only present at low concentration, as shown in Figure 5.

From Table III we see that the potential necessary to oxidize cobalt when both of the irons are in their reduced state (E_1) is different from the potential necessary when either one or both are in their oxidized state (E_6 and E_8). In addition the potentials necessary to oxidize each of the iron sites are the same when cobalt is in its reduced form ($E_2 = E_4$) but not when cobalt is in its oxidized form ($E_3 \neq E_5$). It is interesting that, within our precision, E_5 is not different from E_2 or E_4, and E_3 is greater than E_5, while both reflect Fe oxidation in the presence of an oxidized Co.

The potentials E_2 through E_5 (two-parameter model), relative to E_1, decrease with increasing temperature. Substitution of dmg for nox in the cage shifts the potential of cobalt (E_1 in Table III) to a more positive value, which is consistent in magnitude but opposite in direction compared with the cyclic voltammetry results for the related cobalt clathrochelate compounds $Co(nox)_3(BF)_2$ and $Co(dmg)_3(BF)_2$.

Determination of E_1 required using an ionic strength of 0.1 M. In order to determine if the ionic strength requirement has an effect on the various potentials, a spectrophotometric titration was carried out at this ionic strength and best fit parameters were determined. The resultant potentials (Table II) showed that ionic strength over the range 0–0.1 M has little effect on the potentials.

On the basis of these results, we can conclude that the metal sites do interact with each other and that a minimum of three different potentials are necessary to describe the system (E_1, $E_{2,4,5}$, and E_3). In addition, these potentials are independent of added salt and only slightly dependent on temperature.

It is of interest to consider how the interaction between sites occurs. The apparent lack of a salt dependence of the potentials may suggest that the observed interaction is more likely of a "through bonds" nature than through space. Ion-pair formation would be likely to stabilize the formation of species ROO and OOO, in which two or more charges are next to each other. This, however, assumes that the salt (BF_4^-) is able to get into a position that might promote or hinder any interaction. It also assumes that, at the concentrations used in the experiments where no salt was added, no ion-pair formation is occurring. For a low dielectric solvent such as methylene chloride, ion-pair formation may occur even at the low concentration of BF_4^- present from the oxidant. Thus the through space alternative cannot be ruled out. From crystallographic studies of $Co(dmg)_3(BF)_2$[19] and $Fe(cp)_2$[20] a through space Co–Fe distance of approximately 6.3 Å can be calculated (from a Co–B distance of 3.6 Å in conjunction with a Fe–B distance of 2.0 Å for Fe–C plus a 1.5 Å for C–B with the appropriate angle). A "through bonds" mechanism of interaction requires that five bonds (8.4 Å), including a coordinatively saturated boron atom, be traversed. In bridged ferrocenes coordinatively saturated molecules such as Se[21] and B[22] have been shown to allow some inductive communication to occur. In this instance neither of the two mechanisms can be ruled out although the through space interaction seems to be the more plausible alternative.

Various attempts have been made to observe the internal electron transfer between the Co and Fe centers.[23] Stopped-flow studies of the titration reaction, including any internal electron transfer, have shown it to be complete within ca. 5 ms. Initial temperature-jump experiments, in which equal concentrations of $Co(nox)_3(B(cp)Fe(cp))_2$ and oxidant are intially present, show evidence of a relaxation process in the 100-μs time scale.[24] These studies are being pursued further.

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Supplementary Material Available: Tables of all absorbance data (7 pages). Ordering information is given on any current masthead page.

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Bimetallic μ-Oxo Complexes Formed by Coordination of the Oxo Ligands of $Cp_2Mo{=}O$ and $Cp_2W{=}O$ to Rhodium(I) and Iridium(I) Centers

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The μ-oxo complexes $[Cp_2M{=}O{-}M'(PPh_3)_2(CO)]^+$ (M = Mo, W; M′ = Rh, Ir) have been prepared by solvent displacement from $[M'(CO)(PPh_3)_2(CH_3CN)]^+$ by the oxo ligand of $Cp_2M{=}O$. Crystallographic analysis of the salt $[Cp_2Mo{=}O{-}Rh(PPh_3)_2(CO)][BF_4]\cdot{}^1/_2C_3H_6O\cdot{}^1/_2C_5H_{12}$ [$P2_1/c$, $a = 17.288$ (4) Å, $b = 13.729$ (3) Å, $c = 23.168$ Å, $\beta = 110.49$ (2)°, $V = 5151$ (2) Å^3, $Z = 4$, $R(F) = 6.85\%$, $R_w(F) = 7.42\%$ for 5095 reflections with $F_o \geq 4\sigma(F_o)$] has shown the complex to consist of a square-planar Rh center ligated by the CO, two PPh_3 ligands, and the μ-oxo ligand of the $Cp_2Mo{=}O$ moiety. The Mo—O—Rh linkage is nearly linear (Mo—O—Rh = 167.1 (4)°), and the complex appears best described as having a dative interaction of the oxo ligand with the unsaturated Rh center. Spectroscopic data imply similar structures for the other complexes in this series. ^1H NMR studies show that the $Cp_2M{=}O$ units of these complexes rapidly exchange with CD_3CN solvent and with excess $Cp_2M{=}O$ on the ^1H NMR time scale.

