ring modes with skeletal modes is, in general, slight. Some of the ring modes show extensive mixing of symmetry coordinates of different types; thus in the E block of $Cr(\pi\text{-}C_6H_6)(CO)_3$ the frequency at 1448 cm^{-1} is best labeled ν_{19} [ν(CC)] although mixing with ν_{18} [β(CH)] at 965 cm^{-1} is pronounced. For the deuterated compound, ν_{19} (1292 cm^{-1}) is less heavily mixed with ν_{18} (791 cm^{-1}), but ν_{18} and ν_{10} (762 cm^{-1}) are now heavily mixed. Many of the skeletal modes show contributions from more than one symmetry coordinate. In particular, the chromium–carbon stretching modes are very extensively mixed; this is to be expected as they are mechanically coupled and have similar frequencies. In both the A_1 and E blocks and with both isotopic molecules, the mixing of the chromium–carbon stretching modes is so extensive as to render meaningless descriptions in terms of either ν(Cr–C) or ν(Cr–C^r).

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Registry No. $Cr(\pi\text{-}C_6H_6)(CO)_3$, 12082-08-5; $Cr(\pi\text{-}C_6D_6)(CO)_3$, 38095-88-4.

Supplementary Material Available. Further information on the details of the vibrational analysis will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th Street, N.W., Washington, D.C. 20036. Remit check or money order for \$4.50 for photocopy or \$2.50 for microfiche, referring to code number AIC40694Z.

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Reactions of Ethylene Coordinated to Molybdenum, Tungsten, and Iron

W. H. KNOTH

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Nitrogen, phosphorus, and oxygen nucleophiles, as well as cyanide ion, add to ethylene in $CpMo(CO)_3C_2H_4^+$,[1] $CpW(CO)_3C_2H_4^+$, and $CpFe(CO)_2C_2H_4^+$ to form β-substituted ethylmetal derivatives. Deprotonation of cationic products containing an N–H bond, e.g., $CpW(CO)_3CH_2CH_2NH_3^+$, leads to an insertion–cyclization reaction.

Introduction

The reactivity of coordinated olefinic ligands has been of continual interest for over a decade (see ref 2 and references therein). However, there have been relatively few studies on simple coordinated monoolefins. Recently, coordinated ethylene in $CpFe(CO)_2C_2H_4^+$ was shown to be subject to the facile addition of anionic carbon nucleophiles (L) to form $CpFe(CO)_2CH_2CH_2L$[2] and to the addition of triphenylphosphine, methylamine, and methoxide ion to form $CpFe(CO)_2CH_2CH_2PPh_3^+$,[2b] $CpFe(CO)_2CH_2CH_2N(H)CH_3$,[3] and $CpFe(CO)_2CH_2CH_2OCH_3$,[3] respectively. In addition, ammonia and amines have been found to react with simple monoolefins in certain palladium and platinum complexes.[4]

This paper is concerned mainly with the addition of ammonia and other nucleophiles to coordinated ethylene in $CpM(CO)_3C_2H_4^+$ (M = Mo, W) and with further transformations of the reaction products. Further examples of nucleophilic additions to $CpFe(CO)_2C_2H_4^+$ are described and compared with the molybdenum and tungsten systems and some related chemistry arising from the reaction of ethylene oxide with $CpM(CO)_3^-$ (M = Wo, W) is presented.

Results and Discussion

Ammonia readily adds to ethylene in $CpFe(CO)_2C_2H_4^+$ (I), $CpMo(CO)_3C_2H_4^+$ (II), and $CpW(CO)_3C_2H_4^+$ (III). The isolated products tend to be dialkylated; e.g., $[CpFe(CO)_2CH_2CH_2]_2NH_2^+$ (IV), $[CpMo(CO)_3CH_2CH_2]_2NH_2^+$ (V), and $[CpW(CO)_3CH_2CH_2]_2NH_2^+$ (VI) have been obtained, although $CpW(CO)_3CH_2CH_2NH_3^+$ (VII) has also been isolated. Most of this work involved preparation, isolation, and characterization of these cations as the hexafluorophosphate salts. Reactions of I–III with ammonia are facile and exothermic and proceed in good yield when ammonia vapor is passed over the solid salt or through an acetonitrile solution. Deprotonation of V–VII by sodium hydroxide is accompanied by a cyclization–insertion reaction as in eq 2 and 3. If the reaction of ammonia with II is run in benzene, monoalkylation

Table I. Reaction Products of Ethylene Complexes with Amines and $(C_6H_5)_3P$

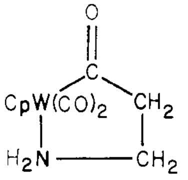
	Coreactant and product[a]				
Metal complex	C_5H_5N	CH_3NH_2	$(CH_3)_2NH$	$(CH_3)_3N$	$(C_6H_5)_3P$
I, $CpFe(CO)_2C_2H_4^+$	1	3	3	1	1
II, $CpMo(CO)_3C_2H_4^+$	1	2	3	1	1
III, $CpW(CO)_3C_2H_4^+$	1	2	1, 2	1	1

[a] 1 = product of type $[\mathrm{CpM(CO)}_{2\text{ or }3}\mathrm{CH_2CH_2L}]^+$; 2 = product of type $[\mathrm{CpM(CO)}_{2\text{ or }3}\mathrm{CH_2CH_2}]_2\mathrm{LH}^+$; 3 = experiment not run.

$$\underset{\mathrm{I}}{\mathrm{CpFe(CO)_2C_2H_4^+}} + 2\mathrm{NH_3} \rightarrow \underset{\mathrm{IV}}{[\mathrm{CpFe(CO)_2C_2H_4}]_2\mathrm{NH_2^+}} + \mathrm{NH_4^+} \qquad (1)$$

$$\mathrm{CpW(CO)_3CH_2CH_2NH_3^+} \xrightarrow{\mathrm{OH^-}}$$

$[\mathrm{CpW(CO)_3CH_2CH_2NH_2}] \rightarrow$

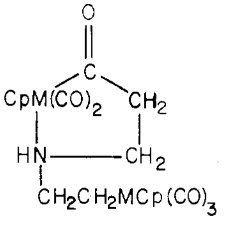


(2)

VIII

$$[\mathrm{CpM(CO)_3CH_2CH_2}]_2\mathrm{NH_2^+} \xrightarrow{\mathrm{OH^-}}$$

$[[\mathrm{CpM(CO)_3CH_2CH_2}]_2\mathrm{NH}] \rightarrow$

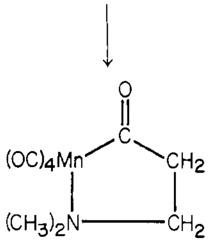


(3)

IXa, M = Mo
b, M = W

predominates but deprotonation is spontaneous and the isolated product is $\mathrm{CpMo(CO)_2COCH_2CH_2NH_2}$ (X), the molybdenum analog of VIII. An X-ray study on X confirms the assigned structure; extensive intermolecular hydrogen bonding between the $\mathrm{NH_2}$ and carbonyl groups clearly identifies the $\mathrm{NH_2}$ group.[5] The structure of VIII follows from the near identity of its infrared spectrum with that of X while the infrared spectra of IXa and IXb are nearly identical with each other and quite similar, in the appropriate regions, to those of VIII and X. Compound VIII has been prepared by Beck from $\mathrm{CpW(CO)_3H}$ and aziridine.[6] The cyclization–insertion reactions involved in the formation of VIII–X are similar to those observed by King[7] when he prepared several transition metal compounds containing a Lewis base β to an $\mathrm{M(CO)}_m$ group as in eq 4. Protonation of IXb by the strong acid $\mathrm{H_2B_{12}Cl_{12}}$[8] occurs at the acyl group to give the carbene complex XI. This is inferred from the lack of an acyl C=O stretch in the infrared spectrum and from the proton NMR spectrum in pyridine which is the same as that of IXb.

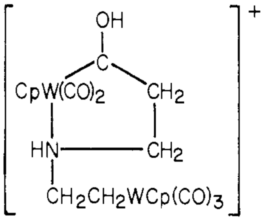
$$\mathrm{Mn(CO)_5^-} + \mathrm{ClCH_2CH_2N(CH_3)_2} \longrightarrow [\mathrm{(OC)_5MnCH_2CH_2N(CH_3)_2}] + \mathrm{Cl^-}$$



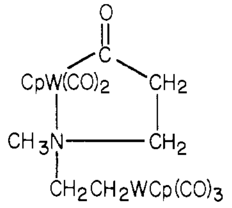
(4)

The reactions of I–III with amines and triphenylphosphine are analogous to their reactions with ammonia as shown in Table I.

