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Synthesis of heteronuclear di- and tri-metal μ-carbyne compounds from the thiocarbyne $[HB(pz)_3](CO)_2W{\equiv}CSMe$

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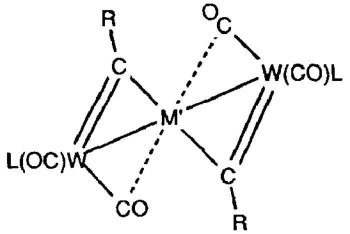
Abstract

The compound $[HB(pz)_3](CO)_2W{\equiv}C{-}SMe$ (**1**) reacts with two equivalents of $(In)Rh(CO)_2$, where In = η^5-indenyl, C_9H_7, in refluxing THF to give the brown-black crystalline μ_3-carbyne $\{(In)_2(\mu\text{-}CO)Rh_2(\mu_3\text{-}CSMe)W(CO)_2[HB(pz)_3]\}$ (**2**) containing a Rh_2W triangle of metal atoms. Compound **2** reacts with $MeOSO_2CF_3$ to methylate the sulfur of the μ_3-CSMe group. A similar trinuclear complex $[(\eta^5\text{-}C_5H_5)_2Ni_2(\mu_3\text{-}CSMe)W(CO)_2[HB(pz)_3]\}$ (**4**) is formed in the reaction of **1** with $[(\eta^5\text{-}C_5H_5)Ni(CO)]_2$. The complex $Pt(C_2H_4)_3$ reacts with two equivalents of **1** to form the trinuclear complex $\{[HB(pz)_3](CO)_2W(\mu_2\text{-}CSMe)\}_2Pt$ (**5**) in which each W–Pt bond is bridged by a carbyne ligand. Like complex **2**, **4** can also be methylated at one of the sulfur atoms. Treatment of $[HB(pz)_3](CO)_2W{\equiv}C{-}SMe$ (**1**) with $(Me_3P)_2Pt(C_2H_4)$ affords the heterobimetallic complex $\{(Me_3P)_2Pt(\mu\text{-}CSMe)W(CO)_2[HB(pz)_3]\}$ (**7**).

Metal-ligand fragments with bonding capabilities similar to acetylenes have been especially useful as building blocks in μ-carbyne cluster syntheses. Among the earliest reactions [1] which demonstrated that the W≡C group could function as a "ligand" similar to acetylene were those involving $(\eta^5\text{-}C_5H_5)(CO)_2W{\equiv}CC_6H_4Me\text{-}4$ and the reagents $Ni(COD)_2$ (COD = cycloocta-1,5-diene), $Pt(\eta\text{-}C_7H_{10})_3$ (C_7H_{10} = bicyclo[2.2.1]heptene) and $Pt(C_2H_4)_3$ [2]. The products are the trimetallic complexes $\{(\eta^5\text{-}C_5H_5)(CO)_2W(\mu\text{-}CC_6H_4Me\text{-}4)\}_2M'$, where M′ = Ni or Pt.



Further studies showed that the compounds $(\eta^5\text{-}C_5H_5)(CO)_2W{\equiv}CR$ (R = C_6H_4Me-4 or Me) combine with a variety of low-valent metal-ligand fragments to afford complexes with bonds between tungsten and other transition elements (Ti, Zr, V, Cr, Mo, W, Mn, Re, Fe, Ru, Os, Co, Rh, Ir, Cu, Ag and Au) [3]. These syntheses provide a versatile route to species containing heteronuclear metal–metal bonds bridged by carbyne ligands [4*].

In this paper, we describe reactions of the thiocarbyne $[HB(pz)_3](CO)_2W{\equiv}C\text{–}SMe$, where $HB(pz)_3^-$ is the hydrotris(1-pyrazolyl)borato ligand, with several metal complexes containing labile ligands. The products of these reactions are new cluster compounds containing metal–metal bonds bridged by a thiocarbyne ligand.

Experimental

General procedures. All reactions, distillations and recrystallizations were carried out under an atmosphere of prepurified N_2, using standard inert atmosphere and Schlenk techniques [5,6] unless stated otherwise. Tetrahydrofuran (THF) and Et_2O were distilled from Na/benzophenone. Hexanes and CH_2Cl_2 were distilled from CaH_2. A Nicolet MX-10 FT spectrophotometer was used to measure IR spectra, and JEOL instruments (FX90Q, FX200 and FX400) were used to measure NMR spectra. Tetramethylsilane (Me_4Si) was the standard of reference for all ^{1}H and ^{13}C NMR spectra; chemical shifts are reported in δ downfield from Me_4Si and coupling constants are in Hz. ^{31}P resonances, downfield from the H_3PO_4 external reference (in a capillary insert), are given in positive values (ppm). ^{195}Pt chemical shifts are to high frequency of $\Xi(^{195}Pt)$ 21.4 MHz. Electron-impact mass spectra (EIMS) were obtained on a Finnigan 4000 spectrometer. Fast atom bombardment (FAB, dithiothreitol/dithioerythritol (5/1) matrix) mass spectra were recorded on a Kratos MS-50 spectrometer. The compounds $[HB(pz)_3](CO)_2W{\equiv}CSMe$ [7], $Pt(COD)_2$ [8], $(In)Rh(C_2H_4)_2$ (In = η^5-indenyl, C_9H_7) [9] and $[CpNi(CO)]_2$ (Cp = η^5-cyclopentadienyl, C_5H_5) [10] were prepared by previously described procedures. All other chemicals were used as received from commercial sources.

