we calculate for $WONp_3Cl$ (**2**), but in **1**, the oxo group is trans to a ligand with a larger "trans effect" than it is in **2**. Therefore the W=O bond length is expected to be shorter in **2** and the force constant, as we find, larger. In the rhenium systems the interaction constant is small and positive.[4c] The difference in the sign of the constant in the W and Re systems is responsible for the finding that in the W system the Raman band is lower in energy than the infrared band; in the rhenium systems the opposite is true. The differences between the two systems are the coordination number and the number of valence electrons, but whether either of these differences is responsible for the change in sign of this interaction constant is not clear.

Equation 4 may be used to calculate the difference in force constants of the bridging oxygen stretches. This difference was calculated for both **1** and [^{18}O]**1**. The average of these two values was used to calculate the position of these asymmetric stretches. These results are shown in Table V. Reasonable agreement between calculated and observed values was obtained by using an average difference in the force constants ($k_R - k_{RR}$) = 2.2 mdyn/Å. Again, the difference compares well with those found for the rhenium systems, which range from 2.13 to 2.47 mdyn/Å.[4c] Equation 3, however, cannot be used to calculate the sum of these constants, and, therefore, their individual values until the symmetric stretch is assigned to a Raman band. As noted above, this band is not expected to shift upon isotopic substitution and is therefore less easy to identify. In the region of the Raman spectrum where a band ascribable to that stretch might be expected are four peaks (at 141, 205, 241, and 271 cm^{-1}) that do not shift upon isotopic substitution. There is no definitive way to choose among these possibilities with the data at hand. All of the force constants and sums and differences of force constants we have calculated for **1**, however, fall in the range of force constants and combinations thereof calculated for the rhenium systems. If force constants are calculated by assuming each of the peaks mentioned above is the symmetric M–O–M stretch, only those using the 205 cm^{-1} value fall into the ranges for analogous force constants in the linear Re_2O_3 complexes. The value calculated for k_R (3.38 mdyn/Å) falls in the range 3.25–3.73 mdyn/Å, while the value calculated for k_{RR} (1.17 mdyn/Å) falls in the range 1.04–1.29 mdyn/Å. We therefore tentatively assign the band at 205 cm^{-1} to the symmetric stretch of the bridging oxygen and accept the values of the force constants calculated above.

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Registry No. 1, 87615-70-1; [^{18}O]**1**, 91841-53-1; **2**, 75846-05-8; [^{18}O]**2**, 91798-61-7; $W(CCMe_3)Np_3$, 68490-69-7; Me_3SiCl, 75-77-4.

Supplementary Material Available: Tables S1 and S2, listings of observed and calculated structure factors and anisotropic thermal parameters (7 pages). Ordering information is given on any current masthead page.

Synthesis, Characterization, and Equilibrium Studies of Group 6B Intramolecular Metalloesters: Crystal Structure of *trans*-(η^5-C_5H_4)$CH_2CH_2O_2CW(CO)_2PPh_3$

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Contribution No. 6984 from the Laboratories of Chemistry, California Institute of Technology, Pasadena, California 91125. Received February 27, 1984

Abstract: Treatment of [(η^5-$C_5H_4CH_2CH_2OH$)$M(CO)_3PR_3$]$^+BF_4^-$ (**1a–d**, M = Mo, W; R = Ph, *p*-tolyl) with base affords solely the neutral intramolecular metalloester, *trans*-(η^5-C_5H_4)$CH_2CH_2O_2CM(CO)_2PR_3$ (**2**). The X-ray structure of **2b** (M = W; R = Ph) (space group $P2_1/n$, a = 8.127 Å, b = 16.823 Å, c = 17.623 Å, β = 101.980°, V = 2357 (1) Å^3, Z = 4) was solved by heavy-atom and Fourier methods and refined by full-matrix least squares to S (goodness-of-fit) = 1.27 and R = 0.043 (5728 reflections). The structural results indicate that there is little or no strain upon coordination of the Cp and ester groups when coupled with the ethylene bridge. Equilibrium studies indicate that $\Delta H°$ and $\Delta S°$ are −1.1 ± 0.6 kcal/mol and 3.2 ± 2.0 eu and −1.9 ± 0.2 kcal/mol and 4.5 ± 0.6 eu for **2c** (M = Mo; R = *p*-tolyl) and **2d** (M = W; R = *p*-tolyl), respectively, for the reaction with MeOH in benzene to form the methyl ester and regenerate the alcohol-substituted Cp. Treatment of the analogous compound (**1g**), in which the alcohol is connected to the Cp by CH_2, with methoxide yields an intramolecular metalloester (**3**) as well. Equilibrium data indicate that the intramolecular metalloester is more stable than the methyl ester, $K_{eq} \leq 3$ M^{-1}. The contrasting compounds with the $(CH_2)_3$ bridge (**1e** and **1f**) yield only the intermolecular methyl esters (**5e** and **5f**). The equilibrium constants are estimated to be ≥230 M^{-1} (**5e**) and ≥117 M^{-1} (**5f**).

New modes of activating small molecules by homogeneous systems have been a major theme in organometallic chemistry. Carbon monoxide has been the target of most recent interest due to scientific and economic developments. The work to be described involves the design of a bifunctional catalyst to accomplish this goal. Scheme I shows a plausible mechanism whereby carbon monoxide and hydrogen may react in the presence of a transition-metal complex and an external nucleophile to give organic products.[2]

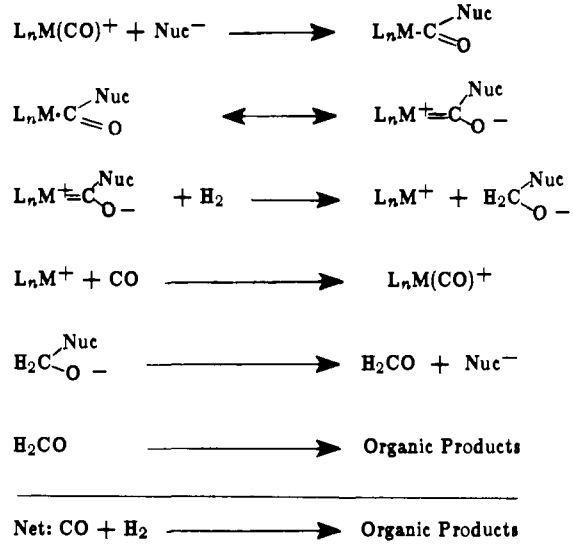
The overall thermodynamics should in all probability be favorable (e.g., for the formation of methanol, $\Delta G_f°$ = −6.0 kcal/mol), and even the unfavorable formation of formaldehyde

(1) Myron A. Bantrell Fellow in chemistry, 1981–1983.

(2) Doxsee, K. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1981**, *103*, 7696.

0002-7863/84/1506-6310$01.50/0

Scheme I

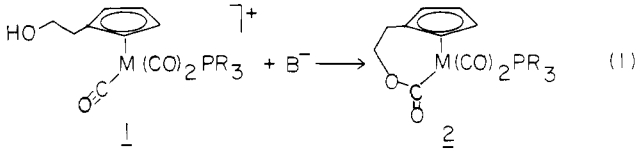


(ΔG_f° = +6.5 kcal/mol) may be mediated to some extent by coordination to the transition-metal center and serve as an intermediate to other products.[3]

To promote attack by the nucleophile at bound carbon monoxide and to enhance the possibility of achieving a catalytic system, we are exploring bifunctional catalysts in which the nucleophile has been incorporated into the transition-metal complex, i.e., as an intramolecular nucleophile. We report herein a complex which allows for the evaluation of the structural features which must be considered in the design of such a system.

Results and Discussion

Compounds of the form $[(CPR')M(CO)_3PR_3]^+BF_4^-$ (R′ ≡ $(CH_2)_nOH$) were synthesized in order to promote and observe intramolecular nucleophilic interaction with bound carbon monoxide. It was believed that the positive charge on the metal center would induce this interaction since the IR stretching frequencies for the carbonyls are in the range of those reported to undergo reaction with amines to give carbamoyl complexes.[4] Yet, aside from intramolecular hydrogen bonding between the alcohol and the $M(CO)_3PR_3$ fragment, no such interaction occurs.[5] However, the cationic complex (**1**) is cleanly converted to the intramolecular metalloester (**2**) by deprotonation of the alcohol with an external base (eq 1).[6]



(1)

1 & 2: a, M=Mo, R=Ph
b, M=W, R=Ph
c, M=Mo, R=p-tolyl
d, M=W, R=p-tolyl

Comparison of the IR, ^1H, and ^{31}P NMR data indicates that the metalloesters (**2**) are analogous to the products formed by methoxide attack on the parent cations (**4**) (Tables I and II). One major difference is the apparent formation of only one isomer as indicated by ^{31}P and ^1H NMR. The proton NMR (Figure 1) and

(3) Stull, D. R.; Westrum, E. F.; Sinke, G. C. "The Chemical Thermodynamics of Organic Chemistry"; Wiley-Interscience: New York, 1969.
(4) Angelici, R. J. *Acc. Chem. Res.* **1972**, *5*, 335.
(5) As evidenced by a dilution study of the IR spectrum in the OH region.
(6) Other intramolecular metalloesters have been synthesized but without the use of a Cp ligand as the means for anchoring the oxygen nucleophile prior to ester formation. See, for example: (a) Heck, R. F.; Boss, C. R. *J. Am. Chem. Soc.* **1964**, *86*, 2580. (b) Murdoch, H. D. *Helv. Chim. Acta* **1947**, *47*, 936. (c) Klemarczyk, P.; Price, T.; Priester, W.; Rosenblum, M. *J. Organomet. Chem.* **1977**, *139*, C25.

