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Synthesis and reactions of the η^2-dithiocarbene $[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)SMe]^+$

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Abstract

The SMe^+ electrophile adds to the carbyne carbon of $[HB(pz)_3](CO)_2W{\equiv}CSMe$ (**1**) to give $[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)SMe]^+$ (**2**), the first example of an η^2-dithiocarbene bonded to the metal through both the carbon and sulfur atoms. Sodium naphthalenide, LiPh and $LiPPh_2$ act as reducing agents when allowed to react with **2** forming a mixture of **1** and $[HB(pz)_3](CO)_2W(\eta^2\text{-}C(SMe)_2SMe]$ (**7**). Reactions of **2** with nucleophiles (Nuc) give the air-stable adducts $[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)(Nuc)SMe]$ (Nuc = SR^-, H^-, CH_3^- and PMe_3). The dithiocarbene **2** also reacts with $CpMo(CO)_3^-$ or $Mn(CO)_5^-$ to give **1** and $CpMo(CO)_3SMe$ or $[Mn(CO)_4SMe]_2$, respectively. Treatment of **2** with excess $^-CH(CO_2Me)_2$ produces air-stable $[HB(pz)_3](CO)_2W[C(SMe){=}C(CO_2Me)_2]$ (**6**, 15%) and (**7**, 45%).

Only a few η^2-thiocarbene complexes $\{(PPh_3)_2[CN(4\text{-}C_6H_4CH_3)](Cl)Os[\eta^2\text{-}C(4\text{-}C_6H_4CH_3)SMe]\}ClO_4$ [1], $\{[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]\}SO_3CF_3$ [2] and $\{Cp(CO)_2W[\eta^2\text{-}CR(SMe)]\}BF_4$ (R = C_6H_4Me-4 [3a], R = Me [3b]), 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.

Experimental

General procedures. All reactions, chromatography, distillations and recrystallizations were carried out under an atmosphere of prepurified N_2, using standard

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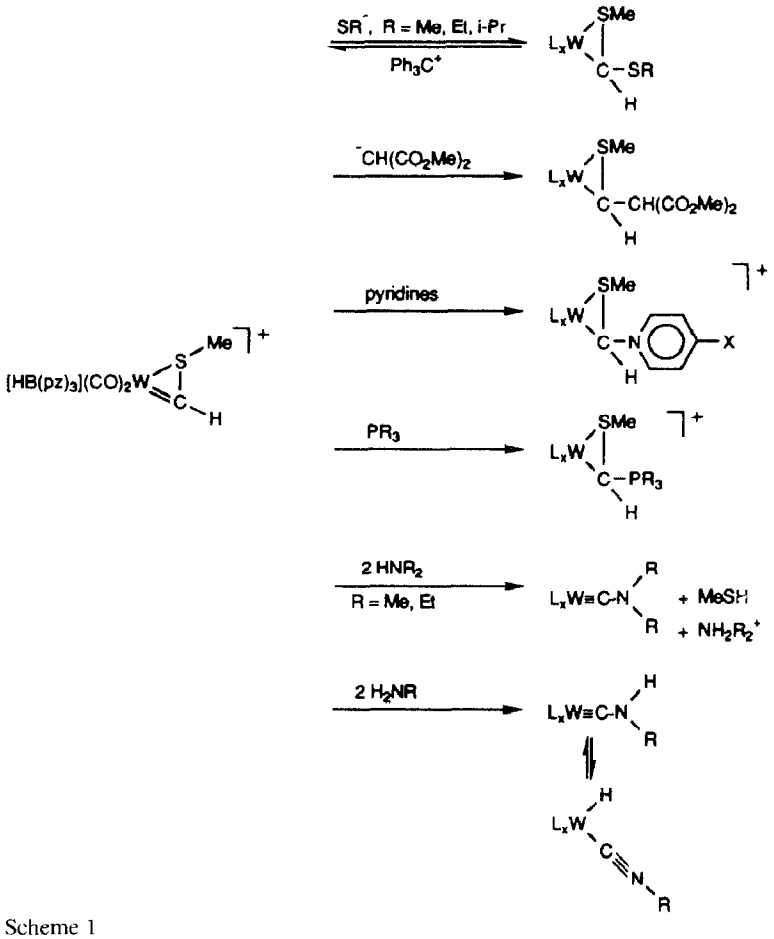


Scheme 1

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 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 ^1H (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 $[HB(pz)_3](CO)_2W{\equiv}C\text{-}SMe$ (**1**) [8], $[Me_2SSMe]SO_3CF_3$ [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.

