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Syntheses and Structures of $[HB(pz)_3](CO)_2(CS)W–Au(PR_3)$. First Examples of a Semibridging CS Ligand

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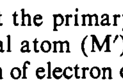
Abstract: Reactions of $[HB(pz)_3](CO)_2W(CS)^-$ with $ClAuPR_3$ (R = Ph or Me) yield the complexes $[HB(pz)_3](CO)_2(CS)W–Au(PR_3)$, which have a semibridging CO and a semibridging CS, the first examples of CS in this bonding mode. X-ray diffraction studies of the complexes show the semibridging CO and CS ligands to be bent: W–C–O (173.4 (7)°) and W–C–S (165.9 (5)°); data are for the PPh_3 complex. The much shorter Au–CS (2.162 (7) Å) than Au–CO (2.720 (8) Å) bond distance indicates a substantially stronger semibridging interaction for CS than CO with the Au. The Au–CO distance is 0.174 Å shorter in the PMe_3 than in the PPh_3 derivative. This result, together with the short Au–CS bond distance, suggests the primary interaction between the semibridging CO and CS groups with Au is a donation of electron density from the Au to the CO and CS π^* orbitals. The J_{PC} coupling constant (7.39 Hz) for the semibridging CO in the PMe_3 compound is larger than that in the PPh_3 compound ($J_{PC} \cong 0$ Hz), and the J_{PC} coupling constant in the PPh_3 compound is much greater for the semibridging CS (34.18 Hz) than for the semibridging CO (~0 Hz).

The similarity of carbon monosulfide (CS) to CO has stimulated much interest in the synthesis and reactivity of CS complexes.[1] The CS group is found as a terminal ligand (e.g., $(CO)_5W(CS)$,[2] $CpFe(CO)_2(CS)^+$,[3] $CpMn(CO)_2(CS))$,[4] as a carbon-bridging ligand (e.g., $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CS)$,[5] $MnPt(\mu\text{-}CS)(CO)_2(PMePh_2)_2Cp)$,[6] and as an end-to-end bridging ligand (e.g., $(dppe)_2(CO)WC{\equiv}SW(CO)_5$.[7] In its complexes, CS is a better σ-donor and π-acceptor than CO[1b] and generally binds more strongly to metals than does CO. The CO ligand participates in 3 types of metal–metal bridging in dinuclear systems:[8] carbon bridging (I), side-on bonding (II), and semibridging (III). Bonding features of these bridging ligands were reviewed recently by Horwitz and Shriver.[9] The side-on bonding CO(II) acts as a four-electron donor, providing two σ electrons to M and two π electrons to M′; both M′–O and M′–C interactions are relatively strong. The semibridging CO group (III) is characterized by different M–C distances ($a < b$) and unequal MCO angles ($\alpha > \beta$); the M′–C interaction is relatively weak. Extended Hückel molecular orbital calculations on $Cp_2M_2(CO)_4$ (M = Cr, Mo)[10] suggest that the primary interaction between the more distant second metal atom (M′) and the semibridging carbonyl ligand is a donation of electron density from M′ into the CO π^* orbitals. As a result, the semibridging CO ligand shows a lower stretching frequency than a comparable terminal CO group.[9] Unlike CO, CS has not been found or suggested to be a side-on or semibridging ligand in any metal complexes until now.



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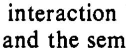

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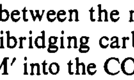
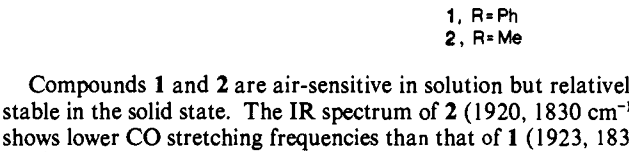


III

Results and Discussion

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

Reactions of $[HB(pz)_3](CO)_2W(CS)^-$ and $ClAu(PR_3)$ in CH_2Cl_2 at room temperature produce orange crystalline complexes $[HB(pz)_3](CO)_2(CS)W–Au(PR_3)$ (eq 1); the low yield (20–30%) is presumably due to incomplete separation of the products since no other CO-containing products are observed during the reaction. In the products, **1** and **2**, the $Au(PR_3)$ moiety has added to the W, as is found in other heterobimetallic Au compounds, e.g., $Cp(CO)_3W–Au(PPh_3)$,[14] $(CO)_4[P(OPh)_3]Mn–Au(PPh_3)$,[15] $(CO)_4Co–Au(PPh_3)$,[16] and $(\eta^3\text{-}C_3H_5)(CO)_3Fe–Au(PPh_3)$.[17]