Table I. IR Stretching Frequencies[a]

M	R	ν(CO), cm^{-1}	ν(C=O), cm^{-1}
	$(\eta^5\text{-}C_5H_4)CH_2CH_2O_2CM(CO)_2PR_3$		
Mo (**2a**)	Ph	1970 (s), 1881 (vs)	1613 (m)
W (**2b**)	Ph	1961 (s), 1868 (vs)	1610 (m)
Mo (**2c**)	*p*-tolyl	1968 (s), 1876 (vs)	1610 (m)
W (**2d**)	*p*-tolyl	1961 (s), 1870 (vs)	1610 (m)
	$(\eta^5\text{-}C_5H_4)CH_2O_2CM(CO)_2PR_3$		
W (**3**)	Ph	1957 (s), 1882 (s)	1598 (m)
	$(\eta^5\text{-}C_5H_5)M(CO)_2PPh_3(CO_2Me)$[b]		
Mo (**4a**)		1960 (s), 1875 (vs)	1610 (m)
W (**4b**)		1950 (s), 1863 (vs)	1608 (m)

[a] CH_2Cl_2 solution. [b] A mixture of the cis and trans compounds.

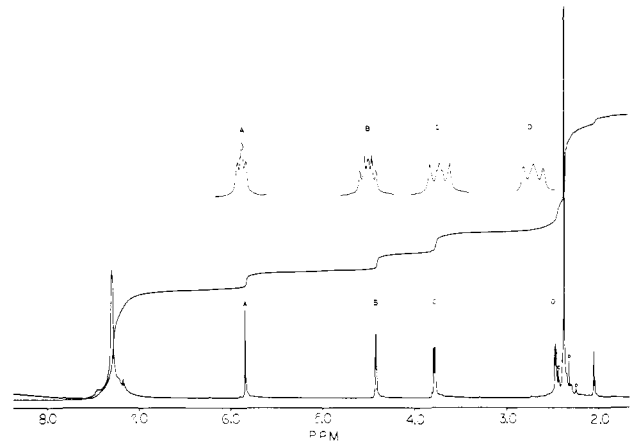


Figure 1. ^1H NMR spectrum (500 MHz) of **2d**. Signals marked with small circles are spinning sidebands.

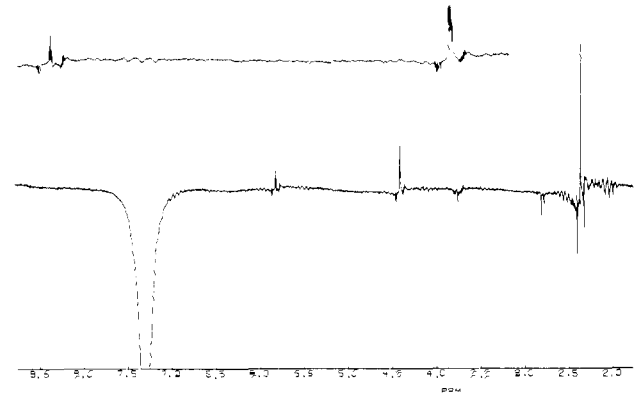


Figure 2. Difference NOE (500 MHz) spectrum of **2d** upon irradiation of ortho *p*-tolyl protons. The upper part of the figure is an expansion of the region from approximately 4.0 to 6.0 ppm.

the fact that the asymmetric carbonyl stretch is more intense than the symmetric stretch in the IR indicates that the single isomer formed is the trans;[7] the chemical shifts and ^{183}W–^{31}P coupling constants are consistent with this (Table II).

Of particular interest with regard to the trans configuration of the ester and phosphine ligands is the complexity of the ^1H NMR signal at 4.30–4.42 ppm in **2** which appears to be a doublet of triplets (although not true binomial triplets). The signal at 5.46–5.84 ppm appears simply as a pseudotriplet. These signals are due to the two pairs of protons on the substituted Cp ring. In a trans arrangement and with a tethered Cp ring, one pair will reside at a much closer proximity to the aryl rings of the phosphine than the other and as such will display an NMR signal shifted upfield, much in the manner of the ligand protons of an iron complex that has been reported.[8]

(7) Craig, P. J.; Edwards, J. *J. Less-Common Met.* **1974**, *36*, 193.
(8) Treichel, P. M.; Shubkin, R. L. *Inorg. Chem.* **1967**, *6*, 1328.

Table II. ^1H and ^{31}P NMR Data[a]

M	R	^1H[b] C_5H_4R (H2 and H5)	^1H[b] C_5H_4R (H_3 and H_4)	^1H[b] CH_2O	^1H[b] $CpCH_2$	^{31}P[c]
			$(\eta^5\text{-}C_5H_4)CH_2CH_2O_2CM(CO)_2PR_3$			
Mo (**2a**)	Ph[d]	5.46	4.30 (J = 3.4)	3.88	2.40	71.07 (s)
W (**2b**)	Ph[d]	5.59	4.35 (J = 3.4)	3.86	2.43	39.98 (J = 212.4)[e]
Mo (**2c**)	*p*-tolyl	5.67	4.37 (J = 3.2)	3.78	2.37	71.61 (s)
W (**2d**)	*p*-tolyl	5.84	4.42 (J = 3.7)	3.77	2.47	40.04 (J = 217.3)[e]
			$(\eta^5\text{-}C_5H_4)CH_2O_2CM(CO)_2PR_3$			
W (**3**)	Ph	6.26	4.41 (J = 3.5)	4.12		37.29 (J = 200.2)[e]

		^1H[b] Cp	^1H[b] CH_3	^{13}P[c]
Mo (**4a**)	cis	5.34 (s)	2.57 (s)	64.55 (s)
	trans	5.15 (d, J = 1.2)	3.48 (s)	73.36 (s)
W (**4b**)	cis	5.47 (s)	2.51 (s)	35.54 (J = 271.0)[e]
	trans	5.25 (d, J = 1.2)	3.45 (s)	42.94 (J = 234.4)[e]

[a] $(CD_3)_2CO$ solution. [b] Chemical shifts in ppm (δ), residual protons of acetone-d_6 used as reference (2.04 ppm). Coupling constants are in Hz. Unless otherwise noted, coupling patterns indicate an AA'BB' system, the coupling constants reported for the Cp protons are attributed to the ^{31}P nucleus. [c] Chemical shifts are in ppm relative to free phosphine under the same conditions. [d] $CDCl_3$ solution. [e] The signal is present as a singlet along with a small doublet due to coupling to the 14% abundance of the ^{183}W nucleus.

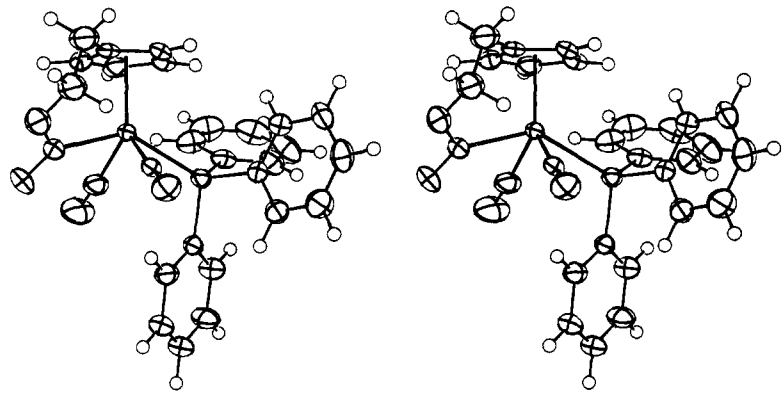


Figure 3. Stereoview of the ORTEP diagram of **2b**. Nonhydrogen atoms are represented by their 50% probability ellipsoids.

A difference Nuclear Overhauser Effect (NOE) experiment performed on **2d** is shown in Figure 2. The 4.42-ppm ^1H NMR signal is due to Cp protons situated in close proximity to the phosphine ligand since an enhancement approximately four times greater than that for the 5.84-ppm signal is observed upon irradiation of the ortho protons of the tolyl phosphine. This suggests that the additional splitting of the signal is due to coupling with the ^{31}P nucleus. The coupling of more than 3 Hz is quite large in comparison to the couplings normally observed for *trans*-$CpM(CO)_2LX$ compounds (1.0–1.5 Hz). (See Figure 4 for numbering.) This is presumably because rotation does not occur about the M–Cp axis, and as such the interaction between the ^{31}P and ^1H nuclei is greater for H_6 and H_7. Accordingly, the interaction between the phosphorus and H_8 and H_5 nuclei is small and no coupling is observed. This appears to be evidence for through-space coupling of the ^1H and ^{31}P nuclei, since through-bond coupling does not explain the difference in the Cp protons. The ^1H NMR spectrum in which H_6 and H_7 were decoupled from H_8 and H_5 displays only a doublet for the signal (J = 3.7 Hz) while the decoupled H_8 and H_5 signal is a singlet. Thus the additional coupling does not arise from the ring protons and is most probably due to P–H coupling. Further support is obtained from the ^{31}P NMR spectrum in which the aryl protons have been selectively decoupled; the ^{31}P signal shape is consistent with two somewhat broad signals separated by approximately 3.5 Hz. The through-space mechanism has been proposed by some[9] and disputed by others[10] as an explanation of the doublet Cp ^1H NMR signal in *trans*-$CpM(CO)_2LX$ compounds.

(9) George, T. A.; Turnipseed, C. D. *Inorg. Chem.* **1973**, *12*, 394.
(10) Kennedy, J. D.; McFarlane, W.; Rycroft, D. S. *Inorg. Chem.* **1973**, *12*, 2742.