Deprotonation of $[\mathrm{CpW(CO)_3CH_2CH_2}]_2\mathrm{N(H)CH_3^+}$ gave both a cyclization–insertion product, XII, analogous to IX, and the simple deprotonated product $[\mathrm{CpW(CO)_3CH_2CH_2}]_2\mathrm{NCH_3}$. The latter is converted to XII by treatment with cyanide ion.



XI



XII

The reversibility of the addition of a neutral ligand to ethylene in I–III depends both on the nucleophile and on the metal. The proton NMR spectrum shows that the addition of water to an acetonitrile solution of $\mathrm{CpFe(CO)_2CH_2CH_2NC_5H_5^+}$ causes rapid dissociation of the pyridine with regeneration of the ethylene complex. The molybdenum and tungsten analogs are unaffected by aqueous acetonitrile but lose the pyridine when treated with hydrochloric acid. The trimethylamine adducts of I–III all decompose slowly in aqueous acetonitrile. The ammonia addition products are more stable but show the same order of stability as the pyridine adducts; i.e., $[\mathrm{CpFe(CO)_2CH_2CH_2}]_2\mathrm{NH_2^+}$ is unaffected by water but is rapidly converted to the ethylene complex by hydrochloric acid while the tungsten and molybdenum analogs are not affected. Refluxing a solution of $[\mathrm{CpMo(CO)_3CH_2CH_2}]_2\mathrm{NH_2^+PF_6^-}$ in an alcohol–hydrochloric acid mixture for 30 sec gave the corresponding chloride salt. Prolonged (16 hr) treatment of $\mathrm{CpW(CO)_3C_2H_4PPh_3^+}$ with methanolic hydrochloric acid causes cleavage of $\mathrm{Ph_3PCH_2CH_3^+}$.

It has been reported[3] that sodium cyanide in water displaces ethylene from $\mathrm{CpFe(CO)_2C_2H_4^+}$. We confirm this but find that tetraethylammonium cyanide in acetonitrile causes only partial loss of ethylene and that the crude product contains an estimated 21% yield of $\mathrm{CpFe(CO)_2CH_2CH_2CN}$.[9] More success was achieved in the reaction of $\mathrm{CpMo(CO)_3C_2H_4^+}$ and $\mathrm{CpFe[P(OPh_3)]_2C_2H_4^+}$ with cyanide. Sodium cyanide in water caused loss of ethylene in both systems but tetraethylammonium cyanide in acetonitrile gave a 33% isolated yield of $\mathrm{CpMo(CO)_3CH_2CH_2CN}$ and a 69% isolated yield of $\mathrm{CpFe[P(OPh_3)]_2CH_2CH_2CN}$. Treatment of the latter with hydrogen (Pd/C catalyzed) gave a low yield of propionitrile.

Although it reacts smoothly with tetraethylammonium cyanide, $\mathrm{CpFe[P(OPh)_3]_2C_2H_4^+}$ does not add ammonia, amines, or triphenylphosphine. Presumably the greater electron density on the iron in $\mathrm{CpFe[P(OPh)_3]_2C_2H_4^+}$ compared to $\mathrm{CpFe(CO)_2C_2H_4^+}$ is transmitted in part to the ethylene, accounting for the decreased electrophilicity.

The possibility of effecting successive substitutions on an ethylene ligand has been demonstrated by the series of reactions

$$CpW(CO)_3C_2H_4^+ + CH_3NH_2 \xrightarrow{-H^+} [CpW(CO)_3C_2H_4]_2NCH_3 \xrightarrow{Ph_3C^+}$$

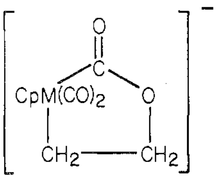
$$CpW(CO)_3\text{-}\pi\text{-}C_2H_3N(CH_3)C_2H_4WCp(CO)_3^+ \xrightarrow{Et_4NCN}$$

$$\underset{\mathrm{X}}{CpW(CO)_3CH_2CH(CN)N(CH_3)C_2H_4WCp(CO)_3}$$

The mode of addition of the tungsten and the nitrile group to the double bond in the final step has not been firmly established; it may be opposite to that shown here.

Recently there was a report[10] of the reaction of ethylene oxide with $CpFe(CO)_2^-$ to form $CpFe(CO)_2CH_2CH_2O^-$. Protonation of this gave $CpFe(CO)_2C_2H_4^+$; $CpFe(CO)_2CH_2CH_2OH$ would be an expected protonation product but apparently was too unstable to isolate. We now find that $CpMo(CO)_3^-$ and $CpW(CO)_3^-$ react similarly with ethylene oxide, forming $CpMo(CO)_3CH_2CH_2O^-$ and $CpW(CO)_3CH_2CH_2O^-$ which readily protonate to form isolable $CpMo(CO)_3CH_2CH_2OH$ and $CpW(CO)_3CH_2CH_2OH$. These alcohols are stable for several weeks at room temperature and longer at lower temperatures; they do decompose slowly with the release of ethylene and are converted to the corresponding ethylene complexes by treatment with strong acids.

The formulas $CpMo(CO)_3CH_2CH_2O^-$ and $CpW(CO)_3CH_2CH_2O^-$ do not adequately represent the structures. The infrared spectra exhibit C=O stretching absorptions at 1580 and 1550 cm^{-1}, respectively, implying structure XIII.



XIIIa, M = Mo
b, M = W

The alternative possibility, that an insertion reaction occurred in the formation of XIII, similar to that occurring in the formation of VIII, is ruled out by the previously mentioned facile conversions to $CpM(CO)_3CH_2CH_2OH$ and $CpM(CO)_3C_2H_4^+$.

Reaction of XIIIa with $CpFe(CO)_2C_2H_4^+$ and with $CpW(CO)_3C_2H_4^+$ and reaction of the latter with XIIIb has given $CpMo(CO)_3CH_2CH_2OCH_2CH_2FeCp(CO)_2$, $CpMo(CO)_3CH_2CH_2OCH_2CH_2WCp(CO)_3$, and $(CpW(CO)_3CH_2CH_2)_2O$. All of these decompose slowly (weeks) with the evolution of ethylene. Spectral data are in Table II.

Experimental Section

Ethylene Complexes. $CpFe(CO)_2C_2H_4^+$. An adaptation of the literature method[11] was used. Triphenylmethyl hexafluorophosphate (7.8 g, 20 mmol) was added to a solution of $CpFe(CO)_2C_2H_5$ (4 g, 19 mmol) in chloroform (30 ml) in a nitrogen atmosphere. The mixture was stirred for 1 hr and then filtered. The filter cake was dissolved in acetone (150 ml) at ambient temperature. Partial evaporation of the solution precipitated yellow $CpFe(CO)_2C_2H_4^+PF_6^-$ (5.2 g, 77%).

$CpMo(CO)_3C_2H_4^+$. This was prepared according to the literature[12] and isolated as the hexafluorophosphate salt.

$CpW(CO)_3C_2H_4^+$. The preparation of $CpW(CO)_3C_2H_4^+$ from $CpW(CO)_3Cl$, aluminum chloride, and ethylene has been reported[13] but a different procedure was used in this work.

A mixture of tungsten hexacarbonyl (35.5 g, 0.1 mol) and sodium cyclopentadienide (10.6 g, 0.12 mol) in tetrahydrofuran (200 ml) was refluxed overnight under nitrogen and allowed to cool. Ethyl iodide (23.4 g, 0.15 mol) was added and the mixture was stirred overnight at ambient temperature. The solvent was removed under vacuum and the residue was extracted with chloroform (200 ml). The extracts were mixed with Ph_3CPF_6 (38.8 g, 0.1 mol) and chloroform (400 ml) and stirred for 3 days. Filtration gave a green solid which was extracted with acetone. Partial concentration of the extracts gave yellow crystalline $CpW(CO)_3C_2H_4^+PF_6^-$ (14.3 g, 28%).

$CpFe[P(OPh)_3]_2C_2H_4^+$. This was prepared from $CpFe[P(OPh)_3]_2I$ according to literature directions.[14]

Reactions. $[CpFe(CO)_2CH_2CH_2]_2NH_2^+$. Ammonia was bubbled through a mixture of $CpFe(CO)_2C_2H_4PF_6$ (2.0 g, 5.7 mmol) and acetonitrile (20 ml) for 10 min. Water (4 ml) was added and the clear solution was partially concentrated to obtain 0.95 g (60%) of $[CpFe(CO)_2CH_2CH_2]_2NH_2^+PF_6^-$. Anal. Calcd for $C_{18}H_{20}F_6NO_2PFe_2$: C, 37.86; H, 3.53; N, 2.45. Found: C, 37.72; H, 3.51; N, 2.54.