(1)

1, R = Ph
2, R = Me

Compounds **1** and **2** are air-sensitive in solution but relatively stable in the solid state. The IR spectrum of **2** (1920, 1830 cm^{-1}) shows lower CO stretching frequencies than that of **1** (1923, 1836 cm^{-1}), as expected for the more electron-donating PMe_3 group. The stretching frequency of the semibridging CO group is assigned

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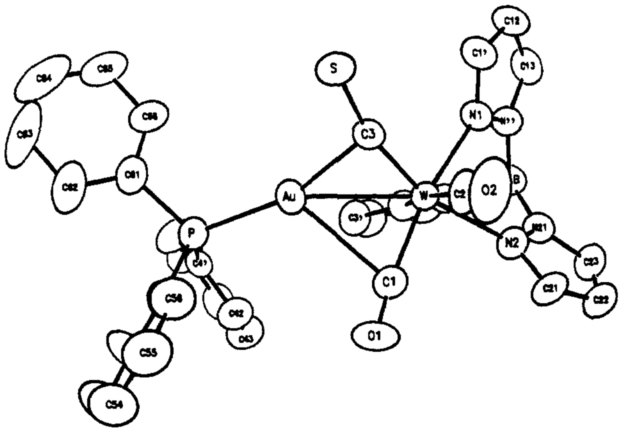

Figure 1. ORTEP plot of [HB(pz)$_3$](CO)$_2$(CS)W–Au(PPh$_3$) (**1**).

to the lower band (**1** (1836 cm^{-1}), **2** (1830 cm^{-1})), for reasons discussed in the introduction. The stretching frequency of the semibridging CS group would also be expected to be lower than that of a comparable terminal CS group, e.g., [HB(pz)$_3$](CO)$_2$W(CS)I, ν(CS) = 1243 cm^{-1}.[13] Unfortunately, the ν(CS) band of the semibridging CS group has not been identified because the HB(pz)$_3^-$ and PPh$_3$ groups also have strong absorptions between 1300 and 1000 cm^{-1}.[18]

The ^{13}C NMR spectrum of **1** at room temperature shows three peaks corresponding to two different CO groups and a CS. The resonance at 226.88 ppm, which is assigned to the terminal CO, has a chemical shift which is similar to that of CO groups in related compounds, e.g., 224.0 ppm for [HB(pz)$_3$](CO)$_2$W(CS)I.[13] The semibriding CO is then assigned to the band at 295.80 ppm. The semibridging CO is shifted downfield more than the terminal CO, as is also found in Cp(CO)$_2$W(μ-C(tolyl)$=$CH$_2$)Pt(PMe$_3$)$_2$[19] and Cp(CO)$_2$W(μ-C(tolyl))Rh(PMe$_3$)(η^5-C$_9$H$_7$).[20] The instability of the compound does not allow high-temperature ^{13}C NMR studies, which might provide information about scrambling of the semibridging and terminal CO groups.[6] The resonance at 301.05 ppm with J_{PC} = 34.18 Hz, which is assigned to the semibridging CS, has a similar chemical shift to that of the terminal CS in [HB(pz)$_3$](CO)$_2$W(CS)I (300.0 ppm).[13] Coupling of the PPh$_3$ phosphorus to the CS (J_{PC} = 34.18 Hz) but not to the CO (J_{PC} $\cong$ 0 Hz) in **1** suggests that there is a stronger interaction between Au and CS than CO. Also in **2**, J_{PC} coupling to the PMe$_3$ phosphorus is greater for CS (J_{PC} = 29.60 Hz) than for CO (J_{PC} = 7.39 Hz). The larger J_{PC} (7.39 Hz) for the semibridging CO in the PMe$_3$ compound, as compared with the PPh$_3$ compound (J_{PC} $\cong$ 0 Hz), suggests a stronger interaction of the semibridging CO with Au in **2** than in **1**; these conclusions are supported by the structural results described below. In W–Pt dinuclear complexes with a semibridging CO interaction with the Pt, it has also been observed that J_{PC} coupling constants are larger for shorter Pt–CO (semibridging) bonds, e.g., Cp(CO)$_2$W(μ-η^1,η^3-CH(tolyl))Pt(PMe$_3$)$_2$ (Pt–CO = 2.27 Å, J_{PC} = 22 Hz)[21] vs. Cp(CO)$_2$W(μ-C(tolyl)$=$CH$_2$)Pt(PMe$_3$)$_2$ (Pt–CO = 2.54 Å, J_{PC} = 11 Hz).[19]