Table III. Summary of Data Collection and Refinement Parameters

formula	$C_{28}H_{23}O_4PW$	
formula wt	638.32	
space group	$P2_1/n$	
a, Å	8.1273 (17)	
b, Å	16.823 (5)	
c, Å	17.623 (3)	
β, deg	101.980 (16)	
V, Å^3	2357.1 (10)	
Z	4	
D_{calcd}, g/cm^3	1.799	
crystal size, mm	0.062 × 0.266 × 0.628	
λ, Å	0.71073	
μ, mm^{-1}	5.10	
2θ limits, deg	4–36	35–56
scan rate, deg/min	4.88	2.02
bkgrd-to-scan time ratio	1.0	0.5
scan width, deg	1.1	1.2 above K_{α_2}
	1.1	1.2 below K_{α_1}
no. of reflections	3657	9066
total no. of av data	5728	
final agreement[a]		
R_F	0.043 (5335)	
R'_F	0.027 (4085)	
S	1.27 (5728)	

[a] Defined in footnote 34; number of reflections given in parentheses.

Isolation of **2b** as a crystalline product has permitted an X-ray structure determination; Table III summarizes details of the data collection and refinement, and Table IV lists atom coordinates. The trans configuration of the metalloester (Figure 3) confirms the spectroscopic assignments. The trans configuration is presumably due to unfavorable steric interactions in the cis isomer since in this isomer the arm bridging the Cp and carbonyl is in

Table IV. Atom Coordinates ($\times 10^4$) and U_{eq}'s (Å^2, $\times 10^4$)

	x	*y*	*z*	U_{eq}
W	2845.2 (2)	1740.4 (1)	973.9 (1)	316
P	1804.3 (13)	2923.5 (7)	1591.7 (5)	314
C(1)	5278 (5)	1121 (4)	996 (3)	509
O(1)	6568 (4)	1414 (3)	885 (3)	783
C(2)	4196 (6)	−148 (3)	1376 (3)	576
O(2)	5432 (4)	306 (3)	1119 (2)	635
C(3)	2592 (6)	−247 (3)	761 (3)	571
C(4)	1779 (5)	521 (3)	482 (2)	389
C(5)	459 (5)	919 (3)	751 (2)	374
C(6)	33 (5)	1608 (3)	304 (2)	406
C(7)	1062 (6)	1649 (3)	−255 (2)	451
C(8)	2151 (5)	993 (3)	−148 (2)	468
C(9)	4306 (6)	2600 (3)	705 (2)	520
O(9)	5076 (6)	3085 (3)	498 (2)	842
C(10)	3658 (5)	1539 (3)	2078 (2)	349
O(10)	4126 (4)	1382 (2)	2733 (2)	540
C(11)	3400 (5)	3660 (3)	2008 (2)	334
C(12)	5000 (5)	3412 (3)	2397 (2)	414
C(13)	6213 (5)	3965 (3)	2719 (3)	447
C(14)	5867 (6)	4772 (3)	2640 (3)	492
C(15)	4304 (6)	5023 (3)	2246 (3)	526
C(16)	3082 (6)	4469 (3)	1941 (2)	438
C(21)	805 (5)	2654 (3)	2402 (2)	327
C(22)	−701 (5)	2243 (3)	2234 (2)	388
C(23)	−1451 (6)	1975 (3)	2828 (3)	453
C(24)	−687 (7)	2107 (3)	3585 (3)	534
C(25)	804 (7)	2518 (4)	3758 (3)	586
C(26)	1563 (6)	2785 (3)	3171 (2)	440
C(31)	179 (5)	3535 (3)	974 (2)	387
C(32)	178 (7)	3612 (3)	190 (3)	504
C(33)	−1016 (8)	4074 (4)	−284 (3)	644
C(34)	−2202 (7)	4461 (4)	23 (3)	668
C(35)	−2215 (7)	4411 (3)	804 (3)	628
C(36)	−1017 (6)	3938 (3)	1277 (3)	485

Table V. Bond Lengths and Angles

bonds	Å	angles	deg
W–P	2.495 (3)	P–W–C(1)	138.5 (4)
W–C(1)	2.233 (15)	R–W–P	115.9 (1)
C(1)–O(1)	1.227 (19)	R–W–C(1)	105.6 (4)
C(2)–O(2)	1.405 (20)	W–C(1)–O(1)	126.2 (11)
C(1)–O(2)	1.390 (18)	O(1)–C(1)–O(2)	111.9 (13)
C(2)–C(3)	1.552 (23)	W–C(1)–O(2)	121.8 (10)
C(3)–C(4)	1.486 (21)	C(1)–O(2)–C(2)	121.4 (12)
C(4)–C(5)	1.441 (19)	O(2)–C(2)–C(3)	112.8 (13)
C(5)–C(6)	1.449 (19)	C(3)–C(4)–C(5)	126.5 (12)
C(6)–C(7)	1.433 (20)	C(3)–C(4)–C(8)	123.2 (12)
C(7)C(8)	1.498 (19)	C(4)–C(5)–C(6)	107.1 (11)
C(4)–C(8)	1.419 (18)	C(8)–C(4)–C(5)	110.2 (11)
W–C(9)	1.943 (14)	C(7)–C(8)–C(4)	106.7 (11)
W–C(10)	1.964 (17)	R–W–C(9)	126.7 (4)
C(9)–O(9)	1.180 (19)	R–W–C(10)	127.9 (5)
C(10)–O(10)	1.186 (20)	C(9)–W–C(10)	105.6 (2)
P–C(11)	1.837 (13)	W–C(9)–O(9)	175.5 (13)
P–C(21)	1.837 (13)	W–C(10)–O(10)	172.7 (14)
P–C(31)	1.853 (14)	W–P–C(11)	116.2 (4)
W–R[a]	2.013 (1)	W–P–C(21)	112.7 (4)
W–C(4)	2.328 (13)	W–P–C(31)	117.6 (4)
W–C(5)	2.385 (13)	W–R–C(4)	88.7 (6)
W–C(6)	2.371 (14)	W–R–C(5)	91.4 (6)
W–C(7)	2.381 (14)	W–R–C(6)	90.7 (7)
W–C(8)	2.339 (12)	W–R–C(7)	90.9 (7)
		W–R–C(8)	88.5 (6)

[a] R ≡ ring centroid of the Cp ring.

too close a proximity to the relatively bulky phosphine ligand. In the less bulky parent methyl ester complexes (**3**) the trans isomer predominates over the cis in solution by approximately 60:40. This predominance is significant when it is considered that there are two possible carbonyls that will yield a cis isomer upon methoxide attack.

A number of relevant bond lengths and angles are given in Table V. The ester moiety is normal, with C—O bond lenghts of 1.39 (2) and 1.41 (2) Å (C(1)—O(2), C(2)—O(2)) and a C=O bond length of 1.23 (2) Å (C(1)—O(1)). Whereas the ester carbonyl stretch is at a slightly lower than normal energy (1610 vs. 1750 cm^{-1}) the C(1)–O(1) bond length does not reflect this change, indicating that the contribution from the carbenoid resonance is not predominant.

Table VI. Best Least-Squares Plane and Torsion Angles

atom	dev[a]	atoms	angle, deg
C(4)	0.006	C(4)–C(3)–C(2)–O(2)	−60.6 (17)
C(5)	−0.014	C(5)–C(4)–C(3)–C(2)	−96.6 (17)
C(6)	0.017	C(8)–C(4)–C(3)–C(2)	89.6 (16)
C(7)	−0.013	C(3)–C(2)–O(2)–C(1)	72.8 (17)
C(8)	0.004	C(2)–O(2)–C(1)–W	−12.4 (18)
W	2.013	C(2)–O(2)–C(1)–O(1)	169.5 (13)
C(3)	−0.089	R–W–C(1)–O(1)	126.6 (13)
C(2)	1.316	R–W–C(1)–O(2)	−51.2 (12)

[a] Deviation in Å from the best Cp plane (C(4) through C(8)).

Table VII. Thermodynamic Parameters for Intra- to Intermolecular Equilibration

M	R	*n*	K_{eq},[a] M^{-1}	$\Delta G°$, kcal	$\Delta H°$, kcal	$\Delta S°$, eu
W	Ph	1	≤4.0	≥−0.7		
Mo	*p*-tolyl	2	32	−2.1	−1.1	3.2
W	*p*-tolyl	2	42	−2.2	−0.9	4.5
Mo	Ph	3	≥230	≤−3.2		
W	Ph	3	≥117	≤−2.8		
			With EtOH			
W	*p*-tolyl	2	91	−2.7	−4.4	−5.8

[a] 25 °C.

