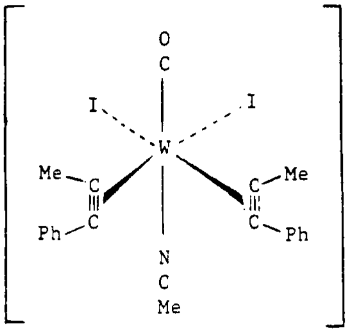

Figure 4. Proposed structure of $[WI_2(CO)(NCMe)(\eta^2\text{-}PhC_2Me)_2]$.

indicated in Figures 1-3. All of the RC_2R type complexes show two sets of R group resonances due to being cis to either carbon monoxide or acetonitrile, except for the bis(*p*-tolyl) complex **9** which shows only one methyl resonance, thus indicating that the methyl groups are too far away from the metal to be affected by other groups coordinated to the metal. All of the other bis PhC_2R complexes show only one R′ resonance indicating that one isomer predominates in these complexes, in accord with infrared spectroscopy. For example, **5** has one C≡CMe resonance at δ −3.12, and it would appear from the crystal structures of **4** and **6** the bond angle involving the group nearest to carbon monoxide is much less and hence on steric grounds it is likely that the methyl groups will be *cis* to the carbon monoxide ligand as shown in Figure 4.

The ^{13}C NMR spectra of both monomeric and dimeric complexes discussed in this paper show alkyne carbon resonances between 194 and 157 ppm which indicates that the alkynes are bonding as rapidly equilibrating 2- and 4-electron donors, each donating an average of three electrons to the metal center. This would allow the complexes to obey the effective atomic number rule which is highly likely because of the diamagnetism of the complexes. Templeton and Ward[2] reported the number of electrons donated by an alkyne can be correlated with the ^{13}C chemical shifts of the coordinated alkyne carbon atoms. The alkyne carbon ^{13}C shifts of complexes **1-9** agrees with the alkynes donating an average of three electrons each to the metal.

Acknowledgment. We thank the SERC for support. We also thank Dr. O. W. Howarth (University of Warwick) for running ^1H and ^{13}C NMR spectra.

Registry No. 1, 111112-42-6; 2, 111187-46-3; 3, 111187-47-4; 4, 111187-48-5; 5, 111187-49-6; 6, 111187-50-9; 7, 111112-43-7; 8, 111112-44-8; 9, 111112-45-9; $[MoI_2(CO)_3(NCMe)_2]$, 102349-56-4; $[Wi_2(CO)_3(NCMe)_2]$, 102382-37-6; MeC_2Me, 503-17-3; MeC_2Ph, 673-32-5; PhC_2Ph, 501-65-5; PhC_2CH_2OH, 1504-58-1; $CH_2ClC_2CH_2Cl$, 821-10-3; *p*-tolC_2*p*-tol, 2789-88-0.

Supplementary Material Available: Tables of remaining dimensions, hydrogen coordinates, and anisotropic thermal parameters in 4 and 6 (8 pages); listings of structure factors (25 pages). Ordering information is given on any current masthead page.

Metal Carbonyl Syntheses. 18.[1] Hydrogen-Bridged Heterobimetallic Complexes: Structural Characterization of $(\eta\text{-}C_5H_5)_2(CO)Nb(\mu\text{-}H)Cr(CO)_5$, $[((\eta\text{-}C_5H_5)_2(CO)Nb)_2(\mu\text{-}H)]^+[Mn(CO)_5]^-$, and $(\eta\text{-}C_5H_5)_2(CO)Ta(\mu\text{-}H)Mn_2(CO)_9$