Comparable yields were obtained in benzene. Quantitative conversions (by NMR analysis) were obtained when $C_5H_5Fe(CO)_2C_2H_4^+PF_6^-$ was exposed to ammonia vapor without solvent.

Attempted deprotonation of $[C_5H_5Fe(CO)_2C_2H_4]_2NH_2^+$ by reaction with sodium hydroxide has not given pure products; reaction with warm aqueous alcoholic hydrochloric acid rapidly regenerates $C_5H_5Fe(CO)_2C_2H_4^+$.

A mixture of $[CpFe(CO)_2CH_2CH_2]_2NH_2^+PF_6^-$ (0.3 g, 0.52 mmol) and tetraethylammonium cyanide (0.2 g, 1.3 mmol) in acetonitrile (7 ml) was stirred briefly and filtered. Dilution of the filtrate with 5 drops of water caused the separation of crystalline yellow $[CpFe(CO)_2CH_2CH_2]_2NH_2CN$. Anal. Calcd for $C_{19}H_{20}N_2O_4Fe_2$: C, 50.48; H, 4.46; N, 6.20. Found: C, 49.56; H, 4.61; N, 5.45.

$CpFe(CO)_2CH_2CH_2N(CH_3)_3^+$. Trimethylamine was bubbled into a solution of $CpFe(CO)_2C_2H_4^+PF_6^-$ (2.5 g, 7.1 mmol) in acetonitrile (25 ml) until reaction ceased. The solution was filtered; the filtrate was concentrated to a small volume and then diluted with benzene to precipitate crystalline $CpFe(CO)_2CH_2CH_2N(CH_3)_3^+\ PF_6^-$ (2.74 g, 94%; mp 134–139° dec), which was dried at ambient temperature under vacuum. Anal. Calcd for $C_{12}H_{18}F_6FeNO_2P$: C, 35.23; H, 4.43; N, 3.42; F, 27.87; Fe, 13.65; P, 7.51. Found: C, 35.38; H, 4.44; N, 3.29; F, 28.16; Fe, 13.70; P, 7.57.

A sample of $CpFe(CO)_2CH_2CH_2N(CH_3)_3^+PF_6^-$ was treated with warm aqueous alcoholic sodium hydroxide. Crystalline $[C_5H_5Fe(CO)_2]_2$ was obtained. The same product was found when a second sample was treated with aqueous acetonitrile for 24 hr.

$CpFe(CO)_2CH_2CH_2NC_5H_5^+$. Two grams (5.7 mmol) of $C_5H_5Fe(CO)_2C_2H_4^+PF_6^-$ was dissolved in pyridine (10 ml). Dilution of the clear solution with benzene (15 ml) caused the separation of crystalline yellow $CpFe(CO)_2CH_2CH_2NC_5H_5^+PF_6^-$ (2.2 g, 90%; mp 96–105° dec). Heating at 80° causes loss of pyridine; the analytical sample was dried at ambient temperature. Anal. Calcd for $CpC_{14}H_{14}F_6FeNO_2P$: C, 39.19; H, 3.29; N, 3.27; F, 26.57; Fe, 13.01. Found: C, 38.57; H, 2.95; N, 3.03; F, 27.32; Fe, 12.98. The addition of water to the NMR sample solution caused rapid dissociation of the pyridine with regeneration of the ethylene complex.

$CpFe(CO)_2CH_2CH_2P(C_6H_5)_3^+$. A mixture of $CpFe(CO)_2C_2H_4^+PF_6^-$ (2.0 g, 5.7 mmol), triphenylphosphine (1.8 g, 6.9 mmol), and acetonitrile (25 ml) was stirred in a nitrogen atmosphere for 30 min and then filtered. The filtrate was diluted with ether until it was cloudy and then allowed to stand for 3 hr. Filtration gave 2.2 g (63%) of yellow-orange crystalline $CpFe(CO)_2CH_2CH_2P(C_6H_5)_3^+PF_6^-$. Anal. Calcd for $C_{27}H_{24}F_6FeO_2P_2$: C, 52.96; H, 3.95. Found: C, 52.95; H, 4.04.

$CpFe(CO)_2CH_2CH_2CN$. Tetraethylammonium cyanide (1.5 g, 10 mmol) was added to a solution of $CpFe(CO)_2C_2H_4^+PF_6^-$ (2.0 g, 5.7 mmol) in acetonitrile (15 ml) in a nitrogen atmosphere. Slight bubbling was noted. The mixture was evaporated to dryness and the residue was extracted several times with benzene. The benzene extracts were combined and evaporated and the new residue was extracted with ethyl ether. Evaporation of the ether extracts left 0.4 g of a red oil which was shown by proton NMR analysis to contain 70% (21% yield) $CpFe(CO)_2CH_2CH_2CN$.[9]

$CpFe[P(OPh)_3]_2CH_2CH_2CN$. Tetraethylammonium cyanide (0.15 g, 1.0 mmol) was added to $CpFe[P(OPh)_3]_2C_2H_4^+BF_4^-$ (0.5 g, 0.58 mmol) in acetonitrile (15 ml) in a nitrogen atmosphere. After 1 hr the solvent was removed, leaving a yellow solid which was extracted with benzene. The addition of hexane to the filtered extracts caused the slow separation of yellow, crystalline $CpFe[P(OPh)_3]_2CH_2CH_2CN$ (0.32 g, 69%). The analytical sample was recrystallized again from benzene–hexane. Anal. Calcd for $C_{44}H_{39}FeNO_6P_2$: C, 66.42; H, 4.94; N, 1.76; O, 12.07. Found: C, 66.72; H, 5.33; N, 1.73; O, 11.87.

$CpMo(CO)_2COCH_2CH_2NH_2$. Ammonia was passed through a mixture of $CpMo(CO)_3C_2H_4^+PF_6^-$ (3.0 g, 7.2 mmol) and benzene (80 ml) for 25 min. The mixture was filtered and the filter cake was added to 40 ml of acetone. This mixture was shaken with 10 ml of