The C-bridging CS ligand in Cp$_2$Fe$_2$(CO)$_2$(μ-CO)(μ-CS),[22] Cp$_2$Fe$_2$(CO)$_2$(μ-CS)$_2$,[1f] MnPt(μ-CS)(CO)$_2$(PMePh$_2$)$_2$Cp,[6] and Cp(PMe$_3$)CoMnCp(CO)(μ-CO)(μ-CS)[23] can be alkylated (R$^+$) at the sulfur atom to give bridging thiocarbyne complexes, M(μ-CSR)M′. However, methylation of **1** with (Me$_3$O)PF$_6$ in CH$_2$Cl$_2$ at room temperature for 20 min cleaves the W–Au bond to give the terminal thiocarbyne [HB(pz)$_3$](CO)$_2$W($\equiv$CSMe), a compound which was prepared earlier via the reaction of [HB(pz)$_3$](CO)$_2$W(CS)$^-$ with MeI.[12b]

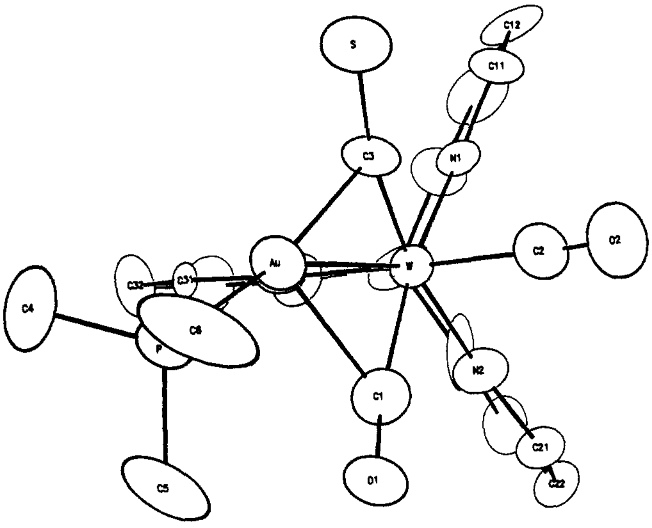

Figure 2. ORTEP plot of [HB(pz)$_3$](CO)$_2$(CS)W–Au(PMe$_3$) (**2**), view down the B–W bond.

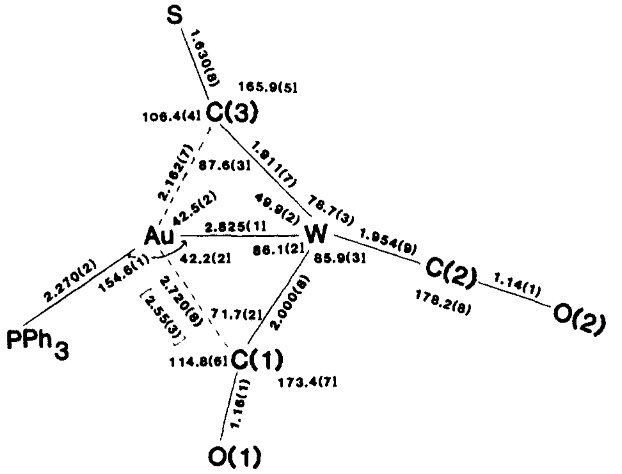

Figure 3. Bond distances and angles around the semibridging CS and CO and terminal CO ligands in the complex [HB(pz)$_3$](CO)$_2$(CS)W–AuPPh$_3$ (**1**). The significant difference between **1** and **2** is in the Au–C(1) distance; this distance in complex **2** is shown in square brackets.

Structure and Bonding Descriptions of [HB(pz)$_3$](CO)$_2$(CS)W–Au(PR$_3$), 1 (R = Ph) and 2 (R = Me). Single-crystal X-ray diffraction studies of **1** and **2** show these molecules to have similar structures (Figures 1 and 2) with a W–Au bond bridged by semibridging CS and CO ligands; the major difference between the structures of **1** and **2** is the Au–C(1) distance, which is discussed later. Figure 3 contains bond distances and angles around the semibridging CS and CO and terminal CO ligands in complex **1**. Selected bond distances and bond angles for **1** and **2** are given in table I. Since the bond distances and angles are more precise for **1** (R = 3.1%) than **2** (R = 5.2%), complex **1** will be discussed in greater detail. First we compare the structure of **1** with that of the closely related Cp(CO)$_3$W–Au(PPh$_3$),[14] in which two of the CO groups are semibridging. The W–Au bond distance (2.8248 (4) Å) in **1** is somewhat longer than those found in Cp(CO)$_3$W–Au(PPh$_3$) (2.698 (3) Å) and Cp(CO)$_2$W–Au(PPh$_3$)(μ-CH(tolyl)) (2.729 (1) Å).[24] Several features of the structure of **1** are consistent with the presence of a semibridging CO group. The W–C(2) bond distance (1.954 (9) Å) is shorter than W–C(1) (2.000 (8) Å), and the C(2)–O(2) bond distance (1.14 (1) Å) appears to be shorter than C(1)–O(1) (1.16 (1) Å).