Introduction

A large number of organometallic oxo-bridged complexes are known,[1] but relatively few are heterometallic and fewer yet have oxo bridges between metals widely separated in the periodic table. Particularly important are complexes with oxo bridges between transition metals in groups 4–6 and those in groups 8–10,[2] in part because such compounds can provide insight into the chemistry that occurs at the interface between a metal and its oxide support during catalytic reactions of the later transition metals supported on oxides of the earlier metal (e.g., TiO_2, MoO_3). We have sought the preparation of such oxo-bridged complexes using the

Table I. Crystallographic Data for $[Cp_2Mo{=}O{-}Rh(PPh_3)_2(CO)][BF_4]\cdot{}^1/_2C_3H_6O\cdot{}^1/_2C_5H_{12}$ (**3**)

formula	$C_{47}H_{40}BF_4O_2P_2RhW\cdot{}^1/_2C_3H_6O\cdot{}^1/_2C_5H_{12}$	Z	4
		D(calc), g/cm^{-3}	1.221
fw	946.59	T, K	293
space group	$P2_1/c$	μ, cm^{-1}	6.62
a, Å	17.288 (4)	radiation λ, Å	0.71073
b, Å	13.729 (3)	$R(F)$, %	6.85
c, Å	23.168 (5)	$R_w(F)$, %	7.42
β, deg	110.49 (2)		
V, Å^3	5151 (2)		

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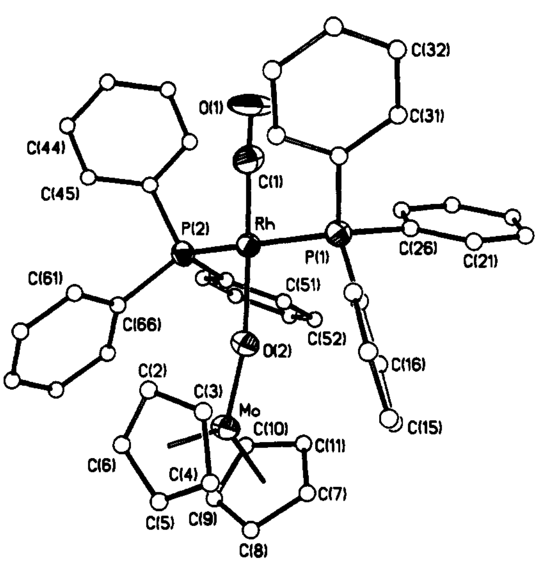
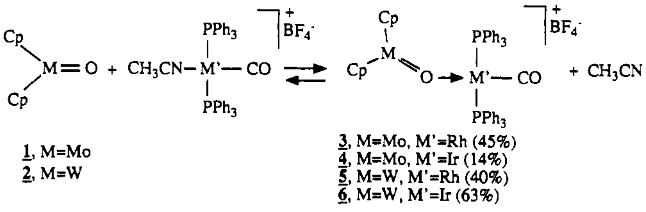


Figure 1. ORTEP drawing of $[Cp_2Mo{=}O{-}Rh(CO)(PPh_3)_2]^+$ (3) with thermal ellipsoids drawn at the 40% probability level.

"bridge-assisted" reaction[3] in which an oxo ligand on one metal displaces a labile ligand from a second metal. This route is one of the most powerful for the synthesis of bimetallic phosphido, carbene, carbyne, and hydride complexes,[3] but it has not been used extensively for the preparation of compounds with bridging oxo ligands.[2a-d,4] As described herein, we have found that the oxo complexes $Cp_2M{=}O$ (**1**, M = Mo; **2**, M = W)[5] are ideally suited for this purpose, as they readily displace weakly coordinated CH_3CN from Rh(I) and Ir(I) centers to form bimetallic μ-oxo compounds. One remarkable property of these new complexes is the ease with which they exchange the $Cp_2M{=}O$ moiety with excess $Cp_2M{=}O$ and with CD_3CN solvent. The oxo complexes **1** and **2** were chosen for this study because the oxo ligands of these complexes have been shown to be sufficiently nucleophilic to add to a variety of electrophilic substrates.[6] This is in part because the oxo ligands of **1** and **2** function only as $2e^-$ donors to the metal and thereby render the oxo ligand more electron rich than in the majority of oxo complexes which formally possess $4e^-$-donating oxygen atoms.

Results

Syntheses and Spectroscopic Characterization. The oxo complexes **1** and **2** have been found to readily displace acetonitrile from the cationic complexes $[M(PPh_3)_2(CO)(CH_3CN)]^+$ (M = Rh,[7] Ir[8]) to form the new bimetallic μ-oxo complexes **3**–**6** (eq 1).