Table II. Spectral Data

	τ(H)[a]			ν,[b] cm^{-1}	
Compd[c]	CH_3, C_6H_5, or NC_5H_5	C_5H_5	CH_2[d]	C≡O	C=O
$CpFe(CO)_2C_2H_4^+$ (I)		4.47 (5)	6.30 (4)	2100–2040	
$CpMo(CO)_3C_2H_4^+$ (II)		4.09 (5)	6.66 (4)	2100–2000	
$CpW(CO)_3C_2H_4^+$ (III)		4.00 (5)	7.04 (4)	2100–2000	
$[CpFe(CO)_2CH_2CH_2]_2NH_2^+$ (IV)		5.07 (5)	7.0 (2), 8.8 (2)	2000, 1940	
$[CpMo(CO)_3CH_2CH_2]_2NH_2^+$ (V)		4.55 (5)	6.8 (2), 8.62 (2)	2040, 1930	
$[CpW(CO)_3CH_2CH_2]_2NH_2^+$ (VI)		4.45 (5)	6.9 (2), 8.5 (2)	2040, 1950–1900	
$CpW(CO)_3CH_2CH_2NH_3^+$ (VII)		4.40 (5)	6.85 (2), 8.5 (2)	2040, 1950–1900	
$CpW(CO)_2COCH_2CH_2NH_2$ (VIII)				1950, 1810	1600, 1530 (C=O, NH_2)
$CpMo(CO)_2COCH_2CH_2N(H)$-$CH_2CH_2MoCp(CO)_3$ (IXa)		4.52 (5) 4.79 (5)	6.6–9.0 (8)	2030, 1940, 1840	1710,[f] 1590
$CpW(CO)_2COCH_2CH_2NH$-$CH_2CH_2WCp(CO)_3$[e] (IXb)		4.42 (5) 4.47 (5)	6.0–8.5 (8)	2030, 1950, 1840	1600
$CpMo(CO)_2COCH_2CH_2NH_2$ (X)		4.8 (5)	7.3–8.0 (4)	1950, 1820	1590, 1540 (C=O, NH_2)
$CpW(CO)_2C(OH)CH_2CH_2N(H)$-$CH_2CH_2WCp(CO)_3^+$ (XI)		4.42 (5) 4.47 (5)	6.0–8.5 (8)	2000, 1960, 1920	1710[f]
$CpFe(CO)_2CH_2CH_2NC_5H_5^+$	1.2–2.3 (5)	5.0 (5)	5.5 (2), 8.4 (2)	2100–1950	
$CpMo(CO)_3CH_2CH_2NC_5H_5^+$	1.2–2.3 (5)	4.5 (5)	5.35 (2), 8.2 (2)	2030, 1930	
$CpW(CO)_3CH_2CH_2NC_5H_5^+$	1.2–2.3 (5)	4.44 (5)	5.4 (2), 8.1 (2)	2030, 1940	
$[CpMo(CO)_3CH_2CH_2]_2N(H)CH_3^+$				2030, 1940	
$[CpW(CO)_3CH_2CH_2]_2N(H)CH_3^+$	7.3 (3)	4.4 (5)	6.8 (2), 8.5 (2)	2020, 1900	
$[CpW(CO)_3CH_2CH_2]_2N(CH_3)_2^+$	7.15 (6)	4.28 (10)	6.70 (4), 8.5 (4)	2040, 1950	
$CpW(CO)_3CH_2CH_2N(H)(CH_3)_2^+$	7.15 (6)	4.28 (5)	6.75 (2), 8.5 (2)	2040, 1940	
$CpFe(CO)_2CH_2CH_2N(CH_3)_3^+$	7.12 (9)	5.05 (5)	6.72 (2), 8.77 (2)	2040, 1940	
$CpMo(CO)_3CH_2CH_2N(CH_3)_3^+$	7.08 (9)	4.52 (5)	6.65 (2), 8.5 (2)	2040, 1940	
$CpW(CO)_3CH_2CH_2N(CH_3)_3^+$	7.10 (9)	4.4 (5)	6.7 (2), 8.5 (2)	2030, 1930	
$CpFe(CO)_2CH_2CH_2P(C_6H_5)_3^+$	2.1–2.4 (15)	5.05 (5)	6.75 (2), 8.75 (2)	2000, 1940	
$CpMo(CO)_3CH_2CH_2P(C_6H_5)_3^+$	2.1–2.4 (15)	4.4 (5)	6.7 (2), 8.5 (2)	2030, 1940	
$CpW(CO)_3CH_2CH_2P(C_6H_5)_3^+$	2.1–2.4 (15)	4.4 (5)	6.65 (2), 8.5 (2)	2020, 1940	
$CpW(CO)_2COCH_2CH_2N(CH_3)$-$CH_2CH_2WCp(CO)_3$ (XII)				2020, 1930, 1850	1600
$[CpW(CO)_3CH_2CH_2]_2NCH_3$	7.54 (3)	4.56 (10)	8.17 (4), 7.07 (4)	2020, 1900	
$CpFe(CO)_2CH_2CH_2CN$[g]		5.80 (5)	7.9 (2), 8.8 (2)		
$CpFe[P(OC_6H_5)_3]_2CH_2CH_2CN$[h]	2.6–3.15 (30)	6.05 (5)[i]	7.52 (2), 8.55 (2)		j
$CpMo(CO)_3CH_2CH_2CN$[g]		5.5 (5)	7.8 (2), 8.7 (2)	2040–1900	j
$CpW(CO)_3$-π-$C_2H_3N(CH_3)CH_2$-$CH_2WCp(CO)_3^+$				2040, 1940	
$CpW(CO)_3CH_2CH(CN)N(CH_3)$-$CH_2CH_2WCp(CO)_3$				2020, 1940	
$CpMo(CO)_2COOCH_2CH_2^-$[k] (XIIIa)	6.52 (4) 6.7 (6)	4.90 (5)	5.3–9.0 (4)	1900, 1800	1560
$CpMo(CO)_3CH_2CH_2OH$				2020, 1940	
$CpW(CO)_2COOCH_2CH_2^-$[k] (XIIIb)	6.52 (4) 6.7 (6)	4.78 (5)	5.8–8.6 (4)	1900, 1800	1550
$CpW(CO)_3CH_2CH_2OH$		4.48 (5)	6.4 (2), 8.4 (2)	2030, 1940	
$CpMo(CO)_3CH_2CH_2OCH_2CH_2$-$FeCp(CO)_2$		4.58 (5) 5.12 (5)	6.5 (4), 8.1 (2) 8.5 (2)	2000, 1920, 1880	
$CpMo(CO)_3CH_2CH_2OCH_2CH_2$-$WCp(CO)_3$		4.68 (5) 4.53 (5)	6.15 (4), 8.04 (4)	2000, 1900	
$[CpW(CO)_3CH_2CH_2]_2O$[e]		4.58 (10)	6.4 (4), 8.4 (4)	2000, 1900	
$CpW(CO)_3OCH_2CH_2WCp(CO)_3$[l]		4.34 (5) 4.66 (5)	5.1 (2), 8.0 (2)	2000, 1900	

[a] Internal standard TMS, 10.0; all spectra in CD_3CN unless otherwise noted. [b] Nujol mull. [c] Data were determined on all cations as PF_6^- salts except for XI which was a $B_{12}Cl_{12}^{2-}$ salt. [d] All CH_2 resonances were multiplets except in ethylene complexes, which exhibited singlets. [e] NMR in C_5D_5N. [f] C=O of retained acetone; see Experimental Section. [g] NMR in C_6D_6. [h] NMR in $CDCl_3$. [i] Triplet; $J = 1$ Hz. [j] ν_{CN} 2290 cm^{-1}. [k] Data were determined on sodium salt; peaks at τ 6.52 and 6.7 due to solvation with 1,2-dimethoxyethane. [l] NMR in CD_2Cl_2.

10% aqueous sodium hydroxide briefly. The aqueous sodium hydroxide layer was removed and discarded and the acetone layer was diluted with water until it became turbid (ca. 50–60 ml of water). The solution was clarified by warming slightly; more water was added until slight turbidity was again noted and the solution was allowed to stand overnight. Crystalline $CpMo(CO)_2COCH_2CH_2NH_2$ (0.83 g, 40%) separated. The same product is obtained if the sodium hydroxide treatment is omitted but the purity is not as satisfactory. Anal. Calcd for $C_{10}H_{11}MoNO_3$: C, 41.54; H, 3.84; N, 4.84; mol wt 289. Found: C, 41.39; H, 3.55; N, 4.75; mol wt 294 (boiling point in CH_3CN).

$[CpMo(CO)_3CH_2CH_2]_2NH_2^+$. Ammonia vapors were passed over solid $CpMo(CO)_3C_2H_4^+PF_6^-$ (3 g, 7.2 mmol) for 20 min. The crude product was a mixture of 70% $[CpMo(CO)_3CH_2CH_2]_2NH_2^+PF_6^-$ and 30% $CpMo(CO)_2COCH_2CH_2NH_2$ by NMR analysis. This mixture was washed with alcohol (this is essential) and the insoluble portion was recrystallized from aqueous acetonitrile to obtain 0.61 g (24%) of $[CpMo(CO)_3CH_2CH_2]_2NH_2^+PF_6^-$. Anal. Calcd for $C_{20}H_{20}F_6Mo_2NO_6P$: C, 33.96; H, 2.85; N, 1.98; F, 16.12. Found: C, 33.84; H, 2.74; N, 2.22; F, 15.89.

A mixture of $[CpMo(CO)_3CH_2CH_2]_2NH_2^+PF_6^-$ (0.88 g, 1.2 mmol), alcohol (20 ml), and concentrated hydrochloric acid (4 ml) was heated to boiling for about 30 sec, filtered, and allowed to cool. The resulting crystalline product was recrystallized from alcohol to obtain $[CpMo(CO)_3CH_2CH_2]_2NH_2Cl$. Anal. Calcd for $C_{20}H_{20}ClMo_2NO_6$: C, 40.19; H, 3.37; N, 2.34; O, 16.06; Cl, 5.93. Found: C, 39.69; H, 3.39; N, 2.34; O, 16.05; Cl, 7.49. The infrared spectra of the hydrochloride and the corresponding PF_6^- salt were virtually identical in the C≡O region; the spectrum of the PF_6^- salt had an N–H stretching absorption at 3300 cm^{-1}, and the spectrum of the hydrochloride has bands at 2700–2800 cm^{-1} that may be attributed to N–H hydrogen bonded to the chlorine.

$Cp\overline{Mo(CO)_2COCH_2CH_2N}(H)CH_2CH_2Mo(CO)_3Cp$. Ammonia vapor was passed over solid $CpMo(CO)_3C_2H_4^+PF_6^-$ (3.0 g, 7.2 mmol) for 15 min with occasional agitation. In a nitrogen atmosphere the crude product was dissolved in acetone (25 ml) and this solution was shaken with 1.6 g of sodium hydroxide in 6 ml of water for 1 min. The aqueous sodium hydroxide layer was removed; the acetone layer was filtered and diluted with water until it became slightly turbid. It was clarified by warming and then allowed to stand for 2 hr. Filtration gave crystalline $Cp\overline{Mo(CO)_2COCH_2CH_2N}(H)CH_2CH_2Mo(CO)_3Cp$ (0.6 g). Proton NMR analysis revealed the retention of 0.3 molar equiv of acetone which was not removed even on drying at 80°. The product is not stable in air. Anal. Calcd for $C_5H_5Mo(CO)_2COC_2H_4N(H)C_2H_4Mo(CO)_3C_5H_5 \cdot 0.3(CH_3)_2CO$: C, 43.38; H, 3.62; N, 2.42; O, 17.42; mol wt 579. Found: C, 43.39; H, 3.78; N, 2.57; O, 17.52; mol wt 575 (boiling point in acetone).