Table 1

IR data for the complexes in CH_2Cl_2 solvent

Complex	IR ν(CO) (cm^{-1})
$[HB(pz)_3](CO)_2W{\equiv}C\text{-}SMe$ (**1**)	1973s, 1885s
$\{[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)SMe]\}(SO_3CF_3)$ (**2**-SO_3CF_3)	2047m, 1965s
$[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)SMe]$ (**3**)	1930s, 1804s
$[HB(pz)_3](CO)_2W[\eta^2\text{-}C(Me)(SMe)SMe]$ (**4**)	1921s, 1800s
$\{[HB(pz)_3](CO)_2W[\eta^2\text{-}C(PMe_3)(SMe)SMe]\}$ (SO_3CF_3) (**5**-SO_3CF_3)	1948s, 1835s
$[HB(pz)_3](CO)_2W[C(SMe){=}C(CO_2Me)_2]$ (**6**)	1962s, 1854s, 1710m, 1689m
$[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)_2SMe]$ (**7**)	1929s, 1818s
$[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)(SEt)SMe]$ (**8**)	1927s, 1806s
$[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)(SPh)SMe]$ (**9**)	1928s, 1808s
$[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)(4\text{-}SC_6H_4\text{-}Me)SMe]$ (**10**)	1931s, 1815s

Synthesis of $\{[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)SMe]\}SO_3CF_3$ (**2**-SO_3CF_3). To a solution of the thiocarbyne compound **1** (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,

Table 2

^1H NMR data for the complexes in CD_2Cl_2 solvent at room temperature [a]

Complex	H3 of pz [b]	H5 of pz [b]	H4 of pz [b]	Other
1	7.93 (br)	7.71 (br)	6.27 (br)	2.70 (SMe)
2-SO_3CF_3	8.01 (d), 7.93 (d), 7.91 (d), 7.89 (d), 7.79 (t) [c]		6.48 (m)	3.36 (WSMe), 2.46 (CSMe)
3 [d]	8.10 (d, A) (B, not resolved)	7.65 (d, A) 7.69 (d, B)	6.24 (t, A) [c] 6.26 (br, B)	5.39, 4.89 [e] (CH; B, A); 2.47, 2.35 (SMe, A); 2.59, 1.57 (SMe, B)
4	8.72 (d), 8.13 (d), 7.87 (d), 7.68 (m), 7.59 (d)		6.26 (t) [c], 6.20 (m)	2.50, 2.17 (SMe); 1.46 (CMe)
5-SO_3CF_3 [f]	8.54 (d), 8.26 (d), 8.20 (d) 8.02 (d), 7.91 (d), 7.76 (d)		6.52 (t) [c], 6.39 (t) [c], 6.30 (t) [c]	3.01, 2.40 (SMe); 1.52 (PMe_3) [g]
6	8.01 (br)	7.71	6.27 (br)	3.79, 3.78 (CO_2Me); 2.34 (WSMe)
7	7.95 (br)	7.66	6.22	2.62 (WSMe) [h]; 2.35, 2.19 (CSMe)
8 [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]
9 [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)
10 [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)

[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 Hz. [f] CD_3NO_2 solvent. [g] J(PH) 12.7 Hz. [h] J(WH) 2.2 Hz. [i] Three isomers; see Discussion. [j] t, J 7.4 Hz. [k] Arene resonances 7.34 (d, J 8.2 Hz), 7.19 (d, J 7.9 Hz), 7.04 (d, J 7.9 Hz).

Table 3

$^{13}C\{H\}$ NMR data for the complexes in CD_2Cl_2 solvent at room temperature [a]

Complex	CO	C3 of pz	C5 of pz	C4 of pz	other
1 [b]	224.7	144.9	135.2	105.7	264.4 (W≡C); 17.4 (SMe)
2-SO_3CF_3 [c]	216.3	148.3	139.9	109.5	230.5 (W=C); 29.1 (WSMe);
	215.3	146.3	139.3	108.9	26.5 (CSMe)
		146.2	139.1	108.7	
4	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	
5-SO_3CF_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	
6	228.2	144.2	135.7	106.3	201.2 (W–C=C); 128.4 (W–C=C);
	225.2				168.4, 163.1 (CO_2Me); 52.1,
					51.9 (OMe); 27.9 (WSMe)
7	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 Hz.

microcrystals of **2**-SO_3CF_3 (0.143 g, 91%). Anal. Found: C, 25.05; H, 2.36; N, 11.94. $C_{15}H_{16}BF_3N_6O_5S_3W$ calcd.: C, 25.44; H, 2.28; N, 11.87%. FAB-MS: m/e 559 (parent cation, M^+), 503 ($M^+ - 2CO$).