(1)

As discussed below, the reactions of eq 1 are reversible but under the conditions used for the synthesis of **3**–**6**, ^1H NMR monitoring indicated the equilibria to lie completely to the right. However, the isolated yields are reduced due to decomposition during the isolation procedure. Complexes **3**–**6** were isolated as microcrystalline solids, and the structure of the Mo—O—Rh complex **3** has been fully defined by an X-ray diffraction study, the results of which are shown in Figure 1. The structure shows the square-planar Rh(I) center to be ligated by the $Cp_2Mo{=}O$ moiety in what appears to be best described as a dative O→Rh interaction with a slightly bent (167.1 (4)°) Mo—O—Rh bond. The spectroscopic data summarized in the Experimental Section for compounds **3**–**6** are consistent with the crystallographically determined structure of **3** and imply similar structures for all four compounds. Particularly important is the observance of a single broad ^{17}O NMR resonance at δ 504 for the W—O—Ir complex **6** that was prepared from ^{17}O-labeled $Cp_2W{=}O$. This resonance is shifted significantly upfield from that of free $Cp_2W{=}O$ at δ 775, implying the maintenance of the μ-oxo linkage in solution since established correlations have shown that the ^{17}O NMR resonances of bridging oxo ligands are substantially upfield from those of terminal oxo ligands.[9]

The infrared analysis of compounds **3**–**6** has been particularly informative. First, the carbonyl stretching frequencies for the single CO ligand of these complexes indicate that the trans influence of the $Cp_2M{=}O$ ligand is similar to that of chloride. This is clearly indicated by comparing the ν_{CO} frequency of the W—O—Ir complex **6** (1965 cm^{-1}) to that of *trans*-$IrCl(CO)(PPh_3)_2$ (1963 cm^{-1}). Also important in the IR spectra of complexes **3**–**6** is a band in the 800–840-cm^{-1} region attributed to the $\nu_{M-O-M'}$ vibration. This assignment is supported by the shift of the 837-cm^{-1} band of the W—O—Ir complex **6** to 803 cm^{-1} when the complex was prepared from ^{18}O-labeled $Cp_2W{=}O$. Of special significance is the fact that the $\nu_{M-O-M'}$ bands are only slightly shifted from the $\nu_{M=O}$ band of the parent $Cp_2M{=}O$ complexes (e.g., $\nu_{W=O}$ = 865 cm^{-1}). The relatively small shift of 28 cm^{-1} upon coordination of $Cp_2W{=}O$ to Ir in forming complex **6** signals the relative weakness of this bonding, as also indicated by the NMR-exchange studies described below. This 28-cm^{-1} shift compares well to the reported 26-cm^{-1} decrease in the $\nu_{W=O}$ stretching frequency of the compound $(Cl(CH_2Bu^t)_3W{=}O$ when its oxygen atom was coordinated to the Lewis acid $AlCl_3$.[4c]

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Table II. Atomic Coordinates (×10⁴) and Isotropic Thermal Parameters (Å² × 10³) for $[Cp_2Mo{=}O{-}Rh(PPh_3)_2(CO)][BF_4]\cdot{}^1/_2C_3H_6O\cdot{}^1/_2C_5H_{12}$ (3)

	x	*y*	*z*	*U*[a]
Rh	1915.8 (4)	1984.5 (5)	2433.1 (3)	37.5 (3)*
Mo	4241.0 (5)	1820.3 (7)	2858.4 (4)	51.3 (3)*
P(1)	1951 (1)	2142 (2)	3447 (1)	40.2 (9)*
P(2)	1801 (1)	2210 (2)	1407 (1)	40.5 (9)*
C(1)	800 (6)	1867 (9)	2191 (4)	65 (5)*
O(1)	118 (4)	1810 (7)	2081 (4)	101 (4)*
O(2)	3166 (3)	2048 (5)	2682 (3)	51 (3)*
C(2)	3853 (8)	185 (8)	2797 (6)	82 (6)*
C(3)	4147 (8)	393 (8)	3403 (6)	90 (7)*
C(4)	4980 (9)	681 (9)	3586 (6)	110 (7)*
C(5)	5188 (8)	554 (9)	3059 (8)	112 (8)*
C(6)	4493 (8)	281 (10)	2569 (7)	104 (7)*
C(7)	5011 (8)	3166 (10)	3336 (6)	99 (7)*
C(8)	5482 (8)	2627 (12)	3028 (8)	144 (10)*
C(9)	5026 (10)	2657 (13)	2384 (7)	128 (9)*
C(10)	4322 (8)	3251 (10)	2335 (7)	98 (7)*
C(11)	4299 (9)	3556 (10)	2873 (6)	94 (7)*
C(12)	2944 (4)	1012 (5)	4452 (3)	74 (5)*
C(13)	3689	772	4913	102 (7)*
C(14)	4385	1352	5008	87 (6)*
C(15)	4337	2172	4641	73 (5)*
C(16)	3592	2412	4180	53 (4)*
C(17)	2895	1832	4085	47 (4)*
C(21)	1995 (4)	3769 (5)	4191 (2)	59 (5)*
C(22)	1829	4737	4288	75 (5)*
C(23)	1429	5338	3786	99 (7)*
C(24)	1195	4970	3188	110 (8)*
C(25)	1362	4002	3092	74 (5)*
C(26)	1762	3401	3593	46 (4)*
C(31)	714 (4)	1812 (4)	3973 (3)	62 (5)*
C(32)	129	1235	4100	85 (6)*
C(33)	−18	286	3873	85 (6)*
C(34)	421	−87	3519	91 (7)*
C(35)	1006	490	3392	69 (5)*
C(36)	1152	1439	3619	48 (4)*
C(41)	147 (4)	2594 (5)	821 (3)	65 (5)*
C(42)	−634	2488	371	75 (6)*
C(43)	−757	1817	−105	88 (6)*
C(44)	−99	1251	−131	87 (6)*
C(45)	682	1357	320	65 (5)*
C(46)	805	2029	796	47 (4)*
C(51)	2289 (4)	4094 (5)	1789 (2)	55 (4)*
C(52)	2424	5076	1702	72 (5)*
C(53)	2251	5440	1108	78 (6)*
C(54)	1944	4822	600	82 (6)*
C(55)	1809	3840	687	63 (5)*
C(56)	1982	3476	1281	46 (4)*
C(61)	2473 (4)	484 (4)	1236 (3)	65 (5)*
C(62)	2991	−130	1057	78 (5)*
C(63)	3545	261	803	85 (6)*
C(64)	3581	1267	729	80 (6)*
C(65)	3063	1881	908	64 (5)*
C(66)	2509	1489	1162	45 (4)*
C(71)	3783 (13)	6069 (17)	3627 (11)	63 (6)
C(72)	3710 (19)	6983 (20)	3645 (14)	118 (10)
C(73)	3980 (15)	5456 (17)	4102 (11)	79 (7)
O(74)	3731 (11)	5950 (14)	3114 (9)	106 (6)
C(75)	1662 (17)	8396 (22)	2230 (13)	81 (7)
C(76)	1953 (15)	9146 (21)	2401 (12)	91 (8)
C(77)	1942 (23)	7821 (28)	1917 (18)	145 (14)
C(78)	977 (39)	8864 (46)	1972 (29)	114 (19)
C(79)	1373 (43)	7835 (51)	2434 (32)	131 (22)
B	3113 (1)	7356 (1)	135 (1)	169 (14)*
F(1)	2863 (4)	7466 (6)	592 (3)	148 (6)*
F(2)	3752 (5)	7891 (8)	216 (3)	217 (9)*
F(3)	2536 (4)	7608 (9)	−365 (3)	310 (12)*
F(4)	3301 (8)	6459 (4)	99 (5)	410 (23)*