Comparison of the W—CO bond lengths (1.94 (1) and 1.96 (2) Å for W—C(9) and W—C(10), C≡O bond lengths (1.18 (2) and 1.19 (2) Å), and W—C—O angles (175.5 (13) and 172.7 (14)°) to other CpW compounds containing terminal carbonyls indicates that they are normal.[11,12,13] The average distance from the W atom to the Cp ring carbons (2.361 Å) is quite similar to other reported values (2.366[12] and 2.336 Å[13]) as is the W—R (R ≡ Cp centroid) distance (2.013 (1) Å) to another reported value (2.04 (1) Å).[11] Additionally, the angles between the ligands trans to one another in the piano stool "legs" (105.6 (2)° for C(9)–W–C(10) and 138.5 (4)° for C(1)–W–P) are reasonably similar to those reported for two four-legged Mo(II) complexes: (a) for $CpMo(CO)_2PPh_3(C(O)CH_3)$, C–Mo–P is 132.7 (4)° and OC–Mo–CO is 107.9 (5)°,[14] (b) for $CpMo(CO)_2(GePh_3)(=C(OEt)Ph)$, Ge–Mo–C is 131.8 (3)° and OC–Mo–CO is 105.1 (5)°.[15]

The slightly enlarged C(1)–W–P angle of 138.5° in **2b** may indicate a small distortion due to the constraints imposed by the $(CH_2)_2$ bridging arm. Upon consideration of the bridging arm itself, no unusual bond lengths or angles are noted (Table V) implying little or no strain upon coordination of the ester to W. The torsion angle about C(2)–C(3) of 60.6° (Table VI) is unremarkable when compared to the corresponding value observed in other structures containing analogous C–C–O fragments.[16] Moreover, the Cp plane is roughly perpendicular to the W–R vector (deviation 1°), not unlike the coordination of Cp to other tungsten complexes.[11-13,17] The individual deviation of atoms from the best least-squares plane (Table VI) is quite small, and the

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(13) Conway, A. J.; Gainsford, G. J.; Schrieke, R. R.; Smith, J. D. *J. Chem. Soc., Dalton Trans.* **1975**, 2499.
(14) Churchill, M. R.; Fennessey, J. P. *Inorg. Chem.* **1968**, *7*, 953.
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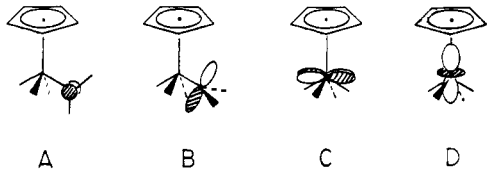
(16) (a) Villa, A. C.; Coghi, L.; Manfredotti, A. G.; Guastini, C. *Cryst. Struct. Commun.* **1974**, *3*, 543. (b) Mikuriya, M.; Torihara, N.; Okawa, H.; Kida, A. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1063. (c) Rêmy, G.; Cottier, L.; Descotes, G.; Faure, R.; Loiseleur, H.; Thomas-David, G. *Acta Crystallogr. Sect. B* **1980**, *B36*, 873.

displacement of C(3) from this plane is not large (0.09 Å), indicating minimal strain at C(4). As such, the ethylene bridge appears to be a reasonable length for linking the ester group and the Cp.

The W–R–C angles (Table V) indicate that the Cp plane is tipped away slightly from the phosphine and toward the ester group. The extent and direction imply that it is probably associated with the bridging arm more than the phosphine since it appears that the Cp is pulled down and twisted about the C(3)–C(4) axis simultaneously by the bridging arm, albeit to a small degree.

The nonbonding distances of the ortho phenyl protons to the H_8 and H_5 and H_6 and H_7 pairs can be calculated and an estimate of the NOE enhancement upon irradiation of the phenyl protons can be made, giving an enhancement ratio of 3 to 1 for the H_6 and H_7 pair over H_8 and H_5. This is in good agreement with experiment (vide supra). In a similar manner, calculation of the average distance between the phosphorus atom and the Cp proton pairs leads to a through-space coupling ratio of 2:1 for the H_6 and H_7 pair over H_8 and H_5.[18] Thus, while the coupling between phosphorus and H_8 and H_5 is expected to occur, it may simply be present at a value below the resolution of the NMR instrument (the calculated coupling constant based on these nonbonding distances is ≤1.5 Hz). The shape of the ^1H NMR signal arising from the H_8 and H_5 pair does not preclude such an explanation since it could quite easily be an unresolved doublet of pseudo-triplets. Regardless, the compound provides an opportunity to examine the putative through-space coupling mechanism. The tethering of the Cp ligand, however, thwarts to some extent an explanation of the difference in J_{HP} between the *cis*- and *trans*-$CpM(CO)_2LX$ compounds since an explanation has been proposed that the difference lies in the tipping of the Cp upon steric interaction between the phosphine and cis or trans X ligands.[19] As discussed above, the overriding factor involved in the configuration of the Cp in **2b** is most probably the orientational requirement of the ethylene bridge.

Also of interest is the orientation of the CO_2R fragment about the W–C(1) bond axis. Calculations indicate that for $CpM(CO)_2LL'$ complexes, where L' is a π donor or acceptor, orientation A is preferred.[20] Orientation B has been calculated to be 15 kcal higher in energy than A in the case of $[CpMo(CO)_2PH_3(=CH_2)]^+$.[20] This can be rationalized upon consideration of the overlap between the available orbitals on the transition-metal center, the d_{xy} and d_{z^2} (C and D), and the p orbital on the ligand; it is better in orientation A with use of d_{xy} orbital. Crystallographic data support the calculations. For example, the acyl complex, $CpMo(CO)_2PPh_3(C(O)Me)$, has a torsion angle for R–Mo–C–Me of approximately 180°[14] as does the neutral carbene complex, $CpMo(CO)_2(GePh_3)(=C(OEt)Ph)$, for R–Mo–C–Ph (where R is the Cp centroid in both cases).[15]



Due to the similarity between the above acyl complex and the metalloester, **2b**, a torsion of 180° for R–W–C(1)–O(1) would be expected to be the preferred geometry. However, as seen in Figure 5 and given in Table VI, the torsion angle is 126.6°, roughly halfway between the 180° conformation and the higher energy 90° conformation. Presumably the determining factor for this is again the orientational requirement of the ethylene bridge since the 180° orientation is unlikely with the arm length involved.

(17) Sieber, W.; Wolfgruber, M.; Neugebauer, D.; Orama, O.; Kreissl, F. R. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **1983**, *38B*, 67.
(18) NOE enhancement falls off as $1/r^6$, whereas through-space coupling decreases as $1/r^3$.
(19) Barnett, K. W.; Beach, D. L.; Gaydos, S. P.; Pollman, T. G. *J. Organomet. Chem.* **1974**, *69*, 121.
(20) Kubáček, P.; Hoffmann, R.; Havlas, Z. *Organometallics* **1982**, *1*, 180.

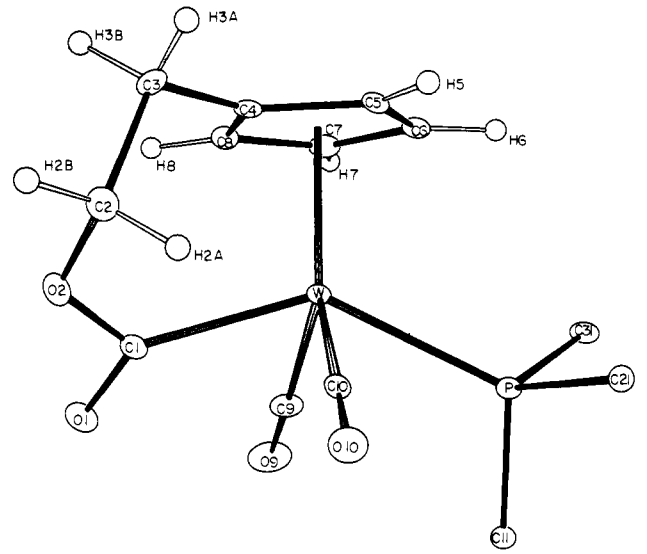
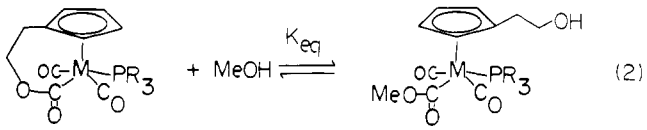


Figure 4. Atom-labeling scheme for the structure of **2b**. Part of the phosphine ligand has been omitted for clarity.

The fact that treatment of **1a–d** with base yields solely the intramolecular esters **2a–d** and none of the intermolecular ester **5** implies that intramolecularity does impart additional drive to the nucleophilic attack at bound CO. In an effort to quantify the effect and to further understand the requirements for catalyst design, equilibrium studies (at ca. 100 mM of **2**) were carried out in which the process shown in eq 2 was examined.



(2)

2 5

Upon reaction of **2c** and **2d** (**2a** and **2b** had insufficient solubility) with methanol in acetone at 25 °C, formation of **5** could be followed by ^1H and ^{31}P NMR since the signals associated with the cis and trans methyl esters obtained appear at shifts quite similar to those of the parent methyl esters. The equilibrium constants obtained are 1.65 ± 0.30 M^{-1} and 1.27 ± 0.15 M^{-1} for **2c** and **2d**, respectively. However, measurements of $\Delta H°$ and $\Delta S°$ in acetone and THF indicate the probable existence of substantial solvent effects. Therefore, equilibrium measurements were obtained in benzene-d_6 in the hope of circumventing any major solvent participation. Figure 6 shows the Van't Hoff plot obtained for the process shown in eq 2, where M is tungsten and R is *p*-tolyl (**2d**). A similar plot is obtained for the molybdenum compound (**2c**). The values found for $\Delta H°$ and $\Delta S°$ are −0.9 ± 0.2 kcal/mol and 4.5 ± 0.6 eu for W and −1.1 ± 0.6 kcal/mol and 3.2 ± 2.0 eu for Mo. These correspond to $\Delta G°$ values of −2.2 ± 0.4 and −2.1 ± 1.2 kcal/mol. Thus, it appears that in the absence of other effects, the process is favored slightly both entropically and enthalpically although both terms are admittedly small.

While it would seem that the entropy should decrease for the process as shown, the entropy gain upon dissociation of the intramolecular arm is apparently sufficiently high to balance the entropy loss associated with the binding of the external alcohol. An additional factor is the clustering of the methanol that is expected to occur in the solvent systems used. As such the entropy of the free methanol may not be as great as would normally be encountered in more polar solvents. The change in enthalpy may be involved with an orientation change of the ester group upon loss of tethering. Presumably the methyl ester is able to attain a more favorable configuration with greater bond overlap than is feasible with the intramolecular ester. This is in general agreement with calculations of analogous systems (vide supra).