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

1		**2**	
(a) Distances (Å)[a]			
W–Au	2.8248 (4)	W–Au	2.824 (1)
W–C(1)	2.000 (8)	W–C(1)	1.985 (28)
W–C(2)	1.954 (9)	W–C(2)	1.966 (30)
W–C(3)	1.911 (7)	W–C(3)	1.905 (24)
W–N(1)	2.223 (6)	W–N(1)	2.221 (20)
W–N(2)	2.212 (6)	W–N(2)	2.293 (21)
W–N(3)	2.243 (6)	W–N(3)	2.242 (20)
Au–S	3.054 (2)	Au–S	3.005 (9)
Au–P	2.270 (2)	Au–P	2.269 (7)
Au–C(1)	2.720 (8)	Au–C(1)	2.546 (28)
Au–C(3)	2.162 (7)	Au–C(3)	2.151 (24)
Au–O(1)	3.374 (7)	Au–O(1)	3.212 (20)
S–C(3)	1.630 (8)	S–C(3)	1.631 (25)
P–C(41)	1.814 (8)	P–C(4)	1.773 (43)
P–C(51)	1.796 (8)	P–C(5)	1.850 (37)
P–C(61)	1.806 (9)	P–C(6)	1.766 (43)
C(1)–O(1)	1.159 (11)	C(1)–O(1)	1.173 (34)
C(2)–O(2)	1.141 (12)	C(2)–O(2)	1.136 (39)
N(11)–B	1.511 (12)	N(11)–B	1.493 (38)
N(21)–B	1.560 (12)	N(21)–B	1.505 (39)
N(31)–B	1.533 (12)	N(31)–B	1.508 (38)
(b) Angles (deg)[a]			
Au–W–C(1)	66.1 (2)	Au–W–C(1)	61.0 (8)
Au–W–C(2)	105.6 (3)	Au–W–C(2)	97.1 (9)
Au–W–C(3)	49.9 (2)	Au–W–C(3)	49.6 (7)
Au–W–N(1)	124.0 (2)	Au–W–N(1)	135.2 (5)
Au–W–N(2)	150.1 (2)	Au–W–N(2)	142.8 (5)
Au–W–N(3)	85.3 (2)	Au–W–N(3)	90.7 (5)
C(1)–W–C(2)	85.9 (3)	C(1)–W–C(2)	90.9 (12)
C(1)–W–C(3)	105.0 (3)	C(1)–W–C(3)	108.4 (11)
C(1)–W–N(1)	167.9 (3)	C(1)–W–N(1)	162.7 (10)
C(1)–W–N(2)	88.7 (3)	C(1)–W–N(2)	83.1 (10)
C(1)–W–N(3)	95.5 (3)	C(1)–W–N(3)	95.0 (10)
C(2)–W–C(3)	78.7 (3)	C(2)–W–C(3)	82.7 (11)
C(2)–W–N(1)	96.7 (3)	C(2)–W–N(1)	92.3 (10)
C(2)–W–N(2)	87.3 (3)	C(2)–W–N(2)	92.7 (10)
C(2)–W–N(3)	168.6 (3)	C(2)–W–N(3)	171.9 (10)
C(3)–W–N(1)	87.2 (3)	C(3)–W–N(1)	88.9 (9)
C(3)–W–N(2)	159.5 (3)	C(3)–W–N(2)	167.5 (9)
C(3)–W–N(3)	111.8 (3)	C(3)–W–N(3)	100.8 (9)
N(1)–W–N(2)	79.6 (2)	N(1)–W–N(2)	79.7 (7)
N(1)–W–N(3)	79.6 (2)	N(1)–W–N(3)	80.5 (7)
N(2)–W–N(3)	81.4 (2)	N(2)–W–N(3)	82.5 (7)
W–Au–P	154.6 (1)	W–Au–P	151.7 (2)
W–Au–C(1)	42.2 (2)	W–Au–C(1)	43.0 (6)
W–Au–C(3)	42.5 (2)	W–Au–C(3)	42.4 (6)
P–Au–C(1)	119.3 (2)	P–Au–C(1)	109.9 (7)
P–Au–C(3)	162.1 (2)	P–Au–C(3)	166.0 (7)
C(1)–Au–C(3)	78.0 (3)	C(1)–Au–C(3)	83.9 (9)
Au–P–C(41)	109.1 (3)	Au–P–C(4)	115.3 (14)
Au–P–C(51)	114.1 (3)	Au–P–C(5)	111.3 (12)
Au–P–C(61)	114.1 (3)	Au–P–C(6)	113.9 (14)
C(41)–P–C(51)	106.5 (4)	C(4)–P–C(5)	103.8 (18)
C(41)–P–C(61)	106.8 (4)	C(4)–P–C(6)	108.5 (20)
C(51)–P–C(61)	105.8 (4)	C(5)–P–C(6)	102.8 (18)
W–C(1)–Au	71.7 (2)	W–C(1)–Au	76.0 (9)
W–C(1)–O(1)	173.4 (7)	W–C(1)–O(1)	169.6 (24)
Au–C(1)–O(1)	114.8 (6)	Au–C(1)–O(1)	114.3 (20)
W–C(2)–O(2)	178.2 (8)	W–C(2)–O(2)	178.3 (27)
W–C(3)–Au	87.6 (3)	W–C(3)–Au	88.0 (9)
W–C(3)–S	165.9 (5)	W–C(3)–S	167.3 (16)
Au–C(3)–S	106.4 (4)	Au–C(3)–S	104.4 (12)