[a] Asterisk represents equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Crystal and Molecular Structure of $[Cp_2Mo{=}O{-}Rh(CO)(PPh_3)_2][BF_4]$. This salt crystallizes in the space group $P2_1/c$ with well-separated cations and anions and with a half-molecule of actone and a half-molecule of pentane solvate in the unit cell. An ORTEP drawing of the complex cation is shown in Figure 1, and relevant crystallographic data are given in Tables I–III. The molecule is best described as a distorted square-planar Rh(I) complex having a donor $Cp_2Mo{=}O$ ligand, with the latter bound to Rh via a slightly bent (167.1 (4)°) Mo—O—Rh linkage. The Mo—O bond distance of 1.786 (6) Å is just slightly longer than the Mo═O distance of 1.721 (2) Å found in $(C_5H_4Me)_2Mo{=}O$,[10] implying little perturbation of the Mo═O unit upon coordination to rhodium. The Rh—O bond length of 2.034 (6) Å is comparable to the 2.044 (4) Å Rh—O distance found in the 2,4-pentanedionate complex $[Rh(CO)_2(C_5H_7O_2)]$[11] but is significantly shorter than the average Rh—O distance of 2.20 Å in $Cp^*Rh[cis\text{-}Nb_2W_2O_{19}]^{2-}$.[2u] The trans influence of the $Cp_2Mo{=}O$ ligand appears similar to that of chloride, as indicated by a comparison of the Rh—CO bond parameters to those of *trans*-$RhCl(CO)(PPh_3)_2$ (Rh—C = 1.821 (5) Å; C—O = 1.141 (6) Å).[12] As noted above, this conclusion was also indicated by an IR analysis of the W—O—Ir complex **6**.

Table III. Selected Bond Distances and Angles for $[Cp_2Mo{=}O{-}Rh(PPh_3)_2(CO)][BF_4]\cdot{}^1/_2C_3H_6O\cdot{}^1/_2C_5H_{12}$ (3)

Bond Distances (Å)			
Rh-P(1)	2.339 (3)	Mo-O(2)	1.78 (6)
Rh-P(2)	2.336 (3)	C(1)-O(1)	1.118 (13)
Rh-C(1)	1.818 (10)	Mo-CNT(1)[a]	2.011 (9)
Rh-O(2)	2.034 (6)	Mo-CNT(2)[a]	2.006 (10)
Bond Angles (deg)			
P(1)-Rh-P(2)	166.7 (1)	C(1)-Rh-O(2)	177.1 (4)
P(1)-Rh-C(1)	88.2 (3)	Rh-O(2)-Mo	167.1 (4)
P(2)-Rh-C(1)	89.7 (3)	CNT(1)-Mo-O(2)	111.9 (4)
P(1)-Rh-O(2)	93.4 (2)	CNT(2)-Mo-O(2)	110.4 (3)
P(2)-Rh-O(2)	89.23 (4)	CNT(1)-Mo-CNT(2)[a]	137.6 (3)

[a] CNT = centroid of η^5-C_5H_5 ring.