As a further study, the tungsten complex was equilibrated with ethanol at various temperatures. The resulting $\Delta H°$ and $\Delta S°$

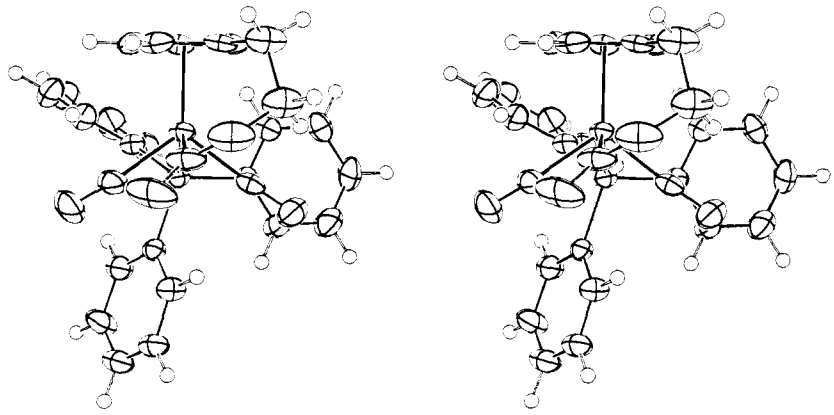


Figure 5. Stereoview of the ORTEP diagram of **2b** looking along C(1)–W–P.

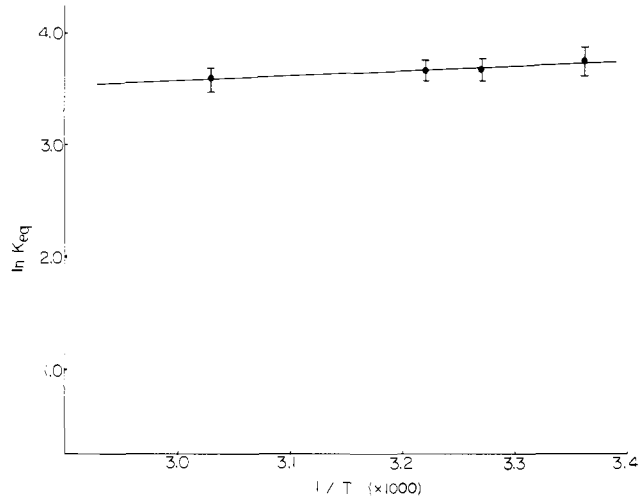


Figure 6. van t'Hoff plot for **2** + MeOH ⇌ **5** with M = W and R = *p*-tolyl in C_6D_6.

values are −4.4 ± 1.3 kcal/mol and −5.8 ± 4.2 eu. The more negative $\Delta H°$ is better determined and may be due to the possibility that the more bulky ethyl group favors the preferred vertical ester orientation to a slightly greater extent than the methyl ester. Nevertheless, the similarity in the thermodynamics implies that there is relatively little difference between the reactions of the two alcohols with the intramolecular ester.

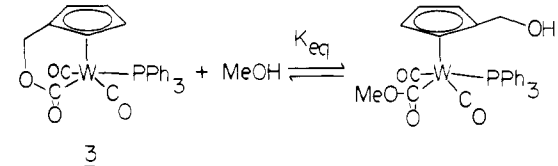
To further explore the requirements of intramolecular activation of CO, cationic complexes in which OH was bound to the Cp by a trimethylene bridge were synthesized (**1e** and **1f**). Treatment of these propanol compounds with methoxide affords only the methyl esters (**5**) unlike the ethanol complexes (see eq 1). Limiting values of the equilibrium constants for the process shown in eq 2 have been found to be ≥230 M^{-1} for the Mo complex (**5e**) in acetone at 25 °C and ≥117 M^{-1} for W (**5f**) in benzene at 25 °C. The corresponding $\Delta G°$ values are ≤−3.2 and ≤2.8 kcal/mol. In actuality, the values are probably more negative since no intramolecular ester is observed in solution with minimal alcohol concentration. It appears then that the trimethylene bridge is unable to achieve the correct orientation, at least in competition with the methyl ester formation (other more sterically bulky bases form the analogous intermolecular esters as well). Molecular models indicate that while the trimethylene bridge is physically possible, steric interactions are expected to occur to a significant extent with the carbonyl ligands, in that the middle CH_2 group appears to achieve close contact. It is also conceivable that the entropy loss may be prohibitively large for intra- vs. intermolecular ester formation.

Finally, since the $(CH_2)_2$ arm appears suited to bridge the cyclopentadienyl and ester groups, and the $(CH_2)_3$ appears to be unsuitable, the question arises whether shortening the arm will allow for intramolecular ester formation. To investigate this possibility the hydroxymethyl derivative, $[(\eta^5\text{-}C_5H_4CH_2OH)M(CO)_3PR_3]^+BF_4^-$ (**1g**), was synthesized. The synthesis is essentially the same as those used for the other cationic complexes; the only difference lies in the formation of the anion, $[CpRM(CO)_3]^-$. Whereas with R = $(CH_2)_2OH$ and $(CH_2)_3OH$ the sodium cyclopentadienide may simply be refluxed with $M(CO)_6$, no clean route to $NaCpCH_2OH$ was available. However, formyl cyclopentadienide, NaCpCHO, may be readily synthesized, and from this the (formyl)$CpW(CO)_3$ anion was obtained.[21] Proton NMR shows the presence of the aldehyde proton at 9.28 ppm, and the CpR protons are shifted downfield from the alcohol-substituted complexes as expected. Additionally, the infrared spectrum indicates higher energy CO stretches as expected for the less electron rich metal center.

Borohydride reduction of the formyl group in ethanol yields the HOMeCp tungsten tricarbonyl anion quite cleanly. Upon so doing, the infrared CO stretches shift back to essentially the same values that are obtained for the hydroxyethyl- and hydroxypropyl-substituted complexes.

Subsequent treatment of **1g** with base affords the intramolecular metalloester **3**. However, while treatment of the hydroxyethyl complexes **1a–d** with base yields the intramolecular metalloesters **2a–d** almost immediately, formation of **3** requires several days under the same conditions. Additionally, the ester that is formed is stable in chloroform and acetone solution for days whereas the $(CH_2)_2$ compound decomposes within hours in the same solvents. As such, it appears that ester formation is slow (i.e., a kinetic barrier) but the overall process is more thermodynamically favored than for the hydroxyethyl derivative.

To understand this better, an intra- vs. intermolecular ester formation study was carried out. As before, methanol was added to a solution of the intramolecular metalloester; however, no methyl ester was observed. A limiting value of K_{eq} of ≤3.5 ± 0.6 M^{-1} was thus obtained for the process given in eq 3. The source of the added stability, with reference to the $(CH_2)_2$ metalloesters, may be better overlap between the carbenoid p and d_{xz} orbitals.



(3)

Consideration of molecular models as well as the bond distances obtained from the crystal structure **2b** indicate that a single methylene should be quite suitable for bridging the distance between the cyclopentadienyl ring and the ester group. No significant distortion of the CH_2 out of the Cp ring plane should be encountered, and the subsequent torsion about the W–C bond is expected to maximize π overlap (vide supra) thus giving rise to additional stabilization.[22] A lower limit of the difference in $\Delta G°$

(21) Hart, W. P.; Macomber, D. W.; Rausch, M. D.; *J. Am. Chem. Soc.* **1980**, *102*, 1196.

(22) A recent crystal structure of **3** confirms these assertions: Coolbaugh, T. S.; Santarsiero, B. D.; Grubbs, R. H., unpublished results.

for metalloester formation with the different bridging arms is 1.5 ± 0.4 kcal/mol with (CH_2) bridge providing the more stable complex.

An additional source of stability may simply be the effective ring size of the lactone-like intramolecular metalloester, since it is known that γ-lactones are favored over their corresponding hydroxy acids while the opposite is true of δ-lactones. This may also account for the lack of formation of the intramolecular metalloester bridged by the $(CH_2)_3$ group since ε-lactones are found to be almost completely disfavored in comparison to the hydroxy acid. Thus, there may be several factors responsible for the stability differences, and the separate determination of these may prove somewhat difficult.

Conclusion

It has been demonstrated that intramolecular activation of carbon monoxide by nucleophilic attack is feasible provided the correct arm length is used in tethering the nucleophile to the anchor ligand. In the above case, where the nucleophile is an alkoxide attached to a Cp ligand via a $(CH_2)_n$ bridge, the value of n plays a key role.

Where $n = 1$ and 2, intramolecular metalloester formation is observed with the $n = 1$ group providing the more stable compound as evidenced by the equilibrium between the intra- and intermolecular esters. The slight instability of the $(CH_2)_2$ bridged complex may make the compound of more interest with respect to possible catalytic usefulness since stable compounds are usually not of importance in catalytic cycles except possibly as sources of reactive intermediates. The lack of reactivity of the (CH_2) bridged ester with chloroform and acetone is in marked contrast to that of the $(CH_2)_2$ bridged complex which is apparently cleaved upon protonation by the solvent as evidenced by the reformation of the alcohol-substituted Cp ligand.[23] On the other hand, the $(CH_2)_3$ bridge system displays little or no propensity for intramolecular metalloester formation. Steric and entropic factors presumably are important since molecular models indicate that the arm should be able to bridge the ester and Cp groups without undue distortion.

