, 104875-82-3; **11**, 104875-84-5; **12**, 104875-86-7; **13**, 104875-85-6; PEt_3, 554-70-1; $PMePh_2$, 1486-28-8; PPh_3, 603-35-0; $(\eta^5\text{-}C_5H_5)(CO)_2W(CS\text{–}DNP)$, 77827-51-1; $P(OMe)_3$, 121-45-9; PPh_2H, 829-85-6.

Supplementary Material Available: Tables of positional parameters of hydrogen atoms, anisotropic thermal parameters, and all bond distances and angles (9 pages); a listing of structure factors (5 pages). Ordering information is given on any current masthead page.

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[43] Jacobson, R. A. *J. Appl. Crystallogr.* **1976**, *9*, 115.

[44] Calculations were carried out on a VAX 11/780 computer. Structure factor calculations and least-squares refinements were done by using the block matrix/full matrix program ALLS (Lapp, R. L.; Jacobson, R. A. U.S. Department of Energy Report IS-4708, Iowa State University, Ames, IA, 1979). Fourier series calculations were done by using the program FOUR (Powell, D. R.; Jacobson, R. A. U.S. Department of Energy Report IS-4737, Iowa State University, Ames, IA, 1980) and for molecular drawings the program ORTEP (Johnson, C. K. U.S. Atomic Energy Commission Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, TN, 1970) was used. An empirical absorption correction was carried out by using diffractometer φ-scan data and the program ABSN (Karcher, B. A. Ph.D. Dissertation, Iowa State University, 1981).