^{1}H NMR Exchange Studies. While complexes **3**–**6** are sufficiently stable to isolate as pure solids, the $Cp_2M{=}O$ portion of the molecules undergoes exchange both with CH_3CN and with excess $Cp_2M{=}O$ at rates convenient for study on the ^{1}H NMR time scale. For example, when any amount of $Cp_2W{=}O$ was added to a solution of $[Cp_2W{=}O{-}Rh(PPh_3)_2(CO)]^+$ (**5**) in CD_2Cl_2 solution at 20 °C, a single cyclopentadienyl resonance was observed lying between that of free $Cp_2W{=}O$ (δ 5.73) and that of **5** (δ 5.14), with the position of the resonance dependent upon the amount of $Cp_2W{=}O$ added. These results indicate that the exchange process shown in eq 2 occurs rapidly on the ^{1}H NMR time scale at 22 °C. *Note that this is not a fluxional process but is instead a rapid chemical transformation.* A shift in the resonance of **5** was observed when as little as 0.1 equiv of $Cp_2W{=}O$ was added. The half-width of the single resonance increased up to the addition of 1 equiv of $Cp_2W{=}O$ and then decreased upon further addition of $Cp_2W{=}O$. A variable-temperature ^{1}H NMR study of this exchange process was conducted by using a CD_2Cl_2 solution containing equimolar quantities of **2** and **5**, and those results are shown in Figure 2. At −75 °C, two separate resonances were observed for the two complexes, indicating slow exchange at this temperature. Upon warming, the resonances broadened, coalesced at −10 °C, and sharpened to a single resonance at 45 °C. These data gave a second-order rate constant at 298 °C of k_2 = 62 400 s⁻¹ M⁻¹. Stated differently, at a $Cp_2W{=}O$ concentration of 0.0667 M the exchange process of eq 2 occurs 8400 times/s. ^{1}H NMR studies showed that similar

$$\underset{\mathbf{2'}}{Cp_2W'{=}O} + \underset{\mathbf{5}}{[Cp_2W{=}O{-}Rh(PPh_3)_2(CO)]^+} \xrightleftharpoons[CD_2Cl_2]{20\ ^\circ C} \underset{\mathbf{5'}}{[Cp_2W'{=}O{-}Rh(PPh_3)_2(CO)]^+} + \underset{\mathbf{2}}{Cp_2W{=}O} \quad (2)$$

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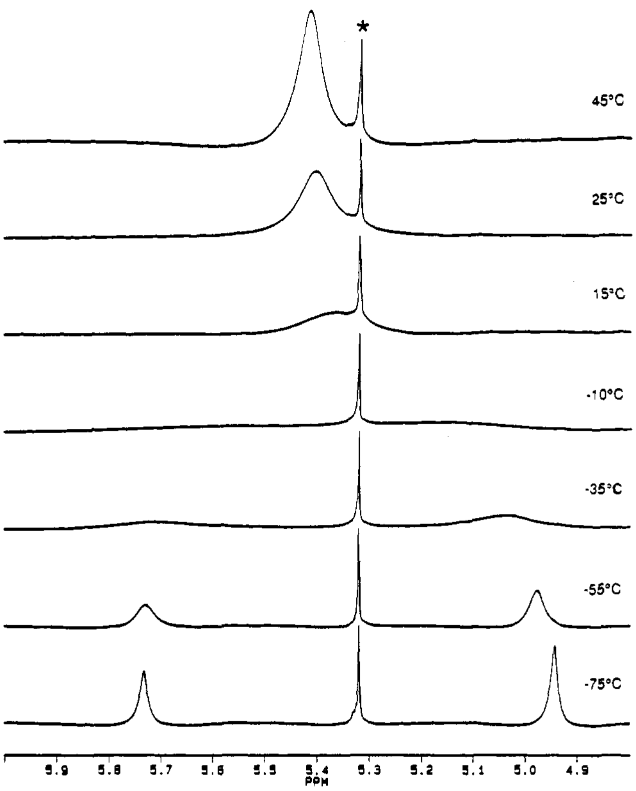

Figure 2. Variable-temperature ^1H NMR spectra for a CD_2Cl_2 solution of $Cp_2W{=}O$ (0.067 M) and complex **5** (0.067 M) showing the cyclopentadienyl proton region from δ 6.0 to 4.8. The resonance marked with the asterisk is due to CH_2Cl_2 impurity.

Table IV. Equilibrium and Thermodynamic Parameters for the Reaction

$$Cp_2M{=}O + [(CD_3CN)M'(PPh_3)_2(CO)]^+ \xrightleftharpoons[CD_2Cl_2]{} [Cp_2M{=}O{-}M'(PPh_3)_2(CO)]^+ + CD_3CN$$

complex	K_{eq}(298 K)	$\Delta H°$, kcal/mol	$\Delta S°_{298}$, cal/(mol deg)
3	25	-0.8 (1)	15 (1)
5	42	-0.9 (1)	8 (1)
6	85	-2.1 (3)	18 (4)

exchange occurred between compounds **3**, **4**, and **6** and the appropriate $Cp_2M{=}O$ reagent, but these processes were not studied in as great a detail.