Consideration of the three cases should enable a better understanding of intramolecular interactions in organometallic compounds. The quantification of these factors will be essential to the design of new bifunctional catalysts and in providing the parameters for the prediction of stereochemical effects in organometallic reactions. Specifically, the study of the reactivity of the metalloesters obtained under various reaction conditions (i.e., with H_2, CO, and hydride reagents) may lead to an understanding of the requirements for the design of a homogeneous catalyst for the reduction of carbon monoxide.

Experimental Section

All reactions were carried out with use of standard Schlenk techniques. Argon used in Schlenk work was purified by passage through columns of BASF RS-11 (Chemalog) and Linde 4Å molecular sieves. Toluene, benzene, and THF were vacuum transferred from sodium benzophenone ketyl. Methylene chloride was stirred over P_2O_5, and acetone was dried over 4Å molecular sieves prior to use. Infrared spectra were obtained from a Perkin-Elmer 257 grating instrument and a Beckman Model IR 4240 spectrometer referenced to the 1601-cm^{-1} stretch of polystyrene. Continuous wave NMR spectra were recorded on a Varian EM-390 instrument with an ambient probe temperature of 34 °C. Fourier transform ^{31}P and ^1H spectra were taken on a JEOL FX-90Q spectrometer operating at 36.2 and 89.56 MHz, respectively, with a probe temperature of 25 °C. All ^{31}P NMR spectra were referenced to an external sample of the appropriate free phosphine in the relevant solvent. Difference NOE and 500-MHz ^1H NMR spectra were recorded on a Bruker WM-500 (500.13 MHz) at 25 °C using the instrument of the Southern California Regional NMR Facility located at Caltech. Melting points were obtained from a Büchi melting point apparatus with all samples placed in glass capillaries under a nitrogen atmosphere and sealed. No temperature corrections were made. Molecular weight determinations were performed by using the isopiestic method, in methylene chloride solution, at room temperature and in vacuo. Elemental analyses were performed by Schwarzkopf Microanalytical of Woodside, New York, Dornis and Kolbe of Mannheim, West Germany, and the analytical facility of the California Institute of Technology.

The parent compounds—$[CpMo(CO)_3]^-Na^+$,[24] $[CpW(CO)_3]^-Li^+$,[25] $CpMo(CO)_3H$,[26] $CpW(CO)_3H$,[26a,27] and $[CpM(CO)_3PR_3]^+BF_4^-$[28]—were prepared according to literature methods.

$[(\eta^5\text{-}C_5H_4(CH_2)_nOH)Mo(CO)_3]^-Na^+$ ($n = 2, 3$). The synthesis where $n = 2$ is given below.

A solution of 300 mg of $[(CpCH_2CH_2OH)Mo(CO)_3]_2$[29] (0.52 mmol) in 60 mL of THF was stirred over excess sodium amalgam (2.1 mmol of Na in 1.5 mL of Hg) under argon at room temperature. After 75 min, the red solution had changed to a pale gold. The solution was transferred away from the amalgam via cannula and filtered on a Schlenk frit. A clear yellow filtrate was obtained from which solvent was removed under reduced pressure. The remaining brown solid was dissolved in 5 mL of THF after which 30 mL of diethyl ether was added causing a pale precipitate to form. This was isolated by cannula filtration, and upon removal of remaining solvent under reduced pressure, 231 mg of the desired product was obtained (75%): $n = 2$, ^1H NMR ($(CD_3)_2CO$), CpR 4.90 (AA′BB′, 4H), CH_2O 3.55 (t, 2 H), $CpCH_2$ 2.46 (t, 2 H), OH variable (s, 1 H); IR (THF) ν(CO), 1900 (s), 1795 (s), 1750 (s). $n = 3$, ^1H NMR ($(CD_3)_2CO$), CpR 4.88 (AA′BB′, 4 H), CH_2O 3.57 (t, 2 H), $CpCH_2$ 2.32 (t, 2 H), CH_2 1.75 (m, 2 H), OH variable (s, 1 H); THF) ν(CO), 1900 (s), 1795 (s), 1742 (s).

$[(\eta^5\text{-}C_5H_4(CH_2)_nOH)W(CO)_3]^-Na^+$ ($n = 2, 3$). The synthesis where $n = 2$ is given below.

An equimolar (22.5 mmol) mixture of $W(CO)_6$ and $NaCpCH_2CH_2OH$ (made freshly from NaH and hydroxyethylcyclopentadiene in THF) was refluxed in 14 mL of THF under argon with stirring. After 12 h, the mixture was cooled to room temperature and filtered. Solvent was removed from the filtrate under reduced pressure until approximately one-half remained. Twenty milliliters of benzene was then added at which point yellow solid began to precipitate. This material was isolated by filtration, and the remaining solvent was removed under reduced pressure. The filtrate was again reduced in volume (to one-fourth) under reduced pressure after which 16 mL of diethyl ether was added causing additional precipitate to form for a total yield of 2.3 g (25.5%): $n = 2$, ^1H NMR ($(CD_3)_2CO$), CpR 4.92 (AA′BB′, 4H), CH_2O 3.54 (t, 2 H), $CpCH_2$ 2.52 (t, 2 H), OH variable (s, 1 H); IR (THF) ν(CO), 1895 (s), 1793 (s), 1742 (s). $n = 3$, ^1H NMR ($(CD_3)_2CO$), CpR 4.92 (AA′BB′, 4H), CH_2O 3.53 (t, 2 H), $CpCH_2$ 2.36 (t, 2 H), CH_2 1.74 (m, 2 H), OH variable (s, 1 H); IR (THF) ν(CO), 1900, 1795, 1745.

$[(\eta^5\text{-}C_5H_4CHO)W(CO)_3]^-Na^+$. The same procedure as that for the alcohol-substituted compounds was followed (43% yield of the THF solvate based on starting $W(CO)_6$): ^1H NMR($(CD_3)_2CO$), CpR(H_2 and H_5) 5.52 (AA′BB′, $J = 2.4$ Hz, 2 H), CpR (H_3 and H_4) 5.11 (AA′BB′, $J = 2.4$ Hz, 2 H), CHO 9.28 (s, 1 H); IR (THF) ν(CO), 1910 (s), 1810 (s), 1775 (m), 1740 (sh).

$[(\eta^5\text{-}C_5H_4CH_2OH)W(CO)_3]^-Na^+$. Using the precedent of other borohydride reductions of formyl Cp complexes,[30,31] 1.16 g of $[CpCHOW(CO)_3]^-Na^+$ (2.5 mmol) was dissolved in 10 mL of dry, degassed ethanol in a small Schlenk tube. One-half of 1 equiv of $NaBH_4$ (48 mg) was added and the mixture was stirred at room temperature for 2 h. Solvent was then removed under reduced pressure yielding a quantitative amount of the product as a tan powder (as the ethanol solvate): ^1H NMR ($(CD_3)_2CO$), CpR(H_2 and H_5) 5.09 (AA′BB′, $J = 2.0$ Hz, 2 H), CpR (H_3 and H_4) 4.90 (AA′BB′, $J = 2.4$ Hz, 2 H), $CpCH_2$ 4.04 (s, 2 H), OH variable (s, 1 H); IR (THF) ν(CO), 1895 (vs), 1792 (vs), 1743 (vs).

$(\eta^5\text{-}C_5H_4(CH_2)_nOH)M(CO)_3H$ (M = Mo, W; $n = 1, 2, 3$). One equivalent of CH_3COOH was added to $[(\eta^5\text{-}C_5H_4(CH_2)_nOH)M(CO)_3]^-Na^+$ in THF (typically 0.5 mmol in 3 mL of THF) under argon with stirring at room temperature. After 10 min, solvent was removed under reduced pressure and the resulting mixture was extracted with benzene (typically 8 times with 2 mL). Solvent was then removed from the combined extracts under reduced pressure giving the product as a gold oil at room temperature (100%). Thermal instability has precluded elemental analysis.

M = W, $n = 1$, ^1H NMR (C_6D_6), CpR 4.66 (AA′BB′, 4 H), CH_2O 3.78 (s, 2H), WH −7.07 (s w/small d, $J = 37.6$ Hz, 1 H), OH variable

(23) Decomposition via decarboxylation of these metalloesters is not observed; however, a possible route is by decarbonylation to yield the alkoxide: Coolbaugh, T. S.; Grubbs, R. H., unpublished results.

(24) Watson, P. L.; Bergman, R. G. *J. Am. Chem. Soc.* **1979**, *101*, 2055.

(25) The synthesis employed was adapted from ref 26a and 26b with the substitution of $W(CH_3CN)_3(CO)_3$ for $W(CO)_6$.

(26) (a) Piper, T. S.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1956**, *3*, 104. (b) Fischer, E. O.; Hafner, W.; Stahl, H. O. *Z. Anorg. Allg. Chem.* **1955**, *282*, 47.

(27) King, R. B.; Fronzagila, A. *Inorg. Chem.* **1966**, *5*, 1837. With the substitution of $W(CH_3CN)_3(CO)_3$ for $W(CO)_6$.

(28) Beck, W.; Schloter, K. *Z. Naturforsch. B.: Anorg. Chem., Org. Chem.* **1978**, *33B*, 1214.

(s, 1 H); IR (C_6D_6) ν(CO), 2018 (s), 1925 (vs).

M = Mo, n = 2, ^{1}H NMR (C_6D_6), CpR 4.75 (AA'BB', 4 H), CH_2O 3.22 (t, 2 H), $CpCH_2$ 2.04 (t, 2 H), MoH −5.30 (s, 1 H), OH variable (s, 1 H); IR (C_6D_6) ν(CO), 2013 (s), 1981 (w), 1932 (s).