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Three examples of complexes from the general class $(\eta\text{-}C_5H_5)_2(CO)M(\mu\text{-}H)M'L_n$, where M = Nb or Ta and $M'L_n$ is a 16-electron fragment, have been structurally characterized. Crystal data for $(\eta\text{-}C_5H_5)_2(CO)Nb(\mu\text{-}H)Cr(CO)_5$ (**1a**): monoclinic; space group $P2_1/n$; a = 919.5 (3), b = 1426.4 (6), c = 1316.0 (3) pm; β = 103.44 (3)°; Z = 4; final R = 0.077 for 2766 reflections used. Crystal data for $[((\eta\text{-}C_5H_5)_2(CO)Nb)_2(\mu\text{-}H)]^+[Mn(CO)_5]^-$ (**2a**): orthorhombic; space group $P2_12_12_1$; a = 1358.3 (3), b = 1556.5 (4), c = 1262.2 (2) pm; Z = 8; final R = 0.045 for 3565 reflections used. Crystal data for $(\eta\text{-}C_5H_5)_2(CO)Ta(\mu\text{-}H)Mn_2(CO)_9$ (**3b**): monoclinic; space group $P2_1/a$; a = 1487.2 (3), b = 1075.6 (2), c = 1559.1 (3) pm; β = 114.04 (1)°; Z = 4; final R = 0.052 for 4469 reflections used. Comparison of structural parameters among these and related complexes indicates all members of this class can be viewed as containing three-center, two-electron M-H-M′ bonds, with the 18-electron $(\eta\text{-}C_5H_5)_2(CO)M\text{-}H$ grouping effectively acting as a two-electron donor to the coordinatively unsaturated $M'L_n$ fragment.

Introduction

While interest in metal-metal bonded organotransition metal complexes has never been lacking, in recent years there has been particular activity aimed at synthesis and characterization of heterobimetallic complexes. There are a number of reasons for this attention;[4] prominent among them is the idea that a complex combining an early and

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[1] Part 17: Hughes, R. P.; Rheingold, A. L.; Herrmann, W. A.; Hubbard, J. L. *J. Organomet. Chem.* **1985**, *286*, 361.

[2] (a) Heidelberg. (b) Notre Dame. (c) München.

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[4] Roberts, D. A.; Geoffroy, G. L. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 6, Chapter 40.

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late transition metal might have exceptional potential for catalyzing reactions such as CO hydrogenation.[4,5] In the course of several independent programs we and others have prepared and structurally characterized a large number of bimetallic compounds with the general formula $(\eta\text{-}C_5H_5)_2(CO)M(\mu\text{-}H)M'L_n$, where M is either Nb or Ta and $[M'L_n]$ is a 16-electron fragment. These complexes share a common structural type—apparently a particularly stable one, as they are obtained under a wide range of preparative conditions. In this paper we will report on several systems (including crystallographic details for three complexes) which have not previously been fully described, compare and discuss structural features common to the entire group, and briefly consider some mechanistic aspects of their formation.

Experimental Section

All reactions were carried out under inert atmosphere, using standard Schlenk and glovebox techniques. Reaction solvents were distilled under argon from sodium benzophenone ketyl before use. $(\eta\text{-}C_5H_5)_2NbH_3$[6] and $(\eta\text{-}C_5H_5)_2TaH_3$[7] were prepared by literature routes. Spectra were recorded on the following instruments: IR, Perkin-Elmer 727B and Beckman 4240; NMR, Varian XL-100 and Brucker WH90; MS, Varian 311-A and MAT CH5.

$(\eta\text{-}C_5H_5)_2(CO)Nb(\mu\text{-}H)Cr(CO)_5$ (1a). A solution of 1.0 g (4.5 mmol) of $Cr(CO)_6$ and ca. 1 g (4.4 mmol) of $(\eta\text{-}C_5H_5)_2NbH_3$ in 250 mL of THF was irradiated in a water-cooled vessel, using a Hanovia high-pressure mercury lamp, for 4 h. The resulting deep red solution was evaporated to dryness; the residue was taken up in benzene and chromatographed on silica gel (1:1 benzene/ether; water-cooled colunn). A red band was eluted and evaporated and the residue recrystallized from 3:1 ether/dichloromethane, yielding 0.81 g (40%) dark red crystals: ^1H NMR $(CDCl_3)$ δ 5.20 (10 H, Cp), −19.45 (1 H, Nb*H*Cr); IR (KBr, cm^{-1}) 2032 (m), 1980 (ms), 1972 (ms), 1951 (s), 1936 (s), 1909 (s,sh), 1903 (vs), 1887 (vs), 1848 (m, sh); IR (acetone, cm^{-1}) 2044 (m) 1947 (vs), 1923 (vs), 1883 (s). MS (assignment, *m/e*, relative intensity): P, 444, 0.13; P − CO, 416, 0.01; P − 4CO, 332, 0.14; P − 5CO, 304, 0.40; P − 6CO, 276, 0.21; $Cp_2NbH(CO)$, 252, 0.21; Cp_2NbH, 224, 1.00. Anal. Calcd for $C_{16}H_{11}CrNbO_6$: C, 43.27; H, 2.50. Found: C, 43.12; H, 2.56.