The same product is obtained (though in less pure form) if the sodium hydroxide treatment is omitted, unless the crude product is washed with alcohol in which case $[C_5H_5Mo(CO)_3CH_2CH_2]_2NH_2^+PF_6^-$ is obtained.

$[CpMo(CO)_3CH_2CH_2]_2NH(CH_3)^+$. Methylamine was passed into a solution of $CpMo(CO)_3C_2H_4^+PF_6^-$ (0.37 g, 0.89 mmol) in acetone (3 ml) until a clear dark red solution formed. This was diluted with water until it was slightly turbid and then allowed to stand. Crystalline $[CpMo(CO)_3CH_2CH_2]_2NH(CH_3)^+PF_6^-$ (0.16 g, 50% separated). Anal. Calcd for $C_{21}H_{22}F_6Mo_2NO_6P$: C, 34.97; H, 3.08; N, 1.94. Found: C, 35.58; H, 3.10; N, 2.14.

$CpMo(CO)_3CH_2CH_2N(CH_3)_3^+$. Trimethylamine was bubbled into a solution of $CpMoC_2H_4^+PF_6^-$ (2.5 g, 6 mmol) in acetonitrile (25 ml) for 5 min. The solution was filtered; concentration of the filtrate to a small volume followed by dilution with benzene precipitated 1.5 g (52%) of $CpMo(CO)_3CH_2CH_2N(CH_3)_3^+PF_6^-$ which was dried in vacuo at ambient temperature. Decomposition occurred on attempted drying of a small portion at 80°. Proton NMR analysis revealed that the analytical sample, dried at ambient temperature, retained about 0.2 molar equiv of benzene. Anal. Calcd for $C_5H_5Mo(CO)_3C_2H_4N(CH_3)_3PF_6 \cdot 0.2C_6H_6$: C, 34.60; H, 3.93; N, 2.84; F, 23.39. Found: C, 34.75; H, 3.85; N, 3.00; F, 22.92.

The addition of water to an acetonitrile solution of $CpMo(CO)_3CH_2CH_2N(CH_3)_3^+PF_6^-$ caused the slow formation of $[CpMo(CO)_3]_2$; ethylene was also detected. In a separate experiment the addition of water to an acetonitrile solution of $CpMo(CO)_3C_2H_4^+$ was also found to cause conversion to $[CpMo(CO)_3]_2$.

$CpMo(CO)_3CH_2CH_2NC_5H_5^+$. A solution of $CpMo(CO)_3C_2H_4^+PF_6^-$ (1.0 g, 2.4 mmol) in pyridine (20 ml) was diluted with water causing the precipitation of $CpMo(CO)_3CH_2CH_2NC_5H_5^+PF_6^-$ as a yellow crystalline solid (0.6 g, 50%). Anal. Calcd for $C_5H_5Mo(CO)_3C_2H_4NC_5H_5PF_6$: C, 36.23; H, 2.84; N, 2.82; P, 6.23; F, 22.92. Found: C, 36.69; H, 2.85; N, 2.80; P, 5.90; F, 23.00.

$CpMo(CO)_3CH_2CH_2P(C_6H_5)_3^+$. A solution of $CpMo(CO)_3C_2H_4^+PF_6^-$ (4.0 g, 9.6 mmol) and triphenylphosphine (3.2 g, 12.2 mmol) in acetonitrile (75 ml) was stirred for 10 min and filtered. The filtrate was diluted to 825 ml with ether and allowed to stand until crystals ceased forming. Filtration gave yellow crystals of $CpMo(CO)_3CH_2CH_2P(C_6H_5)_3^+PF_6^-$, 5.24 g (80%). The analytical sample was dried at 80° in vacuo for 16 hr. Anal. Calcd for $C_{28}H_{24}F_6MoO_3P_2$: C, 49.43; H, 3.56; P, 9.10; F, 16.75. Found: C, 49.54; H, 3.56; P, 9.28; F, 16.43.

$CpMo(CO)_3C_2H_4CN$. Tetraethylammonium cyanide (1.2 g, 7.7 mmol) was added to a solution of $CpMo(CO)_3C_2H_4^+PF_6^-$ (3 g, 7.2 mmol) in acetonitrile (100 ml) in a nitrogen atmosphere. The mixture was stirred 15 min followed by removal of solvent. The residue was extracted with benzene; the extracts were concentrated to a small volume and diluted with hexane. On standing overnight, yellow crystals and a red grease separated. The yellow crystals were $CpMo(CO)_3CH_2CH_2CN$, 0.7 g (33%). Anal. Calcd for $C_{11}H_9MoNO_3$: C, 44.16; H, 3.03; N, 4.68; O, 16.04. Found: C, 44.72; H, 3.05; N, 4.70; O, 16.21.

$[CpW(CO)_3CH_2CH_2]_2NH_2^+$. Ammonia vapors were passed over solid $CpW(CO)_3C_2H_4^+PF_6^-$ (4.0 g, 7.9 mmol) for 10 min with occasional agitation. Proton NMR analysis showed it was 90% converted to $[CpW(CO)_3CH_2CH_2]_2NH_2^+PF_6^-$. Extraction with acetonitrile (80 ml) followed by filtration and dilution of the extract with water (50 ml) gave 1.53 g of $[CpW(CO)_3CH_2CH_2]_2NH_2^+PF_6^-$. Concentration of the filtrate gave an additional 0.45 g for a total yield of 1.98 g (57%). Anal. Calcd for $C_{20}H_{20}F_6NO_6PW_2$: C, 27.20; H, 2.28; N, 1.59; F, 12.91; P. 3.51. Found: C, 27.51; H, 2.20; N, 1.82; F, 13.45; P, 3.42.

Tetraethylammonium cyanide (0.9 g, 5.8 mmol) was added to a mixture of $[CpW(CO)_3CH_2CH_2]_2NH_2^+PF_6^-$ (1.6 g, 1.8 mmol) and acetonitrile (25 ml) which was then stirred for 10 min and filtered. Dropwise addition of water to the filtrate precipitated $[CpW(CO)_3CH_2CH_2]_2NH_2CN$ as a yellow crystalline solid. Anal. Calcd for $C_{21}H_{20}N_2O_6W_2$: C, 33.01; H, 2.64; N, 3.67. Found: C, 33.20; H, 3.32; N, 3.91.

Heating a sample overnight at 70° in vacuo caused loss of HCN and the formation of $Cp\overline{W(CO)_2COCH_2CH_2N}HCH_2CH_2WCp(CO)_3$, identical with that prepared below.

$CpW(CO)_3CH_2CH_2NH_3^+$ and $Cp\overline{W(CO)_2COCH_2CH_2N}H_2$. Ammonia was passed through a mixture of $CpW(CO)_3C_2H_4^+PF_6^-$ (6.0 g, 11.8 mmol) and acetonitrile (50 ml) for 20 min. The reaction mixture was filtered; the filtrate was diluted with water to the cloud point and partially concentrated. Filtration gave 2.0 g (39%) of $[CpW(CO)_3CH_2CH_2]_2NH_2^+PF_6^-$. Concentration of the filtrate to near dryness precipitated 2.4 g (39%) of $CpW(CO)_3CH_2CH_2NH_3^+PF_6^-$ which was isolated and washed well with water. Anal. Calcd for $C_{10}H_{12}F_6NO_3PW$: C, 22.96; H, 2.31; N, 2.68. Found: C, 23.92; H, 2.42; N, 2.83. $[CpW(CO)_3CH_2CH_2]_2NH_2^+PF_6^-$ is insoluble in tetrahydrofuran while the monoalkylated analog is quite soluble.

Addition of tetraethylammonium cyanide to an acetonitrile solution of $CpW(CO)_3CH_2CH_2NH_3^+PF_6^-$, followed by stirring for 10 min and dilution with water, gave crystalline $Cp\overline{W(CO)_2COCH_2CH_2N}H_2$. Anal. Calcd for $C_{10}H_{11}NO_3W$: C, 31.85; H, 2.94; N, 3.71; O, 12.73. Found: C, 31.71; H, 2.84; N, 3.24; O, 12.60.