Reaction of **2** *with* $NaBH_4$. To a solution of **2**-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 × 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)$_2$W[η^2-CH(SMe)SMe] (**3**, 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 **2** *with* $LiCuMe_2$. To a suspension of **2**-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 × 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)$_2$W[η^2-C(SMe)(Me)SMe] (**4**, 0.158 g, 62%). Anal. Found: C, 31.44; H, 3.42; N, 14.53. $C_{15}H_{19}BN_6O_2S_2W$ calcd.: C, 31.38; H, 3.34; N, 14.64%. EIMS (16 or 70 eV): m/e 574 (M^+), 518 ($M^+ - 2CO$).

Reaction of **2** *with* PMe_3. To a solution of **2**-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 $\{[HB(pz)_3](CO)_2W[\eta^2\text{-}C(PMe_3)(SMe)SMe]\}SO_3CF_3$ (**5**-SO_3CF_3, 0.091 g, 74%). Anal. Found: C, 27.68; H, 3.20; N, 10.55. $C_{18}H_{25}BF_3N_6O_5PS_3W$ calcd.: C, 27.57; H, 3.21; N, 10.72%. FAB-MS: *m/e* 635 (parent cation, M^+), 559 ($M^+ - PMe_3$), 503 ($M^+ - PMe_3 - 2CO$).

Reaction of 2 with $NaCH(CO_2Me)_2$. A CH_2Cl_2 mixture (15 ml) containing **2**-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 × 40 cm). Elution with a 1/4 mixture of THF/hexanes removed a pink band of $[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)_2SMe]$ (**7**, 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 $[HB(pz)_3](CO)_2W[C(SMe)=C(CO_2Me)_2]$ (**6**, 0.028 g, 15%). Anal. Found:, C, 33.41; H, 2.93; N, 12.81. $C_{18}H_{19}BN_6O_6SW$ calcd.: C, 33.67; H, 2.98; N, 13.09%. 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 2 with SMe^-. A CH_2Cl_2 mixture (10 ml) containing **2**-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 × 40 cm). The thiocarbyne complex **1** 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 $[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)_2(SMe)]$ (**7**, 0.198 g, 61%). Anal. Found: C, 29.34; H, 3.10; S, 15.92. $C_{15}H_{19}BN_6O_2S_3W$ calcd.: C, 29.72; H, 3.16; S, 15.87%. EIMS (70 eV): *m/e* 606 (M^+), 550 ($M^+ - 2CO$), 503 ($M^+ - 2CO - SMe$).

Reaction of 2 with SEt^-. A CH_2Cl_2 mixture (10 ml) containing **2**-SO_3CF_3 (0.122 g, 0.172 mmol) and NaSEt (0.029 g, 0.344 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 × 30 cm). The thiocarbyne complex **1** 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 $[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)(SEt)(SMe)]$ (**8**, 0.0482 g, 45%). Complex **8** is a mixture of three isomers (see Discussion). Anal. Found: C, 28.90; H, 3.66; S, 13.95. $C_{16}H_{21}BN_6O_2S_3W \cdot CH_2Cl_2$ calcd.: C, 28.95; H, 3.29; S, 13.64%. EIMS (70 eV): *m/e* 620 (M^+), 564 ($M^+ - 2CO$), 461 ($M^+ - 2CO - 2SMe$).

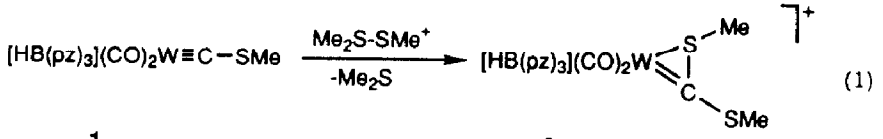
Reaction of 2 with SPh^-. A CH_2Cl_2 mixture (10 ml) containing **2**-SO_3CF_3 (0.152 g, 0.215 mmol) and NaSPh (0.0568 g, 0.430 mmol) was stirred for 2 h. The resulting orange solution was chromatographed on neutral alumina (5–6% H_2O, 2 × 20 cm). An orange band was eluted with CH_2Cl_2. The eluate was concentrated to 10 ml and hexanes (50 ml) were added. This solution was then evaporated to dryness yielding an air-stable, orange powder $[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)(SPh)(SMe)]$ (**9**, 0.0981 g, 68%). Complex **9** is a mixture of two isomers (see Discussion). Anal. Found: C, 36.40; H, 3.58; N, 12.18. $C_{20}H_{21}BN_6O_2S_3W$ calcd.: C, 35.95; H, 3.17; N, 12.58%. EIMS (70 eV): *m/e* 612 ($M^+ - 2CO$).