Synthesis of $\{(In)_2(\mu\text{-}CO)Rh_2(\mu_3\text{-}CSMe)W(CO)_2[HB(pz)_3]\}$ *(2).* Bubbling CO through a THF (50 ml) solution of $(In)Rh(C_2H_4)_2$ (0.60 g, 2.2 mmol) for 10 min produced $(In)Rh(CO)_2$ (IR (THF): ν(CO) 2041, 1979 cm^{-1}). The complex $[HB(pz)_3](CO)_2W{\equiv}CSMe$ (0.56 g, 1.1 mmol) was then added and the solution was refluxed for 24 h. The resulting brown solution was concentrated to ~ 15 ml and hexanes (100 ml) were layered on top of the solution. Cooling to −20 °C for 1 day gave the air-stable, brown-black crystalline product **2** (0.97 g, 91%). Anal. Found: C, 37.57; H, 2.94; N, 7.97; S, 3.38. $C_{32}H_{27}BN_6O_3Rh_2SW$ calcd.: C, 37.36; H, 2.75; N, 7.92; S, 3.02%. EIMS: *m/e* 976 (M^+), 948 (M^+ − CO). IR (THF): ν(CO) 1873s, 1812m, 1798m cm^{-1}. ^{1}H NMR (CD_2Cl_2) [11]: δ (ppm) 7.79 (d, *J* 2.2 Hz, 1H, H3 of pz), 7.71 (m, 3H, H3 and H5 of pz), 7.42 (d, *J* 1.8 Hz, 2H, H5 of pz), 7.21 (dt, *J* 7.3 Hz, *J*(RhH) 0.9, 2H, H5 or H6 of In), 7.01 (dt, *J* 7.5 Hz, *J*(RhH) 0.9 Hz, 2H, H5 or H6 of In), 6.78 (m, 4H, H4 and H7 of In), 6.34 (m, 2H, H1 or H3 of In), 6.24 (pseudo-t, *J* 2.2 Hz, 1H, H4 of pz), 6.19 (pseudo-t, *J* 2.2, 2.0 Hz, 2H, H4 of pz), 5.82 (m, 2H, H1 or H3 of In), 5.73 (pseudo-t, *J* 2.9 Hz, 2H, H2 of In), 0.82 (s, 3H,

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

SMe). $^{13}C\{H\}$NMR ($CDCl_3$) [11]: δ (ppm) 299.1 (t, J(RhC) 25 Hz, μ_3-C); 233.3 (J(WC) 151 Hz, WCO); 219.5 (t, J(RhC) 50 Hz, Rh(μ-CO)); 143.6, 143.2 (C3 of pz); 135.1, 135.0 (C5 of pz); 106.2, 105.0 (C4 of pz); 128.6 (d, J(RhC) 80 Hz), 125.8 (d, J(RhC) 66 Hz), 119.2, 118.9, 116.7, 115.4, 102.3, 88.9, 86.5 (In); 23.0 (SMe).

*Reaction of **2** with $MeOSO_2CF_3$.* A CH_2Cl_2 (40 ml) solution of **2** (0.210 g, 0.215 mmol) and $MeOSO_2CF_3$ (122 μl, 1.08 mmol) was refluxed for 24 h. The volume of the solution was reduced to ~ 20 ml and then hexanes (80 ml) were layered on top. Cooling the solution to −20 ° C for 1 day gave the air-stable, brown-black powdered product $\{(In)_2(\mu\text{-CO})Rh_2(\mu_3\text{-CSMe}_2)W(CO)_2[HB(pz)_3]\}SO_3CF_3$ (**3**, 0.179 g, 73%). Anal. Found: C, 35.02; H, 2.76; N, 7.25. $C_{34}H_{30}BF_3N_6O_6Rh_2S_2W \cdot \frac{1}{2}CH_2Cl_2$ [12*] calcd.: C, 35.04; H, 2.64; N, 7.11%. FAB–MS: m/e 991 (parent cation, M^+), 929 ($M^+ - SMe_2$), 901 ($M^+ - SMe_2 - CO$), 873 ($M^+ - SMe_2 - 2CO$), 845 ($M^+ - SMe_2 - 3CO$). IR (CH_2Cl_2): ν(CO) 1916s, 1838m (br) cm^{-1}. ^1H NMR (CD_2Cl_2): δ (ppm) 7.88 (d, J 2.2 Hz, 2H, H3 of pz), 7.79 (d, J 1.8 Hz, 1H, H3 of pz), 7.76 (d, J 1.8 Hz, 1H, H5 of pz), 7.75 (d, J 1.8 Hz, 2H, H5 of pz), 7.36 (m, 8H, H4–H7 of In), 6.52 (m, 2H, H1 or H3 of In), 6.42 (pseudo-t, J 2.2 Hz, 2H, H4 of pz), 6.28 (pseudo-t, J 2.4, 2.2 Hz, 1H, H4 of pz), 5.86 (m, 2H, H1 or H3 of In), 5.65 (pseudo-t, J 2.8, 2.6 Hz, 2H, H2 of In), 1.29 (s, 6H, SMe_2). $^{13}C\{H\}$ NMR ($CDCl_3$): δ (ppm) 268.6 (t, J(RhC) 32 Hz, μ_3-C; 229.9 (J(WC) 146 Hz, WCO); 212.3 (t, J(RhC) 146 Hz, Rh(μ-CO)); 146.4, 145.0 (C3 of pz); 139.0, 138.3 (C5 of pz); 108.2, 107.9 (C4 of pz); 130.0, 129.6, 123.1, 122.0, 117.9, 117.6, 104.3, 90.4, 89.1 (In); 28.9 (SMe_2).