$(\eta\text{-}C_5H_5)_2(CO)Nb(\mu\text{-}H)Mo(CO)_5$ (1b) was prepared analogously in 37% yield: ^1H NMR $(CDCl_3)$ δ 5.19 (10 H, Cp), −15.47 (1 H, NbHMo); ^{13}C NMR (acetone-d_6) δ 184.87 (Nb(CO)), 180.74 (Mo(CO)), 62.55 (Cp); IR (KBr, cm^{-1}) 2055 (m), 1988 (ms), 1974 (ms), 1960 (s,sh), 1937 (s), 1917 (s,sh), 1909 (vs), 1886 (vs), 1846 (m, sh); IR (acetone, cm^{-1}) 2060 (m), 1949 (vs), 1933 (vs), 1893 (ms). MS (assignment, *m/e* for ^{98}Mo, relative intensity): P, 490, 0.01; P − 2CO, 434, 0.01; P − 3CO, 406, 0.01; P − 4CO, 378, 0.01; P − 5CO, 350, 0.09; P − 6CO, 322, 0.04; $Mo(CO)_6$, 266, 0.06; $Cp_2NbH(CO)$, 252, 0.21; Cp_2NbH, 224, 1.00; Cp_2Nb, 223, 0.93. Anal. Calcd for $C_{16}H_{11}MoNbO_6$: C, 39.37; H, 2.28. Found: C, 39.31; H, 2.33.

$(\eta\text{-}C_5H_5)_2(CO)Nb(\mu\text{-}H)W(CO)_5$ (1c) was prepared analogously in 24% yield or, by carrying out the photolysis at −3 °C, in 49% yield: ^1H NMR $(CDCl_3)$ δ 5.24 (10 H, Cp), −15.77 (1 H, NbHW); IR (KBr, cm^{-1}) 2055 (m), 1982 (ms), 1968 (ms), 1951 (s,sh), 1937 (s), 1905 (s,sh), 1898 (vs), 1880 (vs), 1842 (m, sh); IR (acetone, cm^{-1} (m), 1949 (vs), 1921 (vs), 1889 (m). MS (assignment, *m/e*, relative intensity): P, 576, 0.06; P − CO, 548, 0.01; P − 2CO, 520, 0.06; P − 3CO, 492, 0.09; P − 4CO, 464, 0.07; P − 5CO, 436, 0.20; P − 6CO, 408, 0.09; $W(CO)_6$, 352, 0.06; $Cp_2NbH(CO)$, 252, 0.09; Cp_2NbH, 224, 1.00; Cp_2Nb, 223, 0.60. Anal. Calcd. for $C_{16}H_{11}NbO_6W$: C, 33.36; H, 1.93. Found: C, 33.27; H, 1.95.

Table I. Crystallographic Data

	1a	2a	3b
formula	$C_{16}H_{11}CrNbO_6$	$C_{27}H_{21}MnNb_2O_7$	$C_{20}H_{11}Mn_2TaO_{10}$
cryst dimens, mm	0.3 × 0.1 × 0.16	0.5 × 0.3 × 0.1	0.4 × 0.35 × 0.4
cryst system	monoclinic	orthorhombic	monoclinic
space group	$P2_1/n$	$P2_12_12_1$	$P2_1/a$
a, pm	919.5 (3)	1358.3 (3)	1487.2 (3)
b, pm	1426.4 (6)	1556.5 (4)	1075.6 (2)
c, pm	1316.0 (3)	1262.2 (2)	1559.1 (3)
β, deg.	103.44 (3)		114.04 (1)
V, pm^3	1679×10^6	2669×10^6	2277×10^6
Z	4	8	4
ρ_{calcd}, g/cm^3	1.76	1.735	2.05
μ, cm^{-1}	13.11	12.9	58.4
2θ range, deg	0–60.0	3.5–59	3.5–54.9
no. of reflctns used	2766 ($>2.5\sigma$)	3565 ($>3\sigma$)	4469 ($>3\sigma$)
R_{iso}[a]	0.077		
R_{aniso}[a]	0.045	0.040	0.039
R_w[b]	0.051	0.045	0.052