Complexes **3**–**6** also undergo rapid exchange with CD_3CN, as best illustrated by the Mo—O—Rh complex **3**. When CD_3CN was added in 200-fold excess to CD_2Cl_2 solutions of this complex, a single cyclopentadienyl ^1H NMR resonance was observed between that of the pure complex **3** (δ 4.93) and that of free $Cp_2Mo{=}O$ (δ 5.53). As illustrated by the variable-temperature ^1H NMR spectra shown in Figure 3, upon cooling, the single resonance broadens and shifts toward the resonance position of complex **3**, although the slow-exchange limiting spectrum was not reached in this temperature range. Similar spectral changes were observed for complexes **5** and **6**, but complex **4** was not studied in detail because of its relatively low yield. These data imply the presence of the equilibrium shown in eq 3 with forward and reverse

$$Cp_2Mo{=}O + [(CD_3CN)Rh(PPh_3)_2(CO)]^+ \xrightleftharpoons[CD_2Cl_2]{} [Cp_2Mo{=}O{-}Rh(PPh_3)_2(CO)]^+ + CD_3CN \quad (3)$$

reactions that are fast on the ^1H NMR time scale. The equilibrium constants at 298 K and the associated $\Delta H°$ and $\Delta S°$ values calculated from the temperature dependence of the ^1H NMR spectra are summarized in Table IV. An activation energy of $\Delta G^{\ddagger} \approx 9.0$ kcal/mol was calculated for the forward reaction of eq 3 at the coalescence temperature of −75 °C for both complexes **3** and **5**. Coalescence was not observed for complex **6**, due mainly to the shift in the equilibrium too far in the direction of **6** at low temperatures.

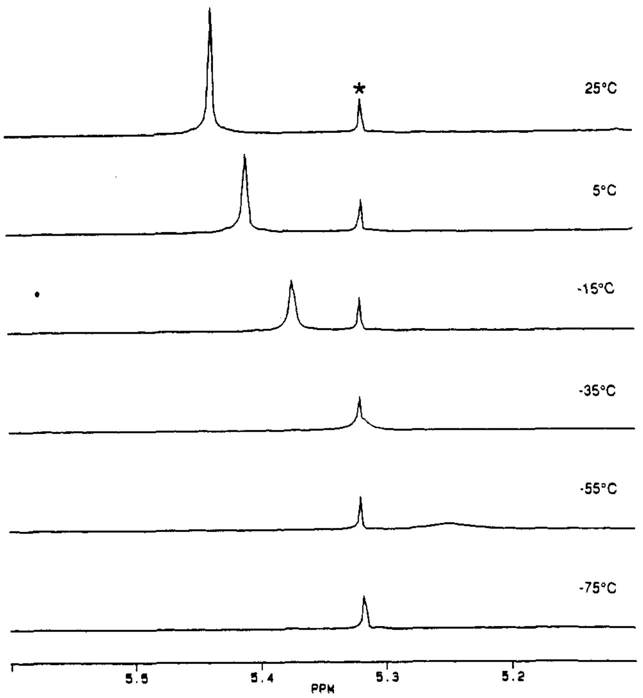

Figure 3. Variable-temperature ^1H NMR spectra of a CD_2Cl_2 solution of $[Cp_2Mo{=}O{-}Rh(CO)(PPh_3)_2]^+$ (**3**, 0.0135 M) and CD_3CN (2.55 M) showing the cyclopentadienyl proton region from δ 5.6 to 5.1. The resonance marked with the asterisk is due to CH_2Cl_2 impurity.

Concluding Remarks

The results reported herein show that the oxo complexes $Cp_2M{=}O$ are sufficiently strong nucleophiles to displace CH_3CN from Rh(I) and Ir(I) centers to form bimetallic μ-oxo complexes that possess weakly coordinated $Cp_2M{=}O$ ligands. The crystallographic data for **3**, the ^1H NMR exchange studies, and the IR analysis summarized above all imply that these complexes are best formulated as donor–acceptor complexes with little covalent character in the Rh—O and Ir—O bonds and with relatively little perturbation in the bonding of the oxo ligand to the Mo(IV) or W(IV) center. The molecules thus resemble the well-known adducts $[M(L)(PPh_3)_2(CO)]^+$ where L is acetonitrile, acetone, THF, and $Me_2S{=}O$,[7,8] although the equilibrium data for eq 3 indicate that the $Cp_2M{=}O$ moiety is a better ligand for the group 9 metal cations than is CH_3CN.

Experimental Section

The compounds $[Ir(PPh_3)_2(CO)(CH_3CN)][BF_4]$,[7] $[Rh(PPh_3)_2(CO)(CH_3CN)][BF_4]$,[8] and $Cp_2M{=}O$ (M = Mo, W)[5] were prepared according to the literature procedures. Solvents were dried by standard methods, and all reactions were conducted under a prepurified N_2 atmosphere by standard Schlenk techniques. All other chemicals were used as received. IR spectra were recorded on an IBM FTIR-32 spectrometer. Field-desorption (FD) mass spectra were obtained by G. Steinmetz and R. J. Hale at the Tennessee Eastman Co., Kingsport, TN. Elemental analyses were obtained from Schwarzkopf Microanalytical Laboratories, Woodside, NY.