*Synthesis of $\{Cp_2Ni_2(\mu_3\text{-CSMe})W(CO)_2[HB(pz)_3]\}$ (**4**).* Refluxing a THF (10 ml) solution of **1** (0.190 g, 0.371 mmol) and $[CpNi(CO)]_2$ (0.112 g, 0.369 mmol) for 3 days produced a brown solution. Layering hexanes (100 ml) on top and then cooling to −20 ° C for 18 h gave the air-stable, brown powdered product **4** (0.146 g, 52%). The product was recrystallized from CH_2Cl_2/hexanes. Anal. Found: C, 35.41; H, 3.12; N, 10.48. $C_{23}H_{23}BN_6Ni_2O_2SW \cdot \frac{1}{2}CH_2Cl_2$ [13*] calcd.: C, 35.19; H, 3.02; N, 10.48%. EIMS: m/e 760 (M^+). IR (THF): ν(CO) 1875vs, 1806s cm^{-1}. ^1H NMR (CD_2Cl_2): δ (ppm) 7.96 (d, J 1.8 Hz, 1H, H3), 7.75 (d, J 2.1 Hz, 1H, H5), 7.66 (d, J 2.1 Hz, 2H, H3), 7.16 (d, J 1.6 Hz, 2H, H5), 6.30 (pseudo-t, J 2.1 Hz, 1H, H4), 6.12 (pseudo-t, J 2.1 Hz, 2H, H4), 5.37 (s, 10H, Cp), 2.27 (s, 3H, SMe). $^{13}C\{H\}$(CD_2Cl_2): δ (ppm) 295.0 (μ_3-C); 236.8 (J(WC) 148 Hz, WCO); 150.6, 149.7 (C3); 140.2, 139.3 (C5); 110.9, 109.9 (C4); 98.3 (Cp); 32.1 (SMe).

*Synthesis of $\{[HB(pz)_3](CO)_2W(\mu_2\text{-CSMe})\}_2Pt$ (**5**).* Ethylene was bubbled through a THF (30 ml) solution of $Pt(COD)_2$ (0.108 g, 0.262 mmol) at 0 ° C for 15 min, thus producing $Pt(C_2H_4)_3$. The thiocarbyne **1** (0.268 g, 0.523 mmol) was then added, and the solution was stirred at room temperature for 3 h. The resulting brown solution was concentrated to ~ 10 ml, and hexanes (100 ml) were layered on top of the solution. Cooling to −20 ° C for 24 h gave the air-stable brown crystalline product **5** (0.272 g, 85%). Anal. Found: C, 26.05; H, 2.37; N, 13.63; S, 5.31. $C_{26}H_{26}B_2N_{12}O_4PtS_2W_2$ calcd.: C, 25.62; H, 2.15; N, 13.79; S, 5.26%. EIMS: m/e 1218 (M^+), 1106 ($M^+ - 4CO$), 1091 ($M^+ - 4CO - Me$), 1076 ($M^+ - 4CO - 2Me$). IR (THF): ν(CO) 1955m, 1925s, 1822m cm^{-1}. ^1H NMR (CD_2Cl_2): δ (ppm) 8.02 (d, J 1.7 Hz, 2H, H3 or H5), 7.99 (d, J 2.5 Hz, 2H, H3 or H5), 7.97 (d, J 2.5 Hz, 2H, H3 or H5), 7.78 (m, 6H, H3 or H5), 6.32 (pseudo-t, J 1.7, 2.5 Hz, 2H, H4), 6.28 (pseudo-t, J 1.7, 2.5 Hz, 4H, H4), 2.38 (s, 6H, SMe). $^{13}C\{H\}$ NMR (CD_2Cl_2): δ (ppm) 290.0 (J(PtC) 842 Hz, J(WC) 159 Hz, μ_2-C); 228.7 (J(PtC) 24 Hz, J(WC)

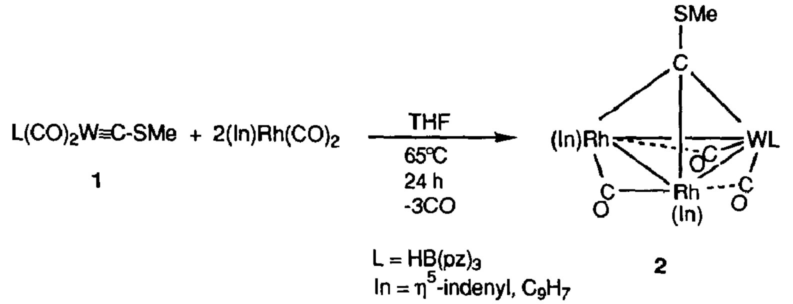
156 Hz, WCO); 226.1 (J(WC) 156 Hz, WCO); 145.9, 144.9 (C3); 136.4, 136.0, 135.9 (C5); 106.7, 106.3 (C4); 23.2 (J(PtC) 76 Hz, SMe). ^{195}Pt{H}NMR (CD_2Cl_2): δ 1604.6.