A solution of $CpW(CO)_3CH_2CH_2NH_3^+PF_6^-$ (1.0 g, 1.9 mmol) in tetrahydrofuran (20 ml) was heated at 50° for 16 hr under 40 psig of carbon monoxide. Crystalline $[CpW(CO)_3CH_2CH_2]_2NH_2^+PF_6^-$ (0.53 g, 62%) slowly separated.

$Cp\overline{W(CO)_2COCH_2CH_2N}HCH_2CH_2W(CO)_3Cp$. A suspension of $[CpW(CO)_3CH_2CH_2]_2NH_2^+PF_6^-$ (1.4 g, 1.6 mmol) in acetone (8 ml) was stirred with water (2 ml) containing 0.52 g of sodium hydroxide. A nitrogen atmosphere was maintained. The layers were separated; dilution of the acetone layer with water gave an oil. This was taken up in warm alcohol, water was added, and the solution was allowed to cool to obtain yellow crystalline $Cp\overline{W(CO)_2COCH_2CH_2N}HCH_2CH_2W(CO)_3Cp$ (0.3 g, 25%). This is air sensitive. Anal. Calcd for $C_{20}H_{19}NO_6W_2$: C, 32.59; H, 2.60; N, 1.90; O, 13.02; mol wt 737. Found: C, 32.65; H, 2.69; N, 2.16; O, 12.79; mol wt 741 (boiling point in acetone).

$[CpW(CO)_3CH_2CH_2]_2NH(CH_3)^+$. Methylamine was passed over solid $CpW(CO)_3C_2H_4^+PF_6^-$ (2.5 g, 2.8 mmol) for 10 min. The resulting sticky orange solid was extracted with acetone. The filtered extracts were diluted with water to precipitate crystalline yellow $[CpW(CO)_3CH_2CH_2]_2NHCH_3^+PF_6^-$ (0.9 g, 36%). Anal. Calcd for $C_{21}H_{22}F_6NO_6PW_2$: C, 28.11; H, 2.47; N, 1.56. Found: C, 28.38; H, 2.36; N, 1.70.

$[CpW(CO)_3CH_2CH_2]NCH_3$ and $Cp\overline{W(CO)_2COCH_2CH_2N}(CH_3)CH_2CH_2W(CO)_3Cp$. Methylamine was passed over $CpW(CO)_3C_2H_4^+PF_6^-$ (2.0 g, 4 mmol) for 5 min with occasional mixing. In a nitrogen atmosphere the resulting orange pasty solid was mixed with acetone (15 ml). A solution of sodium hydroxide (0.64 g) in water (5 ml) was added and the mixture was agitated for several minutes. The water layer was removed. The acetone solution was filtered and the filtrate was diluted with water to separate orange, crystalline $[CpW(CO)_3CH_2CH_2]_2NCH_3$ (0.6 g, 40%). Anal. Calcd for $C_{21}H_{21}NO_6W_2$: C, 33.58; H, 2.82; N, 1.87; mol wt 751. Found: C, 32.81; H, 3.01; N, 2.03; mol wt 800 (boiling point in acetone).

Repeating the above reaction sometimes gave $Cp\overline{W(CO)_2COCH_2CH_2N}(CH_3)CH_2CH_2W(CO)_3Cp$. In addition, this insertion product can be formed from its noninserted precursor by treatment with tetraethylammonium cyanide.

Tetraethylammonium cyanide (0.4 g) was added to $[CpW(CO)_3CH_2CH_2]_2NCH_3$ (0.68 g) in acetonitrile (45 ml) and the mixture was boiled for 3 min in a nitrogen atmosphere, filtered, and diluted with water. Crystalline yellow-orange $Cp\overline{W(CO)_2COCH_2CH_2N}(CH_3)CH_2CH_2W(CO)_3Cp$ separated. Anal. Calcd for $C_{21}H_{21}NO_6W_2$: C, 33.58; H, 2.82; N, 1.87. Found: C, 33.85; H, 2.61; N, 1.99.

$CpW(CO)_3CH_2CH_2]_2N(CH_3)_2^+$. Dimethylamine was passed over $CpW(CO)_3C_2H_4^+PF_6^-$ (2.0 g, 4 mmol) for 10 min. The resulting product was extracted with acetone (15 ml). Ten milliliters of water was added and the mixture was filtered after 10 min to obtain yellow-orange $[CpW(CO)_3CH_2CH_2]_2N(CH_3)_2^+PF_6^-$ (0.59 g). An additional 0.15 g separated from the filtrate after 3 days for a total yield of 0.74 g (40%). Anal. Calcd for $C_{22}H_{24}F_6NO_6PW_2$: C, 28.99; H, 2.65; N, 1.54. Found: C, 29.66; H, 2.90; N, 1.69.

The final filtrate from the above reaction separated crystalline $CpW(CO)_3CH_2CH_2N(H)(CH_3)_2^+PF_6^-$ (0.4 g, 21%) on standing another 24 hr. Anal. Calcd for $C_{12}H_{16}F_6NO_3PW$: C, 26.15; H, 2.93; N, 2.54; P, 5.62. Found: C, 26.67, 26.47; H, 2.93, 2.94; N, 2.62, 2.59; P, 5.35.

The addition of an acetonitrile solution of tetraethylammonium cyanide to $[CpW(CO)_3CH_2CH_2]_2N(CH_3)_2^+PF_6^-$ in acetonitrile caused the slow separation of yellow crystalline $[CpW(CO)_3CH_2CH_2]_2N(CH_3)_2CN$. Anal. Calcd for $C_{21}H_{24}N_2O_6W_2$: C, 34.87; H, 3.05; N, 3.53. Found: C, 34.58; H, 3.22; N, 3.40.

$CpW(CO)_3CH_2CH_2N(CH_3)_3^+$. Trimethylamine was bubbled into a solution of $CpW(CO)_3C_2H_4^+PF_6^-$ (3 g, 5.9 mmol) in acetonitrile (40 ml) for 15 min. The resulting clear solution was diluted with benzene and petroleum ether to precipitate crystalline yellow $CpW(CO)_3CH_2CH_2N(CH_3)_3^+PF_6^-$ (2.7 g, 81%). Proton NMR showed that about 0.27 molar equiv of benzene was retained. Anal. Calcd for $CpW(CO)_3C_2H_4N(CH_3)_3PF_6{\cdot}0.27C_6H_6$: C, 29.98; H, 3.27; N, 2.39; F, 19.47; P, 5.29. Found: C, 30.42, 30.58; H, 3.41, 3.28; N, 2.44, 2.45; F, 19.14; P, 5.00.

$CpW(CO)_3CH_2CH_2NC_5H_5^+$. A solution of $CpW(CO)_3C_2H_4^+PF_6^-$ (1.8 g, 3.6 mmol) in pyridine (30 ml) was prepared and filtered. Dilution of the filtrate with water precipitated yellow crystalline $CpW(CO)_3CH_2CH_2NC_5H_5^+PF_6^-$ (1.64 g, 78%). Anal. Calcd for $C_{15}H_{14}F_6NO_3PW$: C, 30.79; H, 2.41; N, 2.39; F, 19.48. Found: C, 30.93, 31.01; H, 2.26, 2.23; N, 2.30, 2.28; F, 19.59.

$CpW(CO)_3CH_2CH_2P(C_6H_5)_3^+$. A solution of $CpW(CO)_3C_2H_4^+PF_6^-$ (3.0 g, 5.9 mmol) and triphenylphosphine (1.8 g, 6.9 mmol) in acetonitrile (30 ml) was stirred for 30 min and then filtered. The filtrate was diluted with ether until crystals began to separate. The mixture was allowed to stand for 1 hr and then filtered to obtain 3.8 g (84%) of $CpW(CO)CH_2CH_2P(C_6H_5)_3^+PF_6^-$, a light-sensitive yellow solid which was dried at 80° in vacuo. Anal. Calcd for $C_{28}H_{24}F_6O_3P_2W$: C, 43.77; H, 3.15; P, 8.06. Found: C, 43.75; H, 3.25; P, 7.81.

Refluxing a mixture of $[CpW(CO)_3CH_2CH_2]_2NH_2^+PF_6^-$ (0.8 g, 0.9 mmol) and triphenylphosphine (2.0 g, 7.6 mmol) in tetrahydrofuran (30 ml) caused the slow formation of a yellow solution. After a 16-hr reflux period, the solution was concentrated and the concentrate was diluted with ether until it became cloudy. Light yellow crystals of $CpW(CO)_3CH_2CH_2P(C_6H_5)_3^+PF_6^-$ separated on standing.