Preparation of ^{17}O- and ^{18}O-Enriched $Cp_2W{=}O$. A solution of $Cp_2W{=}O$ (200 mg, 0.608 mmol) and 100 μL of 17% $H_2{}^{17}O$ (Cambridge Isotopes Inc.) was allowed to stir for 12 h. The solution was dried over $MgSO_4$ and filtered, and the solvent was removed under vacuum to leave ^{17}O-labeled $Cp_2W{=}O$ [^{17}O NMR (20% CD_2Cl_2/CH_2Cl_2): δ 775 (fwhm = 50 Hz)]. $Cp_2W{=}^{18}O$ was prepared in a similar manner using $Cp_2W{=}O$ (200 mg, 0.608 mmol) and 100 μL of 100% $H_2{}^{18}O$ (MSD Isotopes). All ^{17}O NMR and ^{18}O IR experiments were conducted with complexes prepared from these reagents.

Preparation of $[Cp_2Mo{=}O{-}Rh(PPh_3)_2(CO)][BF_4]$ (3). A solution of $Cp_2Mo{=}O$ (93 mg, 0.385 mmol) in CH_2Cl_2 (15 mL) was filtered through a pad of Celite and added to a CH_2Cl_2 (15 mL) solution of $[Rh(PPh_3)_2(CO)(CH_3CN)][BF_4]$ (200 mg, 0.255 mmol). The solution was allowed to stir for 15 min, the solvent was removed under vacuum, and the flask was exposed to air for 10 min to degrade any remaining

$Cp_2Mo{=}O$. The residue was dissolved in CH_2Cl_2 (25 mL), filtered through a pad of Celite, and the solvent was evaporated under vacuum. Recrystallization from CH_2Cl_2/pentane gave complex **3** as brown needles in 45% yield (133 mg, 0.115 mmol). IR (KBr): $\nu_{CO} = 1981\ cm^{-1}$; $\nu_{Mo-O-Rh} = 800\ cm^{-1}$, FD: m/z 913 ($M + F^+$), 894 (M^+). ^1H NMR (CD_2Cl_2): δ 7.9–6.8 (m, Ph, 30 H), 4.93 (s, Cp, 10 H). ^{31}P NMR (CD_2Cl_2): δ 29.7 (d, $J_{P-Rh} = 133$ Hz). Anal. Calcd for $C_{47}H_{40}BF_4MoO_2P_2Rh{\cdot}2CH_2Cl_2$: C, 51.03; H, 3.64. Found: C, 50.77; H, 3.92.

Preparation of $[Cp_2Mo{=}O{-}Ir(PPh_3)_2(CO)][BF_4]$ (4). Complex **4** was prepared as described above for complex **3** by using $Cp_2Mo{=}O$ (87 mg, 0.362 mmol) and $[Ir(PPh_3)_2(CO)(CH_3CN)][BF_4]$ (210 mg, 0.241 mmol) and was isolated as brown needles in 14% yield (42 mg, 0.034 mmol). IR (KBr): $\nu_{CO} = 1968\ cm^{-1}$; $\nu_{Mo-O-Ir} = 799\ cm^{-1}$. FDMS: m/z 986 (M^+). ^1H NMR (CD_2Cl_2): δ 7.9–7.3 (m, Ph, 30 H), 4.98 (s, Cp, 10 H). ^{31}P NMR (CD_2Cl_2): δ 27.8 (s). Anal. Calcd for $C_{47}H_{40}BF_4IrMoO_2P_2{\cdot}2CH_2Cl_2$: C, 47.31; H, 3.54. Found: C, 47.82; H, 3.36.

Preparation of $[Cp_2W{=}O{-}Rh(PPh_3)_2(CO)][BF_4]$ (5). Complex **5** was prepared as described above for complex **3** by using $Cp_2W{=}O$ (44 mg, 0.133 mmol) and $[Rh(PPh_3)_2(CO)(CH_3CN)][BF_4]$ (95 mg, 0.121 mmol) and was isolated as brown needles in 40% yield (61 mg, 0.049 mmol). IR (KBr): $\nu_{CO} = 1981\ cm^{-1}$; $\nu_{W-O-Rh} = 835\ cm^{-1}$. FDMS: 984 ($M^+$). ^1H NMR (CD_2Cl_2): δ 7.9–7.4 (m, Ph, 30 H), 5.14 (s, Cp, 10 H). ^{31}P NMR (CD_2Cl_2): δ 29.1 (d, $J_{P-Rh} = 132$ Hz). Anal. Calcd for $C_{47}H_{40}BF_4O_2P_2RhW{\cdot}2CH_2Cl_2$: C, 47.38; H, 3.54. Found: C, 47.16; H, 3.39.