Reaction of 2 with $(4\text{-}C_6H_4Me)S^-$. In a procedure similar to the one above, **2**-SO_3CF_3 (0.280 g, 0.395 mmol) was treated in CH_2Cl_2 (10 ml) with $NaS(4\text{-}C_6H_4Me)$ (0.166 g, 0.793 mmol) to give after chromatography an air-stable orange powder

$[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)(S\text{-}4\text{-}C_6H_4Me)SMe]$ (**10**, 0.204 g, 74%). Complex **10** is a mixture of two isomers (see Discussion). Anal. Found: C, 36.50; H, 3.26; S, 14.27. $C_{21}H_{23}BN_6O_2S_3W$ calcd.: C, 36.97; H, 3.40; S, 14.10%. EIMS (16 or 70 eV): *m/e* 626 ($M^+ - 2CO$).

Results and discussion

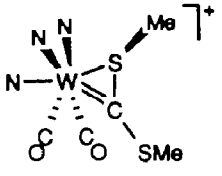
Synthesis of $[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)SMe]^+$ *(2).* The thiocarbyne complex **1** reacts readily at room temperature with the electrophile $[Me_2SSMe]SO_3CF_3$ to give the air-stable dithiocarbene complex **2** in 90–95% yield (eq. 1). A similar



(1)

1 **2**

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 [3]. The purple solid **2**-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 **2** is the same as that



2

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.

The ^1H NMR spectrum of **2** in CD_2Cl_2 shows only one set of resonances both at room temperature and at $-85\,^\circ C$. 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 $-75.5\,^\circ C$, respectively) and $(CO)_4Mo(PhCH_2SCH_2CH_2SCH_2Ph)$ [13] (T_c 33 °C). Thus, it appears that **2** either still inverts at sulfur at $-85\,^\circ C$ or only one isomer is present.

Reactions of **2** *with NaNp and bases.* The thiocarbene complex $[HB(pz)_3](CO)_2W[\eta^2\text{-}C(H)SMe]^+$ is reported to yield a mixture of **1** (10–20%) and $[HB(pz)_3](CO)_2W[\eta^2\text{-}C(H)(SMe)SMe]$ (5–40%) when treated with a variety of bases or sodium naphthalenide (NaNp) [4]. Similarly when $[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)SMe]^+$ (**2**) is treated with one equivalent of NaNp in THF at room temperature, the thiocarbyne **1** and the MeS^- carbene adduct $[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)_2SMe]$ (7) are pro-

duced 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,

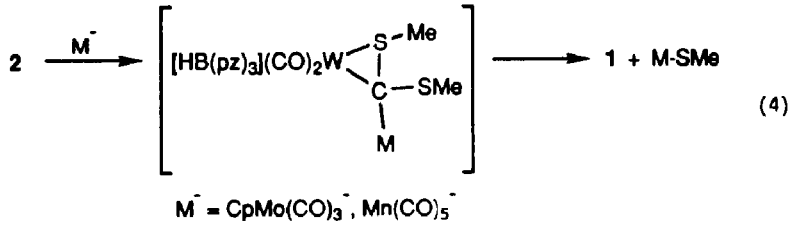
$$\mathbf{2} \xrightarrow{e^-} [HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)SMe]^{\cdot} \rightarrow \mathbf{1} + \cdot SMe \quad (2)$$

$$\cdot SMe \xrightarrow{e^-} {}^-SMe \xrightarrow{\mathbf{2}} [HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)_2SMe] \quad (3)$$

$$\mathbf{7}$$

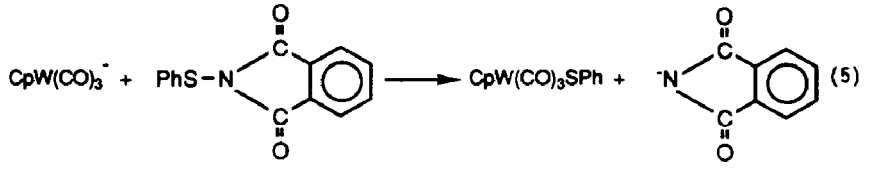
LiPh, $LiPPh_2$ and NaSePh also appear to act as reducing agents, giving **1** (70, 40 and 80%, respectively) and **7** (5, 40 and 5%, respectively). In all of these reactions some insoluble brown decomposition material is also seen. The dithiocarbene **2** does not react with 4-picoline at 40 °C or NEt_2H at 25 °C; however, at 66 °C **2** decomposes in the presence of NEt_2H.