Reaction of 5 with $MeOSO_2CF_3$. After refluxing a CH_2Cl_2 (20 ml) solution of **5** (0.163 g, 0.134 mmol) and $MeOSO_2CF_3$ (18.5 μl, 0.163 mmol) for 48 h, Et_2O (80 ml) was layered on top of the solution, which was then allowed to stand at −20 °C for 18 h to give air-stable brown microcrystals of {[HB(pz)$_3$](CO)$_2$W(μ_2-CSMe$_2$)Pt(μ_2-CSMe)W(CO)$_2$[HB(pz)$_3$]}SO_3CF_3 (**6**, 0.139 g, 75%). Anal. Found: C, 24.43; H, 2.32; N, 11.63. $C_{28}H_{29}B_2F_3N_{12}O_7PtS_3W_2 \cdot \frac{1}{2}CH_2Cl_2$ [12*] calcd.: C, 24.02; H, 2.13; N, 11.80%. FAB–MS: *m/e* 1234 (parent cation, M^+), 1087 ($M^+ - SMe_2 - 3CO$), 1059 ($M^+ - SMe_2 - 4CO$). IR (CH_2Cl_2): ν(CO) 1998s, 1945s, 1855m cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ (ppm) 8.07 (d, J 1.9 Hz, 1H), 8.02 (d, J 2.0 Hz, 1H), 8.00 (d, J 2.1 Hz, 1H), 7.96 (s, 2H), 7.92 (d, J 2.1 Hz, 1H), 7.87 (d, J 2.4 Hz, 1H), 7.84 (m, 3H), 7.80 (d, J 2.4 Hz, 1H), 7.70 (d, J 2.0 Hz, 1H) H3 and H5; 6.46 (pseudo-*t*, J 2.2 Hz, 1H), 6.41 (pseudo-t, J 2.2 Hz, 1H), 6.36 (m, 3H), 6.27 (pseudo-t, J 2.2 Hz, 1H) H4; 2.85 (s, 3H, MeS); 2.63 (s, 3H), 2.28 (s, 3H) Me_2S. ^{13}C{H} NMR (CD_2Cl_2): δ (ppm) 297.7 (μ_2-*C*SMe); 256.4 (μ_2-*C*SMe$_2$); 231.3, 229.8, 227.9, 225.8 (WCO); 150.6, 149.8, 149.5, 148.6, 146.9 (C3); 141.3, 141.0, 140.8, 140.3, 140.1 (C5); 116.6, 111.3, 110.9, 110.7, 110.3 (C4); 35.7, 35.1, 25.9 (Me).

Synthesis of {(Me$_3$P)$_2$Pt(μ-CSMe)W(CO)$_2$[HB(pz)$_3$]} (7). Bis(cycloocta-1,5-diene)platinum (0.231 g, 0.561 mmol) was dissolved in THF (50 ml). After cooling to 0 °C, C_2H_4 was bubbled through the solution for 15 min. The resultant pale yellow solution was treated under ethylene with PMe_3 (115 μl, 1.13 mmol). After stirring (10 min) the C_2H_4 atmosphere was replaced by nitrogen and [HB(pz)$_3$](CO)$_2$W≡CSMe (0.287 g, 0.560 mmol) was added to the solution. After stirring 1.5 h, the resulting red solution was concentrated to ~ 10 ml. Hexanes were layered on top of the solution, and the solution was allowed to stand at −20 °C for 24 h to give air-stable, red, microcrystals of **7** (0.371 g, 77%). Anal. Found: C, 26.48; H, 3.74; N, 9.80; S, 3.61. $C_{19}H_{31}BN_6O_2P_2PtSW$ calcd.: C, 26.56; H, 3.64; N, 9.78; S, 3.73%. IR (THF): ν(CO) 1866s, 1784s cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ (ppm) 8.02 (d, J 1.8 Hz, 1H, H3), 7.75 (d, J 2.2 Hz, 2H, H3), 7.77 (d, J 2.2 Hz, 1H, H5), 7.44 (d, J 1.8 Hz, 2H, H5), 6.28 (pseudo-t, J 2.2, 2.0 Hz, 1H, H4), 6.13 (pseudo-*t*, J 2.2, 2.0 Hz, 2H, H4), 1.83 (d, J(PH) 9.5 Hz, J(PtH) 35.9 Hz, 9H, PMe_3), 1.75 (d, J(PH) 8.1 Hz, J(PtH) 21.2 Hz, (9H, PMe_3), 1.24 (s, 3H, SMe). ^{13}C{H} NMR ($CDCl_3$): δ (ppm) 312.6 (d, J(PC) 64 Hz, J(PtC) 613 Hz, μ_2-C); 225.2 (J(PtC) 43 Hz, J(WC) 168 Hz, WCO); 145.0, 144.8 C(3); 135.0, 134.3 (C5), 106.0, 105.0 (C4); 23.6 (dd; J(PC) 18, 6 Hz; J(PtC) 67 Hz; SMe); 20.4 (d, J(PC) 28 Hz, J(PtC) 82 Hz, PMe_3); 18.3 (d, J(PC) 24 Hz, J(PtC) 52 Hz, PMe_3). ^{31}P{H} NMR ($CDCl_3$): δ (ppm) 140.0 (J(WP) 22 Hz, J(PtP) 3911 Hz), 125.8 (J(PtC) 2678 Hz). ^{195}Pt NMR ($CDCl_3$): δ (ppm) 424 (dd, J(PtP) 3916, 2686 Hz).