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$; isotropic and anisotropic thermal parameters, respectively. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

$[((\eta\text{-}C_5H_5)_2(CO)Nb)_2(\mu\text{-}H)]^+[Mn(CO)_5]^-$ (2a). A solution of 0.11 g (0.5 mmol) of $(\eta\text{-}C_5H_5)_2NbH_3$ and 0.10 g (0.26 mmol) of $Mn_2(CO)_{10}$ in 10 mL of toluene was irradiated in a Pyrex Schlenk tube cooled in an ice–water bath, using a Rayonet photochemical reactor equipped with seven 15-W GE fluorescent lamps ($\lambda_{max} \approx 3600$ Å). After 50 min the resulting cloudy yellow-brown solution was filtered and stored in the dark at 7 °C. The solution gradually turned dark red and, over about 2 weeks, deposited platelike red crystals, insoluble in nonpolar solvents but readily soluble in acetone or dichloromethane: ^1H NMR (acetone-d_6) δ 5.56 (20 H, Cp), −23.44 (1 H, NbHNb), IR (Nujol, cm^{-1}) 2045 (w), 2010 (s), 1975 (m), 1935 (s), 1900 (m), 1890 (m), 1870 (sh), 1850 (m).

$(\eta\text{-}C_5H_5)_2(CO)Ta(\mu\text{-}H)Mn_2(CO)_9$ (3b). A solution of 0.11 g (0.35 mmol) of $(\eta\text{-}C_5H_5)_2TaH_3$ and 0.14 g (0.37 mmol) of $Mn_2(CO)_{10}$ in 7 mL of toluene was irradiated and filtered as described for **2a**. Prolonged storage at 7 °C afforded no precipitation, but addition of an equal volume of hexanes and cooling to −78 °C for 72 h gave cubic purple crystals, sparingly soluble in nonpolar solvents: IR (Nujol, cm^{-1}) 2075 (sh), 1980 (m), 1960 (s), 1940 (m), 1915 (sh).

X-ray Crystallographic Data. Single crystals of the three complexes **1a**, **2a**, and **3b** were obtained as described above. Collection of data (Syntex diffractometers; Mo Kα radiation, 71.069 pm; ambient temperature) and solution and refinement of structures were all routine except as discussed below; details are summarized in Table I.

Heavy atoms in **1a** were located by means of three-dimensional Patterson and difference Fourier analyses, with positions refined anisotropically. The hydrogen atom bridging the two metal atoms was localized by a separate Fourier map that used only low-angle reflections ($2\theta \leq 24.0°$). The hydrogen atoms of the Cp rings were thus located as well but were not further refined; instead they were assigned fixed positions at C–H = 95 pm.

For **2a**, all heavy atoms were readily located by means of three-dimensional Patterson functions and difference Fourier maps; their positions were refined anisotropically. At this point a new difference Fourier map was constructed by using *only low-angle reflections* ($2\theta \leq 24.7°$), revealing a peak in the expected bridging position (as well as those for Cp hydrogen atoms). A hydride at this position refined well by using the entire data set (whereas several other apparent peaks located near the region between the two Nb atoms did not refine well and had high thermal factors; these were discarded). Cp hydrogens were not refined but instead were assigned fixed positions with C–H = 95 pm and $B_{iso} = 5.0 \times 10^4$ pm^2.

The tantalum atom position in **3b** was determined from a three-dimensional Patterson function, and the remaining heavy atoms (Mn, C, O) were located from a series of difference Fourier maps. After refinement, the bridging hydrogen atom was located from difference Fourier maps without the need to resort to the use of low-angle data; hydrogen positions were treated in the same manner as for **2a**.