[a] Estimated standard deviations are given in parentheses.

The W–C(2)–O(2) bond angle is 178.2 (8)°, whereas the W–C(1)–O(1) bond angle (173.4 (7)°) deviates more from 180°; the W–C(1)–O(1) bond angle is close to those (172 (4), 168 (4)°) of the semibridging carbonyls in $Cp(CO)_3W{-}Au(PPh_3)$ and the semibridging Mo–C–O angles (172.5 (5), 172.7 (5)°) in the formylcyclopentadienyl complex, $(\eta\text{-}C_5H_4CHO)(CO)_3Mo{-}Au(PPh_3)$.[25] The Au–C(1) bond distance (2.720 (8) Å) is longer than the distances (2.51 (5), 2.79 (5) Å) of the semibridging CO carbons to Au in $Cp(CO)_3W{-}Au(PPh_3)$ and those 2.528 (6), 2.536 (5) Å) in $(\eta\text{-}C_5H_4CHO)(CO)_3Mo{-}Au(PPh_3)$.[25] The bond distances of the semibridging CO carbons to Au in $(\eta^3\text{-}C_3H_5)(CO)_3Fe{-}Au(PPh_3)$ are 2.595 (7) and 2.569 (7) Å.[17] The Au–O(1) distance is 3.374 (7) Å, too long to be considered a side-on bonding CO.[9] Thus, the C(1)–O(1) ligands in **1** and **2** may be considered semibridging CO groups. The nature of the interaction between the Au atom and the semibridging CO group appears to be one in which Au donates electron density into the semibridging CO ligand π^* orbitals. This conclusion is based on the substantially shorter Au–C(1) distance (2.55 (3) Å) in the more electron-rich PMe_3 complex **2** as compared with that (2.720 (8) Å) in the PPh_3 complex **1**. Although the 14-electron gold(I) center has previously been considered a poor electron donor,[8c,26] it does appear to be a donor in its interaction with the semibridging CO in this system.

The CS ligand in **1** is also in a semibridging position; the Au–S distance is 3.054 (2) Å, long for a side-on bonding CS. As in terminal and C-bridging CS complexes, CS behaves as if it were a better σ-donor and π-acceptor ligand than CO. Thus, the W–C(3) bond distance (1.911 (7) Å) is shorter than both the W–C(1) (2.000 (8) Å) and W–C(2) (1.954 (9) Å) bond distances; it is also somewhat shorter than the W–C bond distance (1.94 (2) Å) to the terminal CS in $(CO)_4(CNC_6H_{11})W(CS)$;[18] however, the latter complex is less electron-rich. The W–C(3)–S bond angle (165.9 (5)°) deviates more from 180° than does that (173.4 (7) Å) of the semibridging CO. The Au–semibridging CS distance, Au–C(3), is much shorter than any Au–semibridging CO distances, the shortest reported distance being 2.52 Å.[14,25] The Au–C(3) distance (2.162 (7) Å) in **1** may be compared with the Au–C(sp) single bond distance (1.94 (2) Å) in (i-Pr)$NH_2AuC{\equiv}CC_6H_5$,[27] the Au–C(sp^2) single bond distance (2.07 (2) Å) in $Ph_3PAuC_6F_5$,[28] and the Au–C(sp^3) single bond distance (2.12 (3) Å) in Ph_3PAuMe.[29] Thus, the Au–C(3) interaction is approaching that of a full bond. The fact that the Au–C(3) distance is substantially shorter than the Au–C(1) distance (2.720 (8) Å) supports the suggestion above that the Au is an electron donor since the better π-accepting CS ligand[1] is expected to form a stronger bond than CO to the Au.