A mixture of $CpW(CO)_3CH_2CH_2P(C_6H_5)_3^+PF_6^-$ (1.0 g), methanol (25 ml), and concentrated hydrochloric acid (5 ml) was refluxed overnight in a nitrogen atmosphere. The resulting black reaction mixture was evaporated to dryness. The black residue was extracted with water. The addition of excess aqueous $H_2B_{12}Cl_{12}$ to the filtered extracts precipitated 0.3 g of a white solid. Proton NMR analysis revealed that this contained $(C_6H_5)_3PCH_2CH_3^+$.

$CpW(CO)_3$-π-$C_2H_3N(CH_3)CH_2CH_2W(CO)_3Cp^+$. A solution of $[CpW(CO)_3CH_2CH_2]_2NCH_3$ (0.43 g, 0.57 mmol) in dichloromethane (10 ml) was added to $Ph_3C^+PF_6^-$ (0.6 g, 1.55 mmol) in dichloromethane (10 ml). A yellow precipitate of $CpW(CO)_3$-π-$C_2H_3N(CH_3)CH_2CH_2W(CO)_3Cp^+PF_6^-$ formed almost immediately (0.37 g, 72%). Anal. Calcd for $C_{21}H_{20}F_6NO_6PW_2$: C, 28.18; H, 2.25; F, 12.74; N, 1.56. Found: C, 28.45; H, 2.45; F, 12.39; N, 1.68. Solubility was too low for a satisfactory NMR spectrum.

$CpW(CO)_3CH_2CH(CN)N(CH_3)CH_2CH_2WCp(CO)_3$. Tetraethylammonium cyanide (0.25 g, 1.8 mmol) was added to a suspension of $CpW(CO)_3$-π-$C_2H_3N(CH_3)CH_2CH_2WCp(CO)_3^+PF_6^-$ (0.45 g, 0.5 mmol) in acetonitrile (10 ml). Dissolution occurred; the mixture was filtered and the filtrate was evaporated to dryness. The residue was extracted with benzene. The addition of hexane to the extract caused the separation of crystalline yellow $CpW(CO)_3CH_2CH(CN)N(CH_3)CH_2CH_2WCp(CO)_3$ (0.05 g, 13%). Anal. Calcd for $C_{22}H_{20}M_2O_6W_2$: C, 34.04; H, 2.60; N, 3.61. Found: C, 34.08; H, 3.09; N, 3.50. The direction of addition of the cyanide is only assumed.

$CpW(CO)_2C(OH)C_2H_4N(H)CH_2CH_2W(CO)_3Cp^+$. A solution of $H_2B_{12}Cl_{12}$[8] (0.6 g, 2.1 mequiv) in water (4 ml) was added to $Cp\overline{W(CO)_2COCH_2CH_2N}(H)CH_2CH_2W(CO)_3Cp$ (0.6 g, 0.81 mmol) in acetone (5 ml). Filtration gave a mixture of orange and yellow solids (starting material plus product). The addition of water to the filtrate precipitated a yellow crystalline product. The original filter cake was again treated with aqueous $H_2B_{12}Cl_{12}$ in acetone and this was repeated until all of the orange starting complex had been converted. The total yield of the crystalline yellow $[Cp\overline{W(CO)_2C(OH)CH_2CH_2N}(H)CH_2CH_2W(CO_3Cp^+]_2B_{12}Cl_{12}^{2-}{\cdot}CH_3COCH_3$ was 0.6 g, 71%. Anal. Calcd for $C_{43}H_{46}B_{12}Cl_{12}N_2O_{13}W_4$: C, 24.71; H, 2.22; N, 1.34; Cl, 20.36. Found: C, 24.48; H, 2.43; N, 1.22; Cl, 19.96. The proton NMR spectrum in pyridine was identical with that of the starting material, $Cp\overline{W(CO)_2COCH_2CH_2N}(H)CH_2CH_2W(CO)_3Cp$, except for the CH_3 groups of acetone. $[CpW(CO)_2C(OH)CH_2CH_2N(H)CH_2CH_2W(CO)_3Cp^+]_2B_{12}Cl_{12}^{2-}$ was recovered from the NMR solution by the addition of water and was identified by infrared analysis.

$CpW(CO)_3CH_2CH_2O^-$. A mixture of tungsten hexacarbonyl (35.5 g, 0.1 mol) and NaC_5H_5 (10.6 g, 0.12 mol) in glyme (1,2-dimethoxyethane, 200 ml) was refluxed overnight in a nitrogen atmosphere. The mixture was filtered. Ethylene oxide was passed through the filtrate for 2 hr. A crystalline yellow solid began to separate after the first hour. Filtration after the reaction period gave 30.8 g (63%) of slightly impure $CpW(CO)_3CH_2CH_2ONa{\cdot}CH_3OCH_2CH_2OCH_3$. A second crop (6.0 g, 12.3%) separated from the filtrate. An analytical sample was obtained by recrystallization from acetone–glyme. Anal. Calcd for $C_{14}H_{19}NaO_6W$: C, 34.31; H, 3.91; Na, 4.69; O, 19.59. Found: C, 34.52; H, 4.04; Na, 5.51; O, 19.65.

$CpW(CO)_3CH_2CH_2OH$. $CpW(CO)_3CH_2CH_2ONa{\cdot}CH_3OCH_2CH_2OCH_3$ (2.0 g, 4.9 mmol) was stirred in acetone (20 ml). Water (4 ml) was added, resulting in almost complete clarification of the solution, which was then filtered. The filtrate was further diluted with water (33 ml), resulting in the slow deposition of needle-shaped crystals of $CpW(CO)_3CH_2CH_2OH$ (1.0 g, 66%). Anal. Calcd for $C_{10}H_{10}O_4W$: C, 31.77; H, 2.67; O, 16.93. Found: C, 32.32; H, 2.78; O, 16.58.

$CpMo(CO)_3CH_2CH_2O^-$. Molybdenum hexacarbonyl (26.4 g, 0.1 mol) and sodium cyclopentadienide (10.6 g, 0.12 mol) were heated in refluxing glyme (200 ml) for 16 hr in a nitrogen atmosphere; the solution was filtered. Evaporation of the filtrate left a bright yellow residue of $NaCpMo(CO)_3$. This was chilled in an ice–water bath and ethylene oxide (300 ml) was condensed onto it. The mixture was stirred overnight during which time the ice–water bath was allowed to warm to room temperature and the ethylene oxide was evaporated. The yellow-orange solid residue was recrystallized by dissolving in warm (not boiling) acetonitrile, filtering, and adding glyme slowly to the filtrate with stirring until crystals started to form. The yield of $CpMo(CO)_3CH_2CH_2ONa{\cdot}CH_3OCH_2CH_2OCH_3$ was 13.9 g, 35%; it was identical by infrared analysis with the material prepared as follows.

Sodium hydride dispersed in oil was added slowly to a solution of $CpMo(CO)_3CH_2CH_2OH$ (1.5 g, 5.2 mmol) in glyme (15 ml) in a nitrogen atmosphere until reaction ceased. The mixture was filtered, and the filter cake was recrystallized from acetonitrile to get $CpMo(CO)_3CH_2CH_2ONa{\cdot}CH_3OCH_2CH_2OCH_3$ (1.04 g, 50%). Anal. Calcd for $C_{14}H_{19}MoNaO_6$: C, 41.80; H, 4.76; Na, 5.71; O, 23.87. Found: C, 42.16; H, 4.98; Na, 6.53; O, 23.50. Treatment of the product with aqueous fluoroboric acid in tetrahydrofuran gave $CpMo(CO)_3C_2H_4^+BF_4^-$.

$CpMo(CO)_3CH_2CH_2OH$. A mixture of NaC_5H_5 (10.6 g, 0.12 mol) and molybdenum hexacarbonyl (26.4 g, 0.1 mol) in glyme (200 ml) was refluxed in a nitrogen atmosphere overnight. The resulting mixture was filtered. Ethylene oxide was bubbled through the filtrate for 2.5 hr. The mixture was again filtered. Ether was added to the filtrate to precipitate 26 g of a solid which was separated and then stirred in water (100 ml) for 5 min in a nitrogen atmosphere. Filtration gave $CpMo(CO)_3CH_2CH_2OH$ (4.0 g, 14%), which was washed four times with water and dried at ambient temperature. This product is somewhat light sensitive and decomposes slowly at 25° with ethylene evolution. Anal. Calcd for $C_{10}H_{10}O_4Mo$: C, 41.40; H, 3.47. Found: C, 41.25; H, 2.89.