Reactions of 2 with $NaMoCp(CO)_3$ and $NaMn(CO)_5$. When treated with $NaMoCp(CO)_3$ in THF at room temperature, the dithiocarbene **2** quantitatively forms the thiocarbyne **1** and $CpMo(CO)_3SMe$ [14] (identified by its IR and ^1H NMR spectra) in ~ 10 min. Similarly, when **2** is treated with $NaMn(CO)_5$ under the same conditions, **1** 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 alternative mechanism would be direct attack of the



(4)

metal anion on the sulfur atom. This is not unreasonable considering that the dithiocarbene **2** 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 [17] (eq. 5). Also, attack by $(Et_2N)_3P$ on the sulfur atom in disulfides has been observed [18].

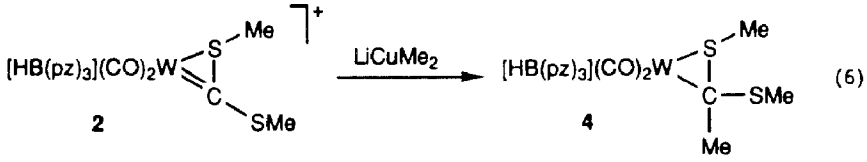


(5)

Reactions of 2 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, **2** forms the air-stable hydride adduct $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)SMe]$ (**3**) quantitatively.

This known compound was identified by comparing its IR and ^{1}H NMR with those reported in the literature [4]. Complex **3** exists as two isomers in solution (vide infra).

The dithiocarbene **2** also reacts with $LiCuMe_2$ to form the Me^- adduct, $[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)(Me)SMe]$ (**4**), in 62% yield (eq. 6). Some decomposi-

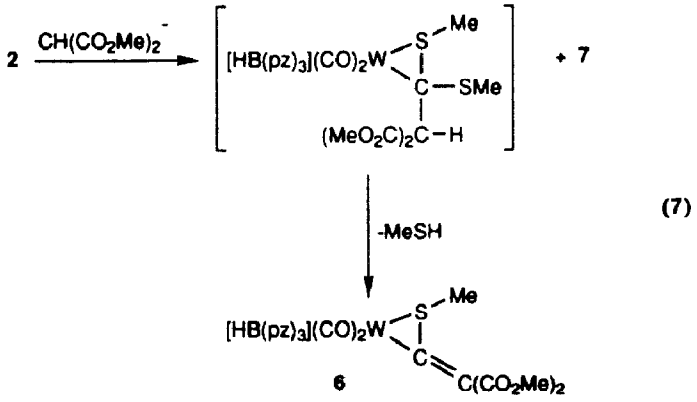


(6)

tion occurs in this reaction but no other products are identified. The $^{13}C\{H\}$ NMR spectrum of **4** exhibits the methine carbon at δ 59.2 ppm, which is similar to the methine carbon shifts reported for $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)SMe]$ (δ 61.8 ppm) [4] and $Cp(CO)Fe[\eta^2\text{-}C(SMe)_2SMe]$ (δ 70.8 ppm) [20].

Trimethylphosphine (PMe_3) adds to the carbene carbon in **2** to produce quantitatively the air-stable adduct $[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)(PMe_3)SMe]^+$ (**5**). Complex **5** was characterized by its elemental analysis, FAB MS, IR (Table 1), ^{1}H NMR (Table 2) and ^{13}C NMR (Table 3) spectra. Chemical shifts were assigned by comparison with the spectra of the thiocarbene adduct $\{[HC(pz)_3](CO)_2W[\eta^2\text{-}CH(PMe_3)SMe]\}(BF_4)_2$ [21]. Unlike **3**, complexes **4** and **5** show only one set of resonances in their ^{1}H NMR spectra (Table 2) at 25 °C, indicating the presence of a single isomer (vide infra).