It is interesting that the Au–CS bond distance is essentially the same in **1** and **2**, whereas the Au–CO distance is considerably shorter in the PMe_3 complex **2**. This suggests that the semibridging CS ligand is less capable of accepting the additional electron density in **2**, whereas the Au–CO interaction is considerably strengthened by it.

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

The W–Au–P bond angle (154.6 (1)°) deviates noticeably from the 180° found in most Au(I) complexes[25,27–29] and is substantially

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smaller than that found in Cp(CO)$_3$W–AuPPh$_3$ (173.8 (3)°). If one assumes Au to prefer linear coordination and one of its ligands is the phosphine, the second ligand should lie on an extension of the P–Au vector. It is interesting that this extension intersects the W–C(3) bond at about its midpoint; perhaps the Au orbitals involved in linear coordination are interacting with W and C(3) at the expense of direct Au–W bonding, which is evident in the longer Au–W bond in this complex as compared with related complexes (see above).

The interplanar angle between the W–C(1)–Au and W–C(3)–Au planes is 138° and 161° in **1** and **2**, respectively. The C(1)→O(1) bond vector lies in the W–C(1)–Au plane (within 0.03°) in **1**, but it is out of this plane slightly (2.04°) pointing toward the semibridging CS in **2**. The C(3)→S bond vector points away from the W–C(3)–Au plane toward the semibridging CO in both **1** (2.29°) and **2** (2.76°).

In conclusion, CS is a better semibridging ligand than CO as suggested by the fact that the CS instead of a second CO is involved in semibridging in **1** and **2**. This conclusion is supported by the much shorter Au–C distance for Au–CS than Au–CO. The more favorable semibridging ability of the CS group appears to be due to its better π^*-acceptor ability as compared with CO, which allows it to interact more strongly with the electron-donating Au atom. Further evidence of the electron-donor ability of the Au is seen in the shorter Au–C distance for the semibridging CO in the more electron-rich PMe$_3$ complex **2** as compared with the PPh$_3$ analogue **1**.

Experimental Section

General Procedures. All reactions were carried out under an N$_2$ atmosphere. Methylene chloride and hexane were dried over CaH$_2$ and distilled under N$_2$. Diethyl ether was distilled from Na–benzophenone under N$_2$. Reagent grade benzene was stored over type 4A molecular sieves. Products were crystallized with use of a layering technique, whereby the compound (30 mg) dissolved in CH$_2$Cl$_2$ (2 mL) was layered with hexane (10 mL) and allowed to sit at 0 °C under a constant N$_2$ atmosphere. Infrared spectra were recorded on a Perkin-Elmer 681 spectrometer; the band positions were calibrated against gaseous CO. ^{1}H NMR spectra were obtained with a Nicolet NT-300 (300 MHz) spectrometer. Proton-decoupled ^{13}C NMR spectra were measured on the same instrument (75.46 MHz). To reduce ^{13}C NMR data collection times, Cr(acac)$_3$ (ca. 0.1 M) was added to the solutions.[32] Chemical shifts of ^{13}C nuclei are reported in δ units with CD$_2$Cl$_2$ (δ = 53.80) as the internal standard. Electron impact mass spectra (EIMS) were obtained on a Finnigan 4000 spectrometer. Elemental microanalyses were performed by Galbraith Laboratories Inc., Knoxville, TN.

Solutions of [(n-Bu)$_4$N]{[HB(pz)$_3$](CO)$_2$W(CS)}[13] were prepared with use of previously described procedures. Ph$_3$PAuCl and Me$_3$PAuCl were purchased from Strem Chemicals, Inc.