Results and discussion

Synthesis of {(In)$_2$(μ-CO)Rh$_2$(μ_3-CSMe)W(CO)$_2$[HB(pz)$_3$]} (2). The thiocarbyne [HB(pz)$_3$](CO)$_2$W≡CSMe (**1**) reacts with two equivalents of (In)Rh(CO)$_2$ in refluxing THF to give air-stable, brown-black microcrystals of **2** in 91% yield (eq. 1). Complex **2** was characterized by microanalysis, and by its ^{1}H, ^{13}C NMR, IR and

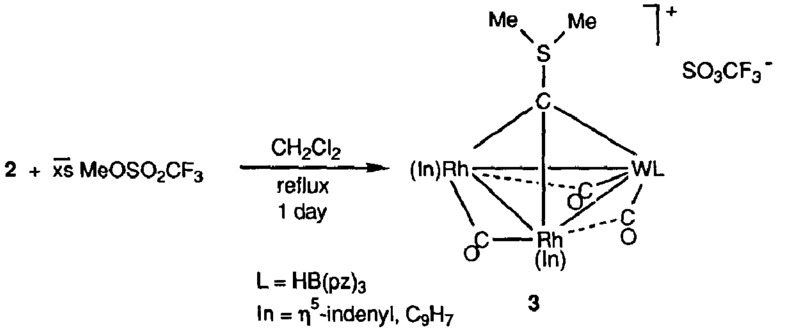


(1)

mass spectra. Three CO stretches are observed in the IR spectrum of **2** (ν(CO) 1873s, 1812m, 1798m cm^{-1}) which are very similar to the ν(CO) (1873s, 1799m cm^{-1}) observed for the analogous complex $\{(In)_2(\mu\text{-}CO)Rh_2(\mu_3\text{-}CMe)W(CO)_2[HB(pz)_3]\}$ [11a*]. The $^{13}C\{H\}$ NMR spectrum of **2** shows a singlet with tungsten satellites at δ 233.3 ppm (J(WC) 151 Hz) which is assigned to the tungsten CO's. A triplet at δ 219.5 ppm (J(RhC) 50 Hz) is assigned to the rhodium μ-CO. These ^{13}C shifts compare well with the CO chemical shifts (δ 233.0 (J(WC) 156 Hz, 220.4 ppm (t, J(RhC) 52 Hz)) reported for $\{(In)_2(\mu\text{-}CO)Rh_2(\mu_3\text{-}CMe)W(CO)_2[HB(pz)_3]\}$. A triplet at δ 299.1 ppm (J(RhC) 25 Hz) is assigned to the μ_3-*C*SMe group. This is ~ 30 ppm upfield of the μ_3-*C*Me signal (δ 329.9 ppm (t, J(RhC) 24 Hz)) observed for $\{(In)_2(\mu\text{-}CO)Rh_2(\mu_3\text{-}CMe)W(CO)_2[HB(pz)_3]\}$. The ^1H NMR spectrum exhibits a singlet at δ 0.82 ppm, which is assigned to the SMe of the bridging carbyne ligand. This resonance occurs much further upfield than the SMe resonance observed for the carbyne $[HB(pz)_3](CO)_2W{\equiv}CSMe$ (δ 2.59 ppm) [7]. It is possible that this unusual upfield shift is due to shielding by the indenyl groups. Presumably the structure of **2** is the same as that of $\{(In)_2(\mu\text{-}CO)Rh_2(\mu_3\text{-}CC_6H_4Me\text{-}4)W(CO)_2[HB(pz)_3]\}$, which was determined by X-ray analysis [11a*].

It was of interest to determine whether or not the SMe group of the bridging alkylidyne ligand in **2** could be replaced by hydrogen or a metal-ligand group. However, complex **2** was found to be unreactive when treated with Raney nickel, $M[CpMo(CO)_3]_2$ (M = Hg or Cd) or $SnCl_2$ in refluxing THF. In addition, no reaction occurred when **2** was photolyzed in the presence of $[CpMo(CO)_3]_2$. Complex reaction mixtures, which could not be characterized, were obtained when **2** was treated with $AgBF_4$ or $HOSO_2CF_3$ in the presence of CO.