Preparation of $[Cp_2W{=}O{-}Ir(PPh_3)_2(CO)][BF_4]$ (6). Complex **6** was prepared as described above for complex **3** by using $Cp_2W\Delta bdO$ (87 mg, 0.265 mmol) and $[Ir(PPh_3)_2(CO)(CH_3CN)][BF_4]$ (210 mg, 0.241 mmol) and was isolated as brown needles in 48% yield (154 mg, 0.116 mmol). IR (KBr): $\nu_{CO} = 1975\ cm^{-1}$; $\nu_{W-^{18}O-Ir} = 837\ cm^{-1}$; $\nu_{W-O-Ir} = 803\ cm^{-1}$. ^1H NMR (CD_2Cl_2): δ 7.9–7.4 (m, Ph, 30 H), 5.14 (s, Cp, 10 H). ^{31}P NMR (CD_2Cl_2): δ 27.8 (s). ^{17}O NMR (20% CD_2Cl_2/CH_2Cl_2): δ 504 (fwhm = 360 Hz). Anal. Calcd for $C_{47}H_{40}BF_4IrO_2P_2W{\cdot}2CH_2Cl_2C$, 44.28; H, 3.68. Found: C, 44.27; H, 3.18.

Variable-Temperature ^1H NMR Studies. All variable-temperature ^1H NMR studies were conducted on a Bruker AM 300 Fourier transform instrument using a Bruker BVT 1000 temperature controller that was standardized (±1 °C) by using both ethylene glycol and methanol as described in the Bruker user's manual AM series. For the exchange studies of complex **5** with excess $Cp_2W{=}O$, the complex (50 mg, 0.040 mmol) and $Cp_2W{=}O$ (**2**) (13.3 mg, 0.040 mmol) were dissolved in 0.6 mL of CD_2Cl_2 and the solution was filtered through a pad of Celite into a 5-mL NMR tube. Spectra were recorded every 10 °C from +45 to −75 °C. The second-order rate constant was calculated at 298 °C, in the fast-exchange region, by using $k = \pi(\Delta\nu)^2/2(W^* - W_0)[Cp_2W{=}O]$, where $\Delta\nu$ is the chemical shift difference between the resonances of **2** and **5** in the absence of exchange, W^* is the peak width at 298 °C during exchange, and W is the combined width of **2** and **5** in absence of exchange.[14] The crossover number was calculated at 298 °C by using crossover no. $= 2(\pi\Delta\nu^2/2(W^* - W_0)$ where $\Delta\nu$, W_0, and W^* are the same as for the k_2 calculation.

For the exchange studies of complex **3** with CD_3CN, the complex (9.3 mg, 0.0081 mmol) was placed in a 5-mL NMR tube to which was added CD_2Cl_2 (500 ± 1 μL) by a micropipet. To this tube was added by a micropipet 100 ± 1 μL of CD_3CN to give CD_3CN and **3** concentrations of 2.55 and 0.0135 M, respectively. Spectra were recorded every 10 °C from −75 to +35 °C. The equilibrium constants at various temperatures were calculated from the position of the resonance relative to those of pure **3** and pure $Cp_2Mo{=}O$ and from the initial concentrations of **3** and CD_3CN. Van't Hoff plots ($\ln K_{eq}$ vs $1/T$, slope $= \Delta H°/R$) gave $\Delta H°$ values. The $\Delta S°$ values were calculated from the relationship $\Delta G°_{298} = \Delta H° - (298)\Delta S°$ with $\Delta G°$ obtained from the value of K_{eq} at 298 K. All values are reported at 95% confidence limits. The values of ΔG^* for complexes **6** and **5** werr calculated from the equilibrium position at coalescence as described in the literature.[15]

Crystal and Molecular Structure of $[Cp_2Mo{=}O{-}Rh(PPh_3)_2(CO)]BF_4{\cdot}{}^1/_2(acetone){\cdot}{}^1/_2(pentane)$ (3). Crystallographic data are summarized in Table I. An orange-brown crystal of **3** grown from acetone/pentane was mounted on a glass fiber; photographic evidence and systematic absences in reflection data provided a unique space group assignment. The data were empirically corrected for absorption by a program that creates a tensor expression relating F_o and F_c (XABS, H. Hope) and corrected for a linear 18% decay in the intensity of the standard reflections (probably due to solvent loss). The structure was solved by direct methods, which yielded the positions of the metal and phosphorus atoms. The lattice also contains disordered molecules of acetone (C(71)–C(73), O(74)) and pentane (C(75)–C(79)) with high thermal parameters. Occupancy refinement for the atoms of both solvent molecules indicated a substoichiometric presence of approximately 0.5; the occupancy was thereafter fixed at 0.5. All non-hydrogen atoms, except for those contained in the solvent molecules, were refined anisotropically. Hydrogen atoms were treated as idealized contributions. The phenyl rings were constrained to rigid, planar hexagons, and the BF_4^- was fixed to a rigid tetrahedral structure. All computations and sources of scattering factors are contained in the SHELXTL program library (G. Sheldrick, Nicolet XRD, Madison, WI). Atomic coordinates are given in Table II, and selected bond distances and angles are listed in Table III.

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Supplementary Material Available: Tables of anisotropic thermal parameters, complete bond lengths and angles, calculated hydrogen atom positions, and crystal data (6 pages); a listing of structure factors (30 pages). Ordering information is given on any current masthead page.

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