$CpW(CO)_3OCH_2CH_2W(CO)_3C_5H_5$ and $CpW(CO)_3CH_2CH_2OCH_2CH_2W(CO)_3Cp$. Three grams (5.9 mmol) of $CpW(CO)_3C_2H_4{}^+PF_6{}^-$ was added to a solution of $CpW(CO)_3CH_2CH_2ONa{\cdot}CH_3OCH_2CH_2OCH_3$ (3.0 g, 7.3 mmol) in acetone (30 ml). The mixture was stirred for 30 min and filtered to get $CpW(CO)_3OCH_2CH_2W(CO)_3Cp$ ("A" 1.15 g, 22%), a yellow crystalline solid. Anal. Calcd for $C_{18}H_{14}O_7W_2$: C, 30.45; H, 1.99; O, 15.77. Found: C, 30.80; H, 2.34; O, 15.05.

The filtrate from the isolation of "A" was allowed to stand an additional 30 min and was then refiltered to obtain $CpW(CO)_3CH_2CH_2OCH_2CH_2W(CO)_3Cp$ ("B" 0.2 g, 4%), also a yellow crystalline solid. Anal. Calcd for $C_{20}H_{18}O_7W_2$: C, 31.69; H, 2.39. Found: C, 31.37; H, 2.77.

The filtrate from the isolation of "B" separated $[CpW(CO)_3]_2$ on further standing.

$CpMo(CO)_3CH_2CH_2OCH_2CH_2W(CO)_3Cp$. Acetone (120 ml), $CpW(CO)_3C_2H_4{}^+PF_6{}^-$ (4.5 g, 8.9 mmol), and $CpMo(CO)_3CH_2CH_2ONa{\cdot}CH_3OCH_2CH_2OCH_3$ (4 g, 10 mmol) were mixed in a nitrogen atmosphere. The mixture was filtered after 10 min. Partial concentration of the filtrate gave a pink solid (2.0 g). The filtrate from the isolation of this solid separated 1.3 g of $[CpMo(CO)_3]_2$ on further standing. The pink solid was recrystallized from methylene chloride–hexane. The lesser soluble fractions were $[CpMo(CO)_3]_2$; the more soluble fraction was $CpMo(CO)_3CH_2CH_2OCH_2CH_2W(CO)_3Cp$, a cream-colored crystalline solid. Anal. Calcd for $C_{20}H_{18}O_7MoW$: C, 36.95; H, 2.79; O, 17.23. Found: C, 36.38; H, 2.75; O, 16.85.

$CpMo(CO)_3CH_2CH_2OCH_2CH_2Fe(CO)_2Cp$. $CpMo(CO)_3CH_2CH_2ONa{\cdot}CH_3OCH_2CH_2OCH_3$ (1.9 g, 4.7 mmol) was added to a mixture of $CpFe(CO)_2C_2H_4{}^+PF_6{}^-$ (1.6 g, 4.6 mmol) and acetonitrile (25 ml). After being stirred for 5 min, the reaction mixture was filtered. Partial concentration of the filtrate gave 1.2 g (53%) of crude $CpMo(CO)_3CH_2CH_2OCH_2CH_2Fe(CO)_2Cp$. Recrystallization of this by dissolution at room temperature in methylene chloride followed by filtration and dilution with hexamethyldisiloxane gave yellow crystals of $CpMo(CO)_3CH_2CH_2OCH_2CH_2Fe(CO)_2Cp$ (0.5 g, 22%). Anal. Calcd for $C_{19}H_{18}O_6FeMo$: C, 46.18; H, 3.67; O, 19.43. Found: C, 45.96; H, 3.66; O, 19.59.

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Registry No. $[CpFe(CO)_2CH_2CH_2]_2NH_2{}^+PF_6{}^-$, 54869-41-9; $[CpFe(CO)_2CH_2CH_2]_2NH_2CN$, 54869-42-0; $CpFe(CO)_2CH_2CH_2N(CH_3)_3{}^+PF_6{}^-$, 54869-44-2; $CpFe(CO)_2CH_2CH_2NC_5H_5{}^+PF_6{}^-$, 54869-60-2; $CpFe(CO)_2CH_2CH_2P(C_6H_5)_3{}^+PF_6{}^-$, 54869-62-4; $CpFe(CO)_2CH_2CH_2CN$, 54869-63-5; $CpFe[P(OPh)_3]_2CH_2CH_2CN$, 54869-64-6; $CpMo(CO)_2COCH_2CH_2NH_2$, 41618-18-2; $[CpMo(CO)_3CH_2CH_2]_2NH_2{}^+PF_6{}^-$, 54869-55-5; $[CpMo(CO)_3CH_2CH_2]_2NH_2Cl$, 54869-56-6; $CpMo(CO)_2COCH_2CH_2N(H)CH_2CH_2Mo(CO)_3Cp$, 54869-53-3; $[CpMo(CO)_3CH_2CH_2]_2NH(CH_3)^+PF_6{}^-$, 54869-58-8; $CpMo(CO)_3CH_2CH_2N(CH_3)_3{}^+PF_6{}^-$, 54869-49-7; $CpMo(CO)_3CH_2CH_2NC_5H_5{}^+PF_6{}^-$, 54869-51-1; $CpMo(CO)_3CH_2CH_2P(C_6H_5)_3{}^+PF_6{}^-$, 54911-56-7; $CpMo(CO)_3CH_2CH_2CN$, 54869-52-2; $[CpW(CO)_3CH_2CH_2]_2NH_2{}^+PF_6{}^-$, 54869-46-4; $[CpW(CO)_3CH_2CH_2]_2NH_2CN$, 54869-47-5; $CpW(CO)_3CH_2CH_2NH_3{}^+PF_6{}^-$, 54869-76-0; $CpW(CO)_2COCH_2CH_2NH_2$, 41618-20-6; $CpW(CO)_2COCH_2CH_2NHCH_2CH_2W(CO)_3Cp$, 54869-86-2; $[CpW(CO)_3CH_2CH_2]_2NHCH_3{}^+PF_6{}^-$, 54869-71-5; $[CpW(CO)_3CH_2CH_2]_2NCH_3$, 54869-70-4; $CpW(CO)_2COCH_2CH_2N(CH_3)CH_2CH_2W(CO)_3Cp$, 54869-85-1; $[CpW(CO)_3CH_2CH_2]_2N(CH_3)_2{}^+PF_6{}^-$, 54869-73-7; $CpW(CO)_3CH_2CH_2N(H)(CH_3)_2{}^+PF_6{}^-$, 54869-84-0; $[CpW(CO)_3CH_2CH_2]_2N(CH_3)_2CN$, 54869-74-8; $CpW(CO)_3CH_2CH_2N(CH_3)_3{}^+PF_6{}^-$, 54869-80-6; $CpW(CO)_3CH_2CH_2NC_5H_5{}^+PF_6{}^-$, 54869-82-8; $CpW(CO)_3CH_2CH_2P(C_6H_5)_3{}^+PF_6{}^-$, 54869-78-2; $CpW(CO)_3\text{-}\pi\text{-}C_2H_3N(CH_3)CH_2CH_2W(CO)_3Cp^+PF_6{}^+$, 54869-66-8; $CpW(CO)_3CH_2CH(CN)N(CH_3)CH_2CH_2WCp(CO)_3$, 54869-67-9; $[CpW(CO)_2C(OH)CH_2CH_2N(H)CH_2CH_2W(CO)_3Cp^+]_2B_{12}Cl_{12}{}^{2-}$, 54869-69-1; $CpW(CO)_3CH_2CH_2ONa$, 54869-39-5; $CpW(CO)_3CH_2CH_2OH$, 54869-38-4; $CpMo(CO)_3CH_2CH_2ONa$, 54869-37-3; $CpMo(CO)_3CH_2CH_2OH$, 54869-36-2; $CpW(CO)_3OCH_2CH_2W(CO)_3Cp$, 54869-35-1; $CpW(CO)_3CH_2CH_2OCH_2CH_2W(CO)_3Cp$, 54869-34-0; $CpMo(CO)_3CH_2CH_2OCH_2CH_2W(CO)_3Cp$, 54869-33-9; $CpMo(CO)_3CH_2CH_2OCH_2CH_2Fe(CO)_2Cp$, 54869-32-8; $CpFe(CO)_2C_2H_4{}^+PF_6{}^-$, 12082-28-9; $CpMo(CO)_3C_2H_4{}^+PF_6{}^-$, 12083-36-2; $CpW(CO)_3C_2H_4{}^+PF_6{}^-$, 12083-42-0; $CpFe[P(OPh)_3]_2C_2H_4{}^+BF_4{}^-$, 33362-33-3; ammonia, 7664-41-7; tetraethylammonium cyanide, 13435-20-6; trimethylamine, 75-50-3; pyridine, 110-86-1; triphenylphosphine, 603-35-0; methylamine, 74-89-5; dimethylamine, 124-40-3.

References and Notes

(1) Cp = η^5-C_5H_5 throughout this paper.

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