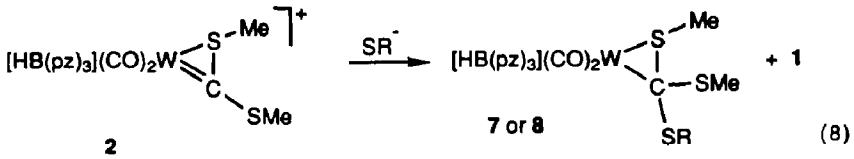
When **2** is treated with an excess of $NaCH(CO_2Me)_2$, two products $[HB(pz)_3](CO)_2W[C(SMe)=C(CO_2Me)_2]$ (**6**, 15%) and $[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)_2SMe]$ (**7**, 45%) are isolated (eq. 7). The reaction is slow (18 h) and insoluble decomposition material is also formed. Complex **6** is a yellow, air-stable solid which was characterized by its elemental analysis, MS, IR (Table 1), ^{1}H 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 208.1 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 **6** 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 107.0 ppm) [22] and $[N(PPh_3)_2][(CO)_4Fe\text{-}CH=C$



(7)

$(CO_2Me)(Me)]$ (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 **6** may involve initial addition of $^-CH(CO_2Me)_2$ to the carbene carbon followed by the rapid elimination of HSMe, which could be promoted by the excess $^-CH(CO_2Me)_2$.

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, **2** reacts with RS^- (R = Me, Et), giving the corresponding air-stable carbene adduct and **1** (eq. 8). However, treating **2** with t-BuS^- does not yield at t-BuS^- adduct but only a mixture of **1** and the MeS^- adduct **7**, in a 9/1 ratio.



2 **7 or 8** (8)

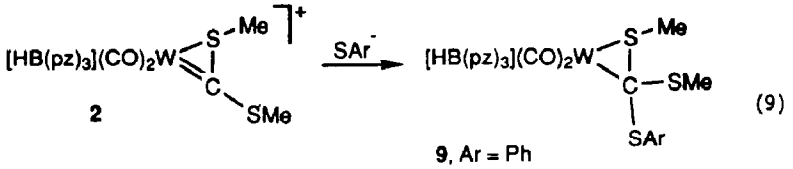
R = Me; 7:1 (9:1)

R = Et; 8:1 (3:2)

Formation of the thiocarbyne complex **1** in these reactions suggests the presence of a competing pathway, that of electron transfer as seen in the reactions of **2** with NaNp (eqs. 2, 3), LiPh, $LiPPh_2$ and NaSePh. The amount of electron transfer as indicated by the amount of **1** formed 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 likely due to the increase in size of RS^- which slows the rate of adduct formation.

The ^1H NMR spectrum of **7** in THF-d_8 shows only one set of resonances at room temperature and at $-95\,^\circ C$. However, the ^1H NMR spectrum of **8** 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_2CH_3 protons. In contrast, the IR spectrum of **8** 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 **2** reacts quantitatively with ArS^- to give only the air-stable carbene adducts (eq. 9). The ^1H NMR spectra (Table 2) of **9** and **10** at room



2 (9)

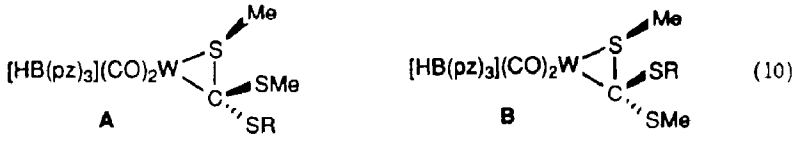
9, Ar = Ph

10, Ar = 4-C_6H_4Me

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_2Cl_2 at 25 °C was observed by ^1H NMR to be 3/2 and 3/1 for **9** and **10**, 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).

Attempts to grow single crystals of **8**, **9**, or **10** 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 **9** and **10**:

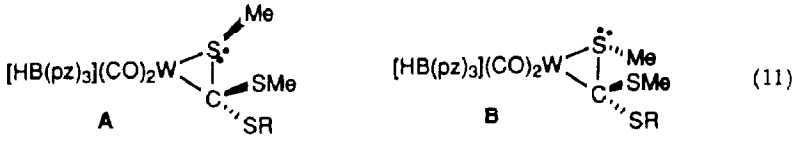
(a) Two isomers would result if attack of the nucleophile at the carbene carbon atom of **2** occurred from above and below the WCS ring (eq. 10). If the two isomers



(10)

were of the type (**A** and **B**) in eq. 10, the MeS^- adduct **7** 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 $\{[HC(pz)_2](CO)_2W[\eta^2\text{-}CH_2(SMe)]\}BF_4$ [21], complexes which also contain equivalent groups on the ring carbon atom. In the reactions of $Li[CuMe_2]$ (eq. 6) and PMe_3 with the dithiocarbene **2**, only one isomer is formed. If **A** and **B** are the isomers shown in eq. 10, the lack of isomers in **5** and **6** may be due to the larger size of the nucleophile, causing it to attack the carbene carbon only from th side opposite the bulky $HB(pz)_3^-$ group. The phosphide complex $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(PPh_2)(SMe)]$ (vide supra) also exists only as one isomer presumably as a result of stereoselective attack by the bulky Ph_2P^- nucleophile [5].