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(5) For recent examples and leading references see: Casey, C. P.; Nief, F. *Organometallics* **1985**, *4*, 1218–20. Ferguson, G. S.; Wolczanski, P. T. *Ibid.* **1985**, *4*, 1601–5.

(6) Labinger, J. A.; Wong, K. S. *J. Organomet. Chem.* **1979**, *170*, 373–84.

(7) Green, M. L. H.; McCleverty, J. A.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1961**, 4854–9.

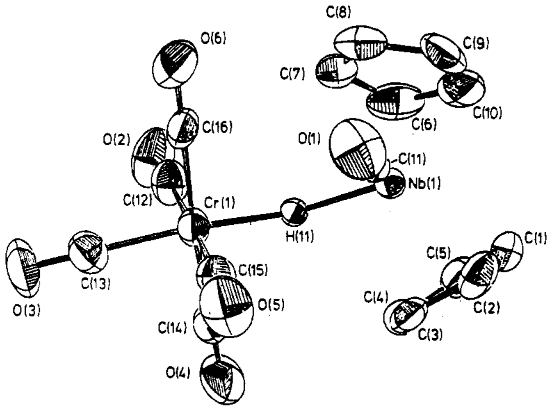

Figure 1. Molecular structure of $(\eta\text{-}C_5H_5)_2(CO)Nb(\mu\text{-}H)Cr(CO)_5$ (**1a**).

Table II. Fractional Atomic Coordinates for 1a[a]

atom	*x*	*y*	*z*
Nb	0.13108 (9)	0.16449 (6)	0.16117 (6)
Cr	−0.11957 (17)	0.06945 (11)	0.29140 (12)
C(1)	0.3867 (12)	0.1499 (9)	0.1633 (9)
C(2)	0.3779 (10)	0.1830 (8)	0.2624 (7)
C(3)	0.3112 (10)	0.1125 (8)	0.3068 (7)
C(4)	0.2873 (11)	0.0344 (7)	0.2385 (9)
C(5)	0.3324 (11)	0.0605 (8)	0.1493 (8)
C(6)	0.0169 (15)	0.1385 (9)	−0.0187 (8)
C(7)	−0.0980 (11)	0.1737 (9)	0.0219 (7)
C(8)	−0.0622 (13)	0.2624 (8)	0.0612 (8)
C(9)	0.0770 (14)	0.2869 (8)	0.0391 (8)
C(10)	0.1213 (14)	0.2110 (9)	−0.0120 (8)
C(11)	0.1108 (12)	0.2690 (6)	0.2645 (8)
O(1)	0.1034 (9)	0.3305 (5)	0.3123 (6)
C(12)	−0.2481 (12)	0.0112 (8)	0.1781 (8)
O(2)	−0.3312 (9)	−0.0258 (7)	0.1115 (6)
C(13)	−0.2474 (12)	0.0313 (7)	0.3738 (8)
O(3)	−0.3256 (9)	0.0068 (6)	0.4240 (6)
C(14)	−0.0063 (12)	−0.0416 (7)	0.3233 (8)
O(4)	0.0641 (10)	−0.1088 (6)	0.3435 (7)
C(15)	0.0028 (11)	0.1305 (7)	0.4072 (7)
O(5)	0.0701 (9)	0.1696 (6)	0.4807 (5)
C(16)	−0.2179 (9)	0.1842 (6)	0.2591 (8)
O(6)	−0.2768 (8)	0.2569 (6)	0.2438 (7)

[a] Estimated standard deviations are given in parentheses.