Reaction of **2** *with* $MeOSO_2CF_3$. When treated with an excess of $MeOSO_2CF_3$ in refluxing CH_2Cl_2, complex **2** is methylated at the sulfur of the bridging alkylidyne group (eq. 2) to give $\{(In)_2(\mu\text{-}CO)Rh_2(\mu_3\text{-}CSMe_2)W(CO)_2[HB(pz)_3]\}SO_3CF_3$ (**3**),

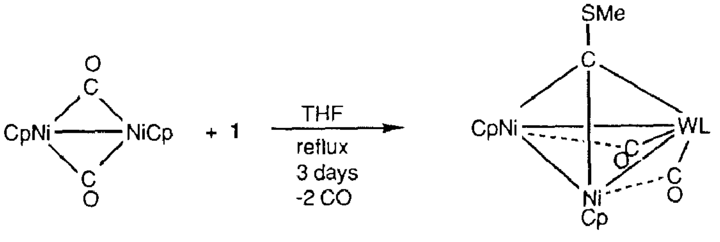


(2)

an air-stable, brown-black powder (73%). Complex **3** was characterized by microanalysis, and by its ^1H, ^{13}C NMR, IR and mass spectra. The IR bands of **3** ($\nu(CO)$ 1916s, 1838m cm^{-1}) are shifted to higher energy as compared with **2** ($\nu(CO)$ 1873s, 1812m, 1798m cm^{-1}) reflecting a higher positive charge on the metals. The ^1H NMR of **3** exhibits a single resonance for the two Me groups at δ 1.29 ppm, indicating that both are bound to sulfur and are equivalent. In the $^{13}C\{H\}$ NMR spectrum, the resonance of the μ_3-C has shifted ~ 30 ppm upfield from the μ_3-C in **2**, to 268.6 ppm (t, $J(RhC)$ 32 Hz). The highest +1 ion in the FAB mass spectrum occurs at m/e 991 and corresponds to the parent cation (M^+). In addition, peaks corresponding to $M^+ - SMe_2$ (m/e 929) and $M^+ - SMe_2 - nCO$ ($n = 1$, 2, 3; $m/e = 901$, 873, 845, respectively) are also observed.

Based on the mass ion observed corresponding to $M^+ - SMe_2$, it was thought that displacement of the SMe_2 group by metal anions might be possible. However, treating **3** with $Na[CpFe(CO)_2]$ in THF produces $[CpFe(CO)_2]_2$ and **2**. Similarly, when **3** is treated with $Na[CpW(CO)_3]$ in THF, the isolated products are $[CpW(CO)_3]_2$, $CpW(CO)_3Me$ and **2**. Complex **3** is also reduced to **2** with one equivalent of sodium naphthalenide (the organic products were not identified).

Synthesis of $\{Cp_2Ni_2(\mu_3\text{-}CSMe)W(CO)_2[HB(pz)_3]\}$ *(4).* Reaction between $[CpNi(\mu\text{-}CO)]_2$ and $[HB(pz)_3](CO)_2W{\equiv}CSMe$ (**1**) in refluxing THF for 3 days gives the expected trimetal cluster **4** in 52% yield (eq. 3). Complex **4** was characterized by microanalysis, the observation of a molecular ion (m/e 760) in the mass spectrum, and NMR spectra. Two CO stretches are observed in the IR spectrum of **4** ($\nu(CO)$ 1875, 1806 cm^{-1}) which are similar to the two tungsten semibridging $\nu(CO)$'s (1873, 1812 cm^{-1}) observed for the analogous rhodium complex **2** and the $\nu(CO)$ bands (1879s, 1817s cm^{-1}) reported for $Cp_2Ni_2(\mu_3\text{-}CC_6H_4Me\text{-}4)W(CO)_2Cp$ [3k]. The $^{13}C\{H\}$ NMR spectrum shows resonances for the μ_3-C at δ 295.0 ppm and for the CO ligands at δ 236.8 ppm ($J(WC)$ 148 Hz).These are comparable to the shifts observed for complex **2** (δ 299.1 and 233.3 ppm ($J(WC)$ 151 Hz) and $Cp_2Ni_2(\mu_3\text{-}CC_6H_4Me\text{-}4)W(CO)_2Cp$ (δ 275.7 ($J(WC)$ 125) and 217.2 ppm ($J(WC)$ 171 Hz)), thus supporting similar structures for the complexes. The ^1H NMR spectrum exhibits a singlet at δ 2.27 ppm assigned to the SMe group. This is in the region typical for SMe groups, unlike the upfield resonance at δ 0.82 ppm observed for the SMe group in **2**, which supports the suggestion that the upfield position in **2** is due to shielding by the indenyl rings (vide infra).