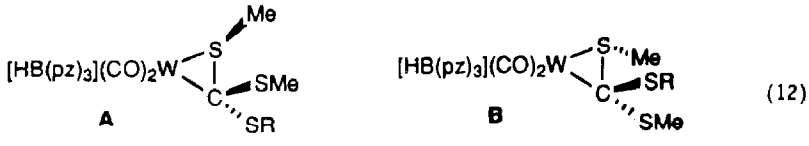
(b) A set of inversion isomers are possible due to the stereogenic center at the coordinated sulfur atom (eq. 11). If the isomers of **9** and **10** result from inversion at



(11)

sulfur, one would expect that similar inversion isomers would be seen for the MeS^- adduct **6**, 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),



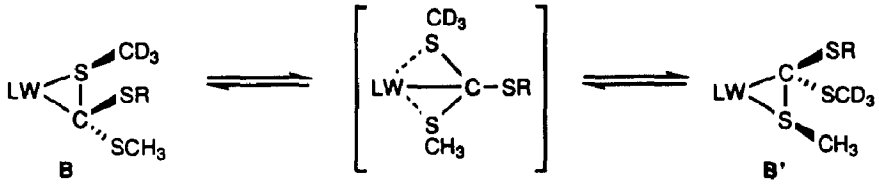
(12)

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 **7**, 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 ^1H 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 ^1H NMR to exist as two interconverting isomers. Thus, it is possible that the isomer ratios (**A**/**B**) observed for complexes **9** and **10** (vide supra) 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 $[HC(pz)_3](CO)_2W[\eta^2\text{-}CH(SR)SMe]^+$ [21].

The deuterated thiocarbene $[HB(pz)_3](CO)_2\overline{W[\eta^2\text{-}C(SCH_3)}\overline{SCD_3}]^+$ was synthesized from $[HB(pz)_3](CO)_2W{\equiv}C\text{-}SCD_3$ [25*] and Me_2SSMe^+ using a procedure analogous to that used for **2**. 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, Ph) 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, $\{Cp(CO)_2W[\eta^3\text{-}C(SMe)_2(4\text{-}C_6H_4Me)]\}(BF_4)_2$,

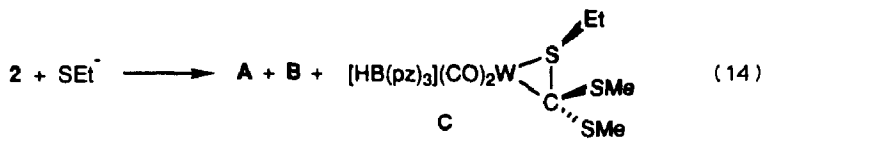


(13)

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

similar to the proposed intermediate has been reported by Kreissl [3]. The exchange process would produce the enantiomer. A non-concerted dissociation 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 $[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)_2SMe]$ (**7**) does not react with excess PMe_3 (25 °C, 48 h) and $[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)(S\text{-}4\text{-}C_6H_4Me)SMe]$ (**10**) does not react with excess MeS^- (25 °C, 48 h), as might be expected of an unsaturated intermediate.

Equation 13 suggests a probable structure for the third isomer (**C**) observed when EtS^- is reacted with **2** (eqs. 8, 14). Isomers **A** and **B** would be of the type in eq. 10.



(14)

Isomer **C** presumably results from interchange of the coordinated SMe group with the uncoordinated SEt group. This scrambling process was verified independently by synthesizing the dithiocarbene $[HB(pz)_3](CO)_2\overline{W[\eta^2\text{-}C(SMe)}\overline{SEt}]^+$ [27*] and then treating it with MeS^-. This reaction produces the same three isomers in the same

* Reference number with asterisk indicates a note in the list of references.

ratio as the reaction of **2** with EtS^-. No interchange of the coordinated SMe group with the uncoordinated SAr group in **9** or **10** 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 $[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)SMe]^+$ (**2**) 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 $\nu(CO)$ absorptions in **2** as compared to $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]^+$ ($\nu(CO)$ 2047m, 1965s cm^{-1} vs. 2067m, 1996s cm^{-1} [2], respectively) indicate that the dithiocarbene **2** may be less electophilic than $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]^+$. This probably accounts for the lack of reaction of **2** with amines, whereas $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]^+$ reacts with amines to give amino-carbyne complexes (Scheme 1).