M = W, n = 2, ^{1}H NMR (C_6D_6), CpR 4.70 (AA'BB', 4H), CH_2 3.29 (t, 2 H), $CpCH_2$ 2.13 (t, 2 H), WH −7.02 (s w/small d, J_{WH} = 37.6 Hz, 1 H), OH variable (s, 1 H); IR (C_6H_6) ν(CO), 2020 (s), 1925 (s).

M = Mo, n = 3, ^{1}H NMR (C_6D_6), CpR 4.63 (AA'BB', 4 H), CH_2O 3.15 (t, 2 H), $CpCH_2$ 2.00 (t, 2 H), CH_2 1.02 (m, 2 H), MoH −5.30 (s, 1 H), OH variable (s, 1 H); IR (C_6D_6) ν(CO), 2020 (s), 1930 (vs).

M = W, n = 3, ^{1}H NMR (C_6D_6), CpR 4.61 (AA'BB', 4 H), CH_2O 3.13 (t, 2 H), $CpCH_2$ 2.01 (t, 2 H), CH_2 1.1, WH −6.99 (s w/small d, J_{WH} = 37.6 Hz, 1 H), OH variable (s, 1 H); IR (C_6H_6) ν(CO), 2017 (s), 1922 (s).

$[(\eta^2$-$C_5H_4(CH_2)_nOH)M(CO)_3PR_3]^+BF_4^-$ (1) (M = Mo, W; n = 1, 2, 3; R = Ph, *p*-tolyl). The method of Beck and Schloter was used.[28] As an example, the synthesis of $[(CpCH_2CH_2OH)W(CO)_3PPh_3]^+BF_4^-$ is given.

A solution of 172.5 mg of $(CpCH_2CH_2OH)W(CO)_3H$ (0.46 mmol) in 4 mL of CH_2Cl_2 under argon was cooled to −30 °C. To this was added 1 equiv of $Ph_3C^+BF_4^-$ (152 mg). Immediately, a dark purple solution was obtained. This was allowed to sit for 5 min after which 1 equiv of triphenylphosphine (121 mg) was added. The solution immediately changed to a red-violet color. The mixture was kept at −30 °C for 1 h with occasional agitation. Following this, the mixture was warmed to room temperature at which point yellow crystalline solids began to form. Diethyl ether (8 mL) was added causing more yellow solids to precipitate. The solid was isolated by filtration and washed 6 times with 2 mL of diethyl ether after which remaining solvent was removed under reduced pressure leaving the product as bright yellow crystalline material (258 mgs, 78.3%).

1g, M = W; n = 1; R = Ph: ^{1}H NMR ($(CD_3)_2CO$), PPh_3 8.27–7.11 (m, 15 H), CpR 6.15 (AA'BB', 4H), CH_2O 4.57 (s, 2 H), OH variable (s, 1 H); ^{31}P NMR ($(CD_3)_2CO$) 19.45 (s w/small d, J_{WP} = 192.9 Hz); IR (CH_2Cl_2) ν(CO), 2050 (s), 1985 (m), 1957 (s).

1a, M = Mo; n = 2; R = Ph: mp 200–206 °C dec; ^{1}H NMR ($(CD_3)_2CO$), PPh_3 7.81–7.31 (m, 15 H), CpR 6.00 (AA'BB', 4 H), CH_2O 3.71 (t, 2 H), $CpCH_2$ 2.64 (t, 2 H), OH variable (s, 1 H); ^{31}P NMR ($(CD_3)_2CO$) 50.18 (s); IR (CH_2Cl_2) ν(CO), 2056 (s), 1995 (sh), 1969 (s).

Anal. Calcd for $C_{28}H_{24}B_1F_4Mo_1O_4P_1$: C, 52.70; H, 3.79. Found: C, 52.76; H, 3.78.

1b, M = W; n = 2; R = Ph: mp 211–215 °C dec; ^{1}H NMR ($(CD_3)_2CO$) PPh_3 7.79–7.24 (m, 15 H), CpR 6.13 (AA'BB', 4H), CH_2O 3.72 (t, 2 H), $CpCH_2$ 2.56 (t, 2 H), OH variable (s, 1 H); ^{31}P NMR ($(CD_3)_2CO$) 19.92 (s w/small d, J_{WP} = 192.9 Hz); IR (CH_2Cl_2) ν(CO), 2050 (s), 1980 (m), 1960(s).

Anal. Calcd for $C_{28}H_{24}B_1F_4O_4P_1W_1$: C, 46.32; H, 3.33. Found: C, 46.15; H, 3.41.

1c, M = Mo; n = 2; R = *p*-tolyl: mp 230–235 °C dec; ^{1}H NMR ($(CD_3)_2CO$) P(*p*-tolyl)$_3$(aryl) 7.89–7.15 (m, 12 H), CpR 5.95 (AA'BB', 4H), CH_2O 3.71 (t, 2 H), $CpCH_2$ 2.63 (t, 2 H), CH_3 2.43, OH not directly observed; ^{31}P NMR ($(CD_3)_2CO$) 50.01 (s); IR (CH_2Cl_2) ν(CO), 2055 (s), 1980 (s), 171 (vs).

Anal. Calcd for $C_{31}H_{30}B_1F_4Mo_1O_4P_1$: C, 54.73; H, 4.44. Found: C, 54.35; H, 4.47.

1d, M = W; n = 2; R = *p*-tolyl: mp 252–254 °C dec; ^{1}H NMR ($(CD_3)_2CO$ P(*p*-tolyl)$_3$(aryl) 7.57–7.14 (m, 12 H), CpR 6.07 (AA'BB', 4 H), CH_2O 3.72 (t, 2 H), $CpCH_2$ 2.73 (t, 2 H), CH_3 2.44 (s, 9 H), OH not directly observed; ^{31}P NMR ($(CD_3)_2CO$) 19.79 (s w/small d, J_{WP} = 190.4 Hz); IR (CH_2Cl_2) ν(CO), 2049 (s), 1975 (sh), 1956 (s).

Anal. Calcd for $C_{31}H_{30}B_1F_4O_4P_1W_1$: C, 48.47, H, 3.94. Found: C, 48.13; H, 4.19.

1e, M = Mo; n = 3; R = Ph: mp 189–191 °C dec; ^{1}H NMR ($(CD_3)_2CO$) PPh_3 7.82–7.28 (m, 15 H), CpR 6.01 (AA'BB', 4 H), CH_2O 3.56 (t, 2 H), $CpCH_2$ 2.57 (t, 2 H), CH_2 1.77 (m, 2 H), OH variable (s, 1 H); ^{31}P NMR ($(CD_3)_2CO$) 49.86 (s); IR (CH_2Cl_2) ν(CO), 2050 (s), 1996 (sh), 1970 (s).

Anal. Calcd for $C_{29}H_{26}B_1F_4Mo_1O_4P_1$: C, 53.40; H, 4.02. Found: C, 53.21; H, 4.27.

1f, M = W; n = 3; R = Ph: mp 142–145° C; ^{1}H NMR ($(CD_3)_2CO$) PPh_3 7.79–7.07 (m, 15 H), CpR 6.13 (m, 4 H), CH_2O 3.56 (t, 2H), $CpCH_2$ 2.66 (t, 2 H), CH_2 1.74 (m, 2 H), OH variable (s, 1 H); ^{31}P NMR ($(CD_3)_2CO$) 19.65 (s w/small d, J_{WP} = 190.4 Hz); IR (CH_2Cl_2) ν(CO), 2050 (m), 1980(sh), 1960 (s).

$(\eta^5$-$C_5H_4)CH_2CH_2O_2CM(CO)_2PPh_3$ (2) (M = Mo, W). The synthesis of the W complex is given below.

A mixture of $[(CpCH_2CH_2OH)W(CO)_3PPh_3]^+BF_4^-$ (108 mg, 0.15 mmol) and NaOMe (10 mgs, 0.19 mmol) was placed in a Schlenk tube under nitrogen. Acetone (1.5 mL) was then added at room temperature at which point all of the material dissolved. Almost immediately, yellow solid precipitated. This was isolated by cannula filtration, and the remaining solvent was removed under pressure leaving the product as a bright yellow solid (0.11 mmol, 70.1%).

2a, M = Mo: mp 160–162 °C dec; ^{1}H NMR ($CDCl_3$) PPh_3 7.56–7.20 (m, 15 H), CpR (H_2 and H_5) 5.46 (AA'XX', 2 H), CpR (H_3 and H_4) 4.30 (m, 2 H), CH_2O 3.88 (AA'BB', 2 H), $CpCH_2$ 2.40 (AA'BB', 2 H); ^{31}P NMR ($CDCl_3$), 71.07 (s); IR (CH_2Cl_2) ν(CO), 1970 (s), 1881 (vs), 1613 (m).

2b, M = W: mp 170–175 °C dec; ^{1}H NMR ($CDCl_3$) PPh_3 7.53–7.31 (m, 15 H), CpR (H_2 and H_5) 5.59 (AA'XX', 2H), CpR (H_3 and H_4) 4.35 (m, 2 H), CH_2O 3.86 (AA'BB', 2 H), $CpCH_2$ 2.43 (AA'BB', 2 H); ^{31}P NMR ($CDCl_3$), 39.98 (s w/small d, J_{WP} = 212.4 Hz); IR (CH_2Cl_2) ν(CO), 1961 (s), 1868 (vs), 1610 (m).

$(\eta^5$-$C_5H_4)CH_2CH_2O_2CM(CO)_2P(p$-tolyl$)_3$ (2) (M = Mo, W). The same procedure was followed as was used for the triphenylphosphine complexes with the exception that the product did not precipitate from acetone solution. Instead, solvent was removed under reduced pressure and the resulting material was extracted with benzene. Upon removal of solvent from the combined extracts, the product was obtained as a yellow, glassy solid (90%).