[HB(pz)$_3$](CO)$_2$(CS)W–AuPPh$_3$ (1). A reaction solution containing [(n-Bu)$_4$N]{[HB(pz)$_3$](CO)$_2$W(CS)} (0.22 mmol) and ClAuPPh$_3$ (109 mg, 0.22 mmol) in 20 mL of CH$_2$Cl$_2$ was stirred at room temperature for 15 min, yielding a red solution, which was evaporated to dryness under reduced pressure. The resulting oily residue was extracted with diethyl ether until the extract was colorless. The extract was filtered through Celite, and the filtrate was evaporated to give an orange solid; recrystallization from CH$_2$Cl$_2$/hexane at 0 °C gave red crystals of **1** (63 mg, 30%). Microscopic crystals were found which were suitable for X-ray analysis. Anal. Calcd for C$_{30}$H$_{25}$AuBN$_6$O$_2$PSW: C, 37.68; H, 2.64; N, 8.79. Found: C, 37.61; H, 2.63; N, 8.65. EIMS (19 eV): m/e 956 (M$^+$), 900 (M$^+$ – 2CO). IR (CH$_2$Cl$_2$): 1923 (s), 1836 (s) cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$): 8.20 (br, H3 of pz), 7.60 (m, H5 of pz and Ph), 6.16 (br, H4 of pz). ^{13}C NMR (CD$_2$Cl$_2$): 301.05 (d, J_{PC} = 34.18 Hz, CS), 295.80 (semibridging CO), 226.88 (CO), 145.87 (C3 of pz), 135.54 (C5 of pz), 105.80 (C4 of pz) [134.38 (d, J_{PC} = 13.47 Hz), 131.86, 130.60, 129.88, 129.43 (d, J_{PC} = 8.54 Hz), Ph].

[HB(pz)$_3$](CO)$_2$(CS)W–AuPMe$_3$ (2). In a procedure similar to that used for **1**, (Me$_3$P)AuCl (160 mg, 0.52 mmol) was allowed to react with [(n-Bu)$_4$N]{[HB(pz)$_3$](CO)$_2$W(CS)} (0.52 mmol) in CH$_2$Cl$_2$ (50 mL) at room temperature for 15 min. The solution was diluted with 70 mL of ether; slow evaporation under reduced pressure funished an orange precipitate. After the solution was decanted, the resulting orange solid was extracted with benzene. The benzene extract was filtered through Celite, and the solution was evaporated to dryness; recrystallization of the residue from CH$_2$Cl$_2$/hexane at 0 °C gave red crystals of **2** (80 mg, 20%), some of which were suitable for X-ray analysis. Anal. Calcd for C$_{15}$H$_{19}$AuBN$_6$O$_2$PSW: C, 23.40; H, 2.49; N, 10.91. Found: C, 22.83; H, 2.57; N, 10.30. EIMS (70 eV): m/e 770 (M$^+$), 714 (M$^+$ – 2CO). IR (CH$_2$Cl$_2$): 1920 (s), 1830 (s) cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$): 8.17 (br, H3 of pz), 7.68 (br, H5 of pz), 6.23 (br, H4 of pz), 1.78 (d, J_{PH} = 9.72 Hz, Me). ^{13}C NMR (CD$_2$Cl$_2$): 295.70 (d, J_{PC} = 29.60 Hz, CS), 293.20 (d, J_{PC} = 7.39 Hz, semibridging CO), 228.11 (CO), 145.81 (C3 of pz), 135.61 (C5 of pz), 105.91 (C4 of pz), 17.81 (d, J_{PC} = 34.61 Hz, Me).

Table II. Summary of Crystal Data and Intensity Data Collection for [HB(pz)$_3$](CO)$_2$(CS)W–Au(PPh$_3$) (**1**) and [HB(pz)$_3$](CO)$_2$(CS)W–Au(PMe$_3$) (**2**)

	1	**2**
formula unit	C$_{30}$H$_{25}$AuBN$_6$O$_2$PSW	C$_{15}$H$_{19}$AuBN$_6$O$_2$PSW
mol wt	956.23	770.02
space group	$P2_1/n$	$Pbca$
a, Å	15.062 (4)	16.956 (3)
b, Å	18.103 (3)	17.173 (3)
c, Å	11.887 (2)	15.053 (2)
α, deg	90	90
β, deg	103.53 (2)	90
γ, deg	90	90
vol, Å^3	3151.2 (12)	4383.4 (14)
Z	4	8
ρ_{calcd}, g/cm^3	2.015	2.333
crystal dimensions, cm	0.05 × 0.05 × 0.045	0.02 × 0.02 × 0.02
diffractometer	DATEX	Syntex P2$_1$
radiation, Å	0.70966	0.71069
monochromator	oriented graphite crystal	oriented graphite crystal
absorption coeff, cm^{-1} (corr appl)	85.12	122.09
ratio min/max transmission	0.544	0.433
ω step scan mode	0.5 s per 0.01°	1° per min
scan width	1.2°	1.0°
background measurement	total 10 s	same as the scan
$2\theta_{max}$, deg	50	45
octants measured	$\pm h,\pm k,l$	h,k,l
reflections measd	5392	3443
independent obsd ($I \geq 3\sigma_I$)	3900	1905
R^a	0.031	0.052
Rw^b	0.038	0.062
S^c	1.258	1.689
secondary extinction^d	0.259 (22) × 10^4	0.070 (19) × 10^4