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References

1 G.R. Clark, T.J. Collins, K. Marsden, W.R. Roper, J. Organomet. Chem., 259 (1983) 215.
2 H.P. Kim, S. Kim, R.A. Jacobson, R.J. Angelici, Organometallics, 3 (1984) 1124.
3 (a) F.R. Kreissl, H. Keller, Angew. Chem., Int. Ed. Engl., 25 (1986) 904; (b) F.R. Kreissl, F.X. Müller, D.L. Wilkinson and G. Müller, Chem. Ber., 122 (1989) 289.
4 H.P. Kim, R.J. Angelici, Organometallics, 5 (1986) 2489.
5 H.P. Kim, S. Kim, R.A. Jacobson, R.J. Angelici, Organometallics, 5 (1986) 2481.
6 D.F. Shriver, M.A. Drezdon, The Manipulation of Air Sensitive Compounds, 2nd edit., John Wiley and Sons, 1986.
7 S. Herzog, J. Dehnert, K. Luhder, in H.B. Jonassen (Ed.), Technique of Inorganic Chemistry, Interscience, New York, Vol. VII, 1969.
8 W.W. Greaves, R.J. Angelici, Inorg. Chem., 20 (1981) 2983.
9 M. Ravenscroft, R.M.G. Roberts, J.G. Tillet, J. Chem. Soc., Perkin Trans. II, (1982) 1569.
10 L.S. Hegedus, Y. Inoue, J. Am. Chem. Soc., 104 (1982) 4917.
11 H.O. House, C.-Y. Chu, J.M. Wilkins, M.J. Umen, J. Org. Chem., 40 (1975) 1460.
12 J.H. Eekhof, H. Hogeveen, R.M. Kellogg, E. Klei, J. Organomet. Chem., 161 (1978) 183.
13 R.J. Cross, G. Hunter, R.C. Massey, J. Chem. Soc., Dalton Trans., (1976) 2015.
14 P.M. Treichel, P.C. Nakagaki, Organometallics, 5 (1986) 711.
15 P.M. Treichel, J.H. Morris, F.G.A. Stone, J. Chem. Soc., (1963) 720.
16 J. Grobe, R. Rau, J. Organomet. Chem., 157 (1978) 281.
17 P.M. Treichel, P.C. Nakagaki, K.J. Haller, J. Organomet. Chem., 327 (1987) 327.
18 D.N. Harpp, J.G. Gleason, J. Am. Chem. Soc., 93 (1971) 2437.
19 (a) F.J. Brown, Prog. Inorg. Chem., 27 (1980) 1. (b) C.P. Casey, React. Intermed., 2 (1981) 135; ibid., 3 (1985) 109.
20 G.N. Glavee, R.J. Angelici, J. Am. Chem. Soc., 111 (1989) 3598.
21 R.A. Doyle, R.J. Angelici, in press.
22 O.A. Gansow, A.R. Burke, R.B. King, M.S. Saran, Inorg. Nucl. Chem. Lett., 10 (1974) 291.
23 T. Mitsudo, H. Watanabe, Y. Watanabe, N. Nitani, Y. Takegami, J. Chem. Soc., Dalton Trans., (1979) 395.
24 R.B. King, M.B. Bisnette, Inorg. Chem., 4 (1965) 486.
25 Synthesized from $Bu_4N\{[HB(pz)_3](CO)_2W(CS)\}$ [26] and CD_3I.
26 W.W. Greaves, R.J. Angelici, J. Organomet. Chem., 191 (1980) 49.
27 $\{[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)SEt]\}SO_3CF_3$ 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 **2**. ^1H NMR (CD_2Cl_2): 7.99 (d, J 2.3 Hz), 7.93 (d, J 2.3 Hz), 7.91 (d, J 2.4 Hz), 7.88 (d, J 2.4 Hz), 7.84 (d, J 2.1 Hz), 7.75 (d, 2.1) H3 and H5; 6.48 (m) H4; 3.81 (q, J 7.5 Hz) SCH_2; 2.42 (s) SMe; 1.55 (t, J 7.5 Hz) Me.