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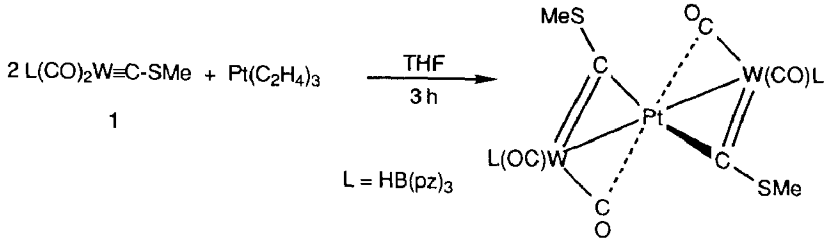
(3)

Synthesis of $\{[HB(pz)_3](CO)_2W(\mu_2\text{-}CSMe)\}_2Pt$ *(5).* Two equivalents of the thiocarbyne **1** react with $Pt(C_2H_4)_3$ in THF at room temperature to give air-stable, brown microcrystals of **5** in 85% yield (eq. 4). Complex **5** was characterized by

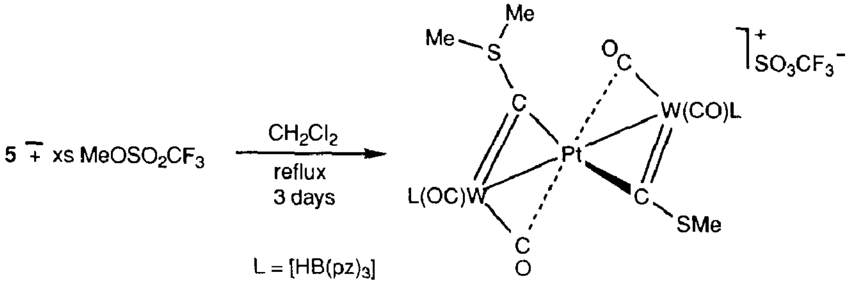


(4)

5

microanalysis, and by its ^{1}H, ^{13}C, ^{195}Pt NMR, IR and mass spectra. Presumably the structure of **5** is the same as that of $\{[HB(pz)_3](CO)_2W(\mu_2\text{-}CMe)\}_2Pt$, which was established by X-ray analysis [14]. Supporting this structure for **5** is the IR spectrum of **5** (ν(CO) 1955m, 1925s, 1822m, cm^{-1}) which is similar to that of $\{[HB(pz)_3](CO)_2W(\mu_2\text{-}CMe)\}_2Pt$ (1956sh, 1931vs, 1792m) [14]. The $^{13}C\{H\}$ NMR spectrum of **5** shows the characteristic resonance (δ 290 ppm, J(PtC) 842 Hz, J(WC) 159 Hz) for an alkylidyne-carbon bridging a metal–metal bond. This is ~ 20 ppm upfield of the μ_2-C (δ 310.3 ppm, J(PtC) 700 Hz, J(WC) 153 Hz) observed for $\{[HB(pz)_3](CO)_2W(\mu_2\text{-}CMe)\}_2Pt$ [14]. Based on the coupling constants, the resonance at δ 228.7 ppm (J(WC) 156 Hz, J(PtC) 24 Hz) is assigned to the semibridging CO's and the resonance at δ 226.1 ppm (J(WC) 156 Hz) is assigned to the terminal CO on each tungsten. The CO shifts in **2** are comparable to the shifts (δ 229.9, 224.6 ppm) reported for $\{[HB(pz)_3](CO)_2W(\mu_2\text{-}CMe)\}_2Pt$. The ^{1}H NMR spectrum of **5** exhibits a singlet at δ 2.38, assigned to the SMe of the bridging carbyne ligand, which is similar to the SMe resonance at δ 2.27 ppm observed for **4** (vide infra). A singlet at 1605 ppm is observed in the $^{195}Pt\{H\}$ NMR spectrum which is comparable to that (δ 1610 ppm) reported for $\{[HB(pz)_3](CO)_2W(\mu_2\text{-}CC_6H_4Me\text{-}4)\}_2Pt$ [14].

When **5** is treated with one equivalent of $HBF_4 \cdot Et_2O$ in CH_2Cl_2, a mixture of products is obtained which could not be separated. An attempt to cleave the C–S bond by photolysis was also unsuccessful (no reaction after 24 h in THF). However, similar to complex **2**, one sulfur atom in **5** can be methylated with $MeOSO_2CF_3$ to give $\{[HB(pz)_3](CO)_2W(\mu_2\text{-}CSMe_2)Pt(\mu_2\text{-}CSMe)W(CO)_2[HB(pz)_3]\}SO_3CF_3$ (**6**, eq. 5). Complex **6** was isolated in 75% yield as air-stable brown microcrystals, and it

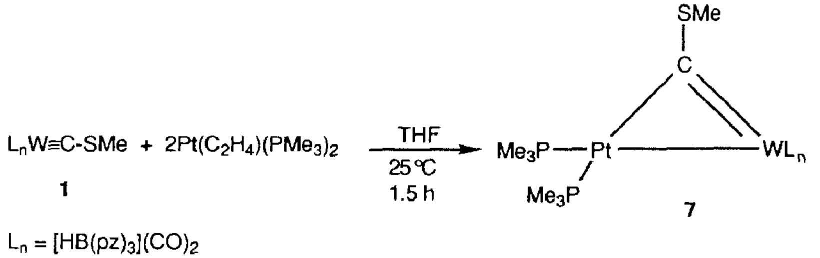


(5)