2c, M = Mo: mp 95–99 °C dec; ^{1}H NMR ($(CD_3)_2CO$) P(*p*-tolyl)$_3$-(aryl) 7.50–7.06 (m, 12 H), CpR (H_2 and H_5) 5.67 (AA'XX', 2 H), CpR (H_3 and H_4) 4.37 (m, 2 H), CH_2O 3.78 (AA'BB', 2 H), $CpCH_2$ 2.37 (AA'BB', 2 H), CH_3 2.37 (s, 9 H); ^{31}P NMR ($(CD_3)_2CO$), 71.61 (s); IR (CH_2Cl_2) ν(CO), 1968 (s), 1876 (vs), 1610 (m).

Anal. Calcd for $C_{31}H_{29}Mo_1O_4P_1$: C, 62.84; H, 4.93. Found: C, 62.68; H, 5.08.

2d, M = W: mp 100–105 °C dec; ^{1}H NMR ($(CD_3)_2CO$) P(*p*-tolyl)$_3$(aryl) 7.32–7.26 (m, 12 H), CpR (H_2 and H_5) 5.84 (AA'XX', 2 H), CpR (H_3 and H_4) 4.42 (m, 2 H), CH_2O 3.77 (AA'BB', 2 H), $CpCH_2$ 2.47 (AA'BB', 2 H), CH_3 2.37 (s, 9 H); ^{31}P NMR ($(CD_3)_2CO$) 40.04 (s w/small d, J_{WP} = 217.3 Hz); IR (CH_2Cl_2) ν(CO), 1961 (s), 1870 (vs), 1610 (m).

Anal. Calcd for $C_{31}H_{29}O_4P_1W_1$: C, 54.72; H, 4.30; mol wt 680.4 g/mol. Found: C, 54.71; H, 4.94; mol wt 680 ± 16 g/mol.

$(\eta^5$-$C_5H_4)CH_2O_2CW(CO)_2PPh_3$ (3). The same procedure was followed as that for the $(CH_2)_2$ bridged triphenylphosphine complexes. The reaction proceeded much more slowly, however, requiring 3 days at room temperature before the product formed as orange crystalline solids.

3: mp 188–190 °C dec; ^{1}H NMR ($(CD_3)_2CO$) PPh_3 7.64–7.26 (m, 15 H), CpR (H_2 and H_5) 6.26 (AA'XX', 2 H), CpR (H_3 and H_4) 4.41 (m, 2 H), CH_2O 4.12 (s); ^{31}P NMR ($(CD_3)_2CO$) 37.29 (s w/small d, J_{PW} = 200.2 Hz); IR (CH_2Cl_2) ν(CO), 1957 (s), 1882 (s), 1598 (m). Molecular weight calculated 624.3 g/mol, found 610 ± 40 g/mol.

$CpM(CO_2Me)(CO)_2PPh_3$ (4) (M = Mo, W). The same procedure was followed as was used for the synthesis of $(\eta^5$-$C_5H_4)CH_2CH_2O_2CM$-$(CO)_2P(p$-tolyl$)_3$ with the substitution of the parent Cp compound instead of the substituted tri-*p*-tolyl cation. The product (a mixture of the cis and trans isomers) was obtained as a glassy orange solid (56%). Thermal instability has precluded elemental analysis.

4a, M = Mo: ^{1}H NMR ($(CD_3)_2CO$) PPh_3 7.60–7.28 (m), Cp cis 5.34 (s), Cp trans 5.15 (d, J = 1.2 Hz), CH_3 trans 3.48 (s), CH_3 cis 2.57 (s); ^{31}P NMR ($(CD_3)_2CO$) trans 73.36 (s), cis 64.55 (s); IR (CH_2Cl_2) ν(CO), 1960 (s), 1875 (s), 1610 (m).

4b, M = W: ^{1}H NMR ($(CD_3)_2CO$) PPh_3 7.54–7.29 (m), Cp cis 5.47 (s), Cp trans 5.25 (d, J = 1.2 Hz), CH_3 trans 3.45 (s), CH_3 cis 2.51 (s); ^{31}P NMR ($(CD_3)_2CO$), trans 42.94 (s w/small d, J_{WP} = 234.4 Hz), cis 35.54 (s w/small d, J_{WP} = 271.0 Hz); IR (CH_2Cl_2) ν(CO), 1950 (s), 1863 (vs), 1608 (m).

X-ray Structure Determination. A thin crystalline plate of $(\eta^5$-$C_5H_4)CH_2CH_2O_2CW(CO)_2PPh_3$ (0.062 × 0.266 × 0.628 mm), obtained after layering pentane on top of a methylene chloride solution and cooling to −20 °C for 2 days, was mounted approximately along the *a* axis in a glass capillary under N_2. A series of oscillation and Weissenberg photographs indicated monoclinic symmetry and the space group $P2_1/n$ ($0k0$ absent for k odd, $h0l$ absent for $h + l$ odd); data were collected on a locally modified Syntex $P2_1$ diffractometer with graphite monochromator and Mo Kα radiation. The unit cell parameters (Table III) were obtained by least-squares refinement of 15 reflections ($30 < 2\theta < 34°$). The three check reflections indicated no decomposition. The data were corrected for absorption ($0.3 < \mu L < 0.7$), and the data were reduced to F_o^2; the form factors for H from Stewart et al.[32] and the *International Tables*

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for X-Ray Crystallography[33] for the other atoms and those for W and P were corrected for anomalous dispersion. The details of data collection are included in Table III.

The position of the W was derived from the Patterson map, and the Fourier map phased on W revealed the remainder of the complex. All H atoms were introduced into the model with fixed coordinates at idealized positions and isotropic $U = 0.076$ Å^2. Least-squares refinement of the non-hydrogen atoms with anisotropic U_{ij}'s, minimizing $\sum w[F_o^2 - (F_c/k)^2]^2$,[34] using all the data (5728 reflections) led to S (goodness of fit) = 1.27 and $R_F = 0.043$; final shift/errors <0.01. The maximum deviations found in the $\Delta\rho$ map are close to W and are about 1.2 e Å^{-3}. All calculations were carried out on a VAX 11/780 computer using the CRYRM system of programs.

Equilibrium Studies

Initial concentrations of **2** were based on the integrated peak areas with respect to added alcohol at time $t = 0$. Subsequent concentrations of **2** and **5** were established by the percentage of the integrated signal intensities of the relevant Cp proton signals in relation to that of the total Cp integration. Temperatures were determined by measurement of $\Delta\nu$(MeOH) with use of equation

$$T(\mathrm{K}) = 406.0 - 0.551|\Delta\nu| - 63.4(\Delta\nu/100)^2$$

$\Delta\nu$ is the difference in Hz between the chemical shifts of the OH and CH_3 signals. The above equation is for 60-MHz values; 90-MHz values must be corrected accordingly.[35]

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Supplementary Material Available: Tables of H-atom coordinates (Table VIII), Gaussian amplitudes (Table IX), and a listing of structure factor amplitudes (Table X) (32 pages). Ordering information is given on any current masthead page.

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(34) The weights, $w = [s + r^2b + (0.02s)^2]^{-1}(Lp/k^2)^2$, s = scan counts, r = scan-to-background time ratio, b = total background counts, k = scale factor of F; $R_F = \sum||F_o| - |F_c||/\sum|F_o|$ (sums of reflections with $I > 0$); $R'_F = R_F$ (sums of reflections with $I > 3\sigma(I)$); $S = [\sum w(F_o^2 - (F_c/k)^2)^2/(n - v)]^{1/2}$, n = number of reflections, v = number of parameters.

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Electron-Transfer-Induced Reactions. A Novel Approach Based on Electrochemical Redox Catalysis. Application to Aromatic Nucleophilic Substitutions

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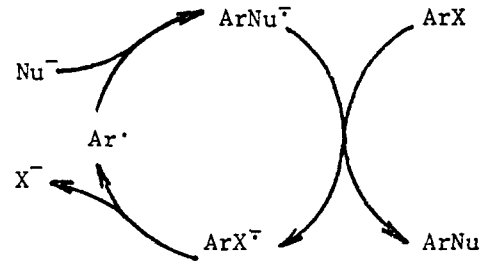
Abstract: A novel approach based on redox catalysis for electrochemical inducement of aromatic nucleophilic substitution is presented. The advantages of this method over the conventional ones are discussed in terms of kinetic and preparative scopes. The capabilities of the method for determining the kinetics of fast nucleophilic attack on an aromatic radical in the context of aromatic nucleophilic substitution is illustrated with the example of the reaction of 2-chlorobenzonitrile with benzenethiolate.

Current interest in aromatic nucleophilic substitutions stems from their important synthetic capabilities.[2] Unfortunately the direct reaction

$$\mathrm{ArX} + \mathrm{Nu}^- \rightarrow \mathrm{ArNu} + \mathrm{X}^- \qquad (1)$$

although thermodynamically possible is often so slow as to be practically impossible. Activation of the reaction via photochemistry or by chemical or electrochemical reduction leads to a considerable increase[2] of the global rate of reaction 1. It is therefore of utmost importance to understand the mechanism of these activation processes. In this connection it has been shown in the past few years[3] that a complete description of the mechanism was attainable by the use of readily available transient electrochemical techniques. Owing to the recent development of electron-transfer-catalyzed reactions,[4] the relevance of these studies to other processes in organic chemistry as well as in coordination and organometallic chemistry is obvious.

Scheme I



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