[a] $R \equiv \sum||F_o| - |F_c||/\sum|F_o|$. [b] $Rw \equiv [\sum\omega(|F_o| - |F_c|)^2/\sum\omega|F_o|^2]^{1/2}$, where $\omega = 1/\sigma_F{}^2$. [c] $S \equiv [\sum\omega(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$, where N$_o$ and N$_v$ are numbers of observations and varied parameters, respectively. [d] Isotropic parameter applied to F_c, based on *P.* Coppens and W. C. Hamilton (*Acta Crystallogr.* **1970**, *A26*, 71) with a polarization factor for the case of a monochromator in the diffracted beam.

X-ray Crystallography. The general procedures for data collection and reduction have been published elsewhere.[33] Details of the data processing and relevant crystallographic data are given in Table II. Computer programs used in this study are summarized in ref 34.

The structures were determined with use of Patterson and electron density function calculations. Hyrogen atoms were included in the

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structure factor calculations at their calculated positions. The positional and anisotropic thermal parameters were refined by block-matrix/full-matrix procedures.

The atomic scattering factors were those from ref 35 modified for the real and imaginary parts of anomalous dispersion.

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Supplementary Material Available: Tables of positional parameters, anisotropic thermal parameters, all bond distances and angles, and structure factors (32 pages). Ordering information is given on any current masthead page.

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Coreceptor Molecules. Synthesis of Metalloreceptors Containing Porphyrin Subunits and Formation of Mixed Substrate Supermolecules by Binding of Organic Substrates and of Metal Ions

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Abstract: Three coreceptor molecules, two macrotetracycles **1** and **2** and one macropentacycle **3**, containing [18]-N_2O_4 macrocyclic and porphyrinic subunits, have been synthesized and characterized. They form metalloreceptors by complexation of transition-metal ions like Zn(II) or Cu(II) with the porphyrin groups. Binding of α,ω-diammonium cations to the [18]-N_2O_4 units occurs with substrate inclusion, yielding η^2-cryptates like **27**, **28**, and **31**, as indicated by very large upfield shifts of the CH_2 proton NMR signals of the substrates. Similarly, these organic cations also bind to the Zn(II)-containing metalloreceptors **19**, **20**, and **22**, giving organic/inorganic *mixed substrate supermolecules*, such as **29**, **30**, and **32**. In these and similar species, the simultaneous complexation of several substrates opens the way to the study of mutual interactions within supramolecular structures and of regulation effects on physical and chemical properties.

Beyond receptor molecules possessing a single binding unit, the chemistry of molecular receptors enters the domain of polytopic coreceptors, macropolycyclic molecules incorporating several binding subunits which may cooperate for the complexation of either several singly bound substrates or of multiply bound polyfunctional substrates.[1,2] Homotopic coreceptors which bind terminal diammonium cations and dicarboxylate anions by means of two identical subunits have been described (see references in ref 1 and below).

Metalloreceptors are heterotopic coreceptors which combine suitable substrate selective binding subunits, such that they can complex both organic substrate(s) and metal cation(s), thus forming mixed substrate supermolecules. As a consequence, interactions and reactions may take place between metal-centered reactive sites and co-bound molecular substrate(s). Such metalloreceptors, -reagents, and -catalysts may also mimic features of metalloproteins.

Earlier examples of a process which may be considered to be of the metalloreceptor type were the formation of molecular cation–anion pairs by a cascade mechanism which involved first complexation of one or two metal cations to a neutral aporeceptor followed by ion pairing between the resulting holoreceptor cation and a molecular anion.[3,4]

We have designed and studied in recent years several metalloreceptor systems (for brief descriptions see ref 1 and 2). We now describe the synthesis of the three coreceptors **1–3** and report their ability to complex *both* metal cations and primary diammonium ions, by means of porphyrin and macrocyclic [18]-N_2O_4 (**12**) subunits, respectively.[5,6]

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