6

was characterized by microanalysis and its ^{1}H, ^{13}C NMR, IR and mass spectra. The IR bands of **6** (ν(CO) 1998s, 1945s, 1855m) are shifted to higher energy as compared with **5** (ν(CO) 1955m, 1925s, 1822m) reflecting the higher positive charge on the metals. The ^{13}C NMR spectrum exhibits two downfield resonances for the bridging alkylidyne groups. The resonance at δ 297.7 ppm is very similar to the μ_2-C resonance (δ 290.0 ppm) observed for **5**, and is assigned to the μ_2-CSMe group. Whereas the resonance at δ 256.4 ppm is shifted ~ 30 ppm upfield from the μ_2-C resonance in **5** and is assigned to the μ_2-$CSMe_2^+$ group. This upfield shift is similar to that (δ 299.1 to 268.6 ppm) observed when **2** is methylated (vide infra). In addition to the different bridging alkylidyne resonances, separate resonances are also observed for each CO (δ 231.3, 229.8, 227.9 and 225.8 ppm), which is consistent with the unsymmetrical structure. The ^1H NMR spectrum of **6** exhibits a separate resonance for each methyl group at room temperature (δ 2.85, 2.63 and 2.28 ppm). However, at 348 K (75 °C), the two upfield resonances coalesce to give a singlet at δ 2.45 ppm. These resonances are assigned to the μ_2-$CSMe_2^+$ ligand, in which the Me groups are diastereotopic at room temperature, but which become equivalent at higher temperatures due to rapid inversion at sulfur. A similar sulfur inversion was observed by Kuhn and Schumann [15] in the $CpFe(CO)(SMe_2)(L)^+$ complexes, where L = PPh_3, CN^-.

Synthesis of $\{(Me_3P)_2Pt(\mu\text{-}CSMe)W(CO)_2[HB(pz)_3]\}$ *(7).* Addition of $[HB(pz)_3](CO)_2W{\equiv}CSMe$ to a THF solution of $Pt(C_2H_4)(PMe_3)_2$ leads to the formation of the air-stable red complex **7** (eq. 6) in 77% yield. Its IR spectrum (in



(6)

THF) contains carbonyl stretching bands at 1866s and 1784s cm^{-1}, which are similar to those (ν(CO) 1914s, 1764s cm^{-1}) reported for $\{(Me_3P)_2Pt(\mu\text{-}CMe)W(CO)_2[HB(pz)_3]\}$ [11a*]. The two PMe_3 ligands in **7** are non-equivalent; however, the $^{31}P\{H\}$ NMR spectrum shows no coupling between the two phosphorus nuclei (δ 140.0, J(PtP) 3911, J(WP) 22 Hz; 125.8 ppm, J(PtP) 2678 Hz). The larger ^{195}Pt–^{31}P and ^{183}W–^{31}P couplings for the signal at δ 140.0 ppm indicate that this resonance is due to the PMe_3 *trans* to the Pt–W bond [16]. In the $^{13}C\{H\}$ NMR spectrum, a resonance was observed at δ 312.6 ppm, appearing as a doublet (J(PC) 64 Hz) with platinum satellites (J(PtC) 613 Hz). The low-field position indicates that it is the bridging carbyne carbon; the magnitude of the ^{195}Pt–^{13}C coupling shows that it is attached to platinum [16,17]. These are similar to the ^{13}C chemical shift (δ 332 ppm) and coupling constants (J(PC) 54 Hz, J(PtC) 644 Hz) reported for the analogous complex $\{(Me_3P)_2Pt(\mu\text{-}CMe)W(CO)_2[HB(pz)_3]\}$ [11a*]. A similar complex $\{(PhMe_2P)_2Pt(\mu\text{-}CC_6H_4Me\text{-}4)W(CO)_2Cp\}$, was characterized by X-ray analysis [18].

When **7** is treated with one equivalent of $HBF_4 \cdot Et_2O$ or $MeOSO_2CF_3$ in CH_2Cl_2, at least two products are obtained. Unfortunately, these could not be separated and thus precluded their characterization. Complex **7** reacts with $SnCl_2$ in THF at 25 °C to give $[HB(pz)_3](CO)_2W{\equiv}C\text{–}SMe$ (**1**) in quantitative yield (by IR).

Conclusions

The reactions discussed in this paper show that the thiocarbyne $[HB(pz)_3](CO)_2W{\equiv}C{-}SMe$ forms heteronuclear complexes similar to those formed by the analogous alkyl and aryl carbynes $[HB(pz)_3](CO)_2W{\equiv}CR$ ($R = Me$, C_6H_4Me-4). However, these latter carbynes appear to act as better ligands in forming heteronuclear complexes, for they also react with various other metal compounds, i.e., AuCl(tetrahydrothiophene) [14], $Ni(COD)_2$ [14], $Mo(CO)_3(MeCN)_3$ [19], $Cp(CO)_2Mo{\equiv}Mo(CO)_2Cp$ [19], $Co_2(CO)_8$ [19], $Fe_2(CO)_9$ [20], to form clusters containing μ_2- and μ_3-carbyne ligands. In contrast, these same metal compounds either do not react with thiocarbyne **1**, or they react and form unstable products which decompose.

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