Table III. Selected Molecular Parameters for 1a

	Bond Lengths, pm		
Nb–Cr	345.3 (2)	Cr–C(15)	188.4 (9)
Cr–H	188.2 (102)	Cr–C(16)	187.0 (9)
Nb–H	182.4 (99)	C(12)–O(2)	114.8 (12)
Nb–C(11)	205.5 (10)	C(13)–O(3)	114.0 (15)
C(11)–O(1)	116.4 (12)	C(14)–O(4)	135.2 (13)
Cr–C(12)	186.9 (10)	C(15)–O(5)	116.3 (11)
Cr–C(13)	185.6 (12)	C(16)–O(6)	116.6 (12)
Cr–C(14)	188.8 (10)	Nb–P(1)	206.9
		Nb–P(2)	206.9
	Bond Angles, deg		
Nb–H–Cr	137.4 (53)	C(12)–Cr–C(14)	177.5 (5)
H–Nb–C(11)	99.1	C(12)–Cr–C(15)	91.4 (4)
Nb–C(11)–O(1)	177.1 (9)	C(12)–Cr–C(16)	91.4 (4)
P(1)–Nb–P(2)[a]	138.35	C(13)–Cr–C(14)	90.9 (5)
Cr–C(12)–O(2)	176.8 (10)	C(13)–Cr–C(15)	90.2 (4)
Cr–C(13)–O(3)	179.2 (9)	C(13)–Cr–C(16)	92.9 (5)
Cr–C(14)–O(4)	179.3 (10)	C(14)–Cr–C(15)	90.7 (4)
Cr–C(15)–O(5)	175.7 (10)	C(14)–Cr–C(16)	175.5 (4)
Cr–C(16)–O(6)	176.9 (9)	C(15)–Cr–C(16)	86.9 (4)
C(12)–Cr–C(13)	88.1 (5)		

[a] P(1) and P(2) are Cp ring centroids.

Molecular structures for the three complexes are shown in Figures 1–3, respectively; in all cases thermal ellipsoids represent 50% probability. Atom positions and selected parameters are

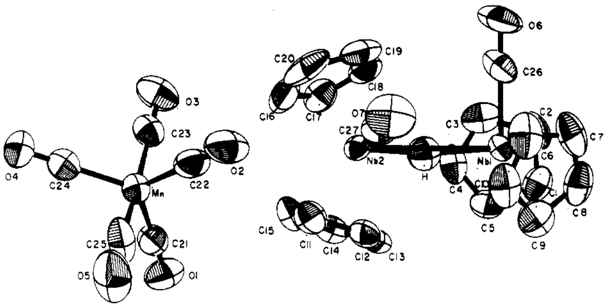

Figure 2. Molecular structure of $[((\eta\text{-}C_5H_5)_2(CO)Nb)_2(\mu\text{-}H)]^+[Mn(CO)_5]^-$ (**2a**).

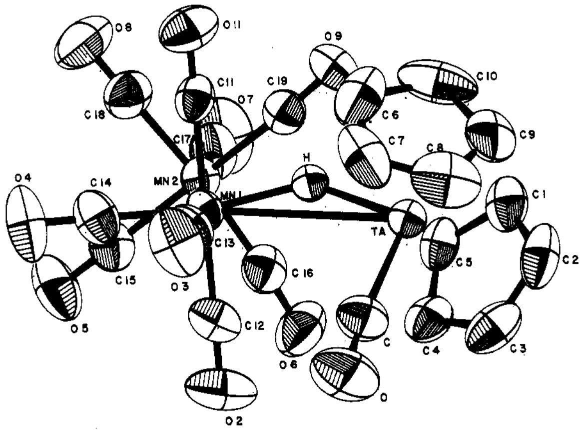

Figure 3. Molecular structure of $(\eta\text{-}C_5H_5)_2(CO)Ta(\mu\text{-}H)Mn_2(CO)_9$ (**3b**).

Table IV. Fractional Atomic Coordinates for 2a[a]

atom	*x*	*y*	*z*
Nb(1)	−0.03393 (3)	0.09918 (3)	0.02133 (4)
Nb(2)	−0.08662 (3)	−0.13461 (3)	−0.03400 (4)
Mn	−0.11780 (6)	−0.51704 (5)	−0.03844 (7)
C(1)	0.0843 (4)	0.1898 (4)	−0.0538 (5)
C(2)	−0.0055 (6)	0.2115 (4)	−0.0988 (5)
C(3)	−0.0354 (5)	0.1388 (5)	−0.1607 (4)
C(4)	0.0377 (6)	0.0769 (4)	−0.1513 (4)
C(5)	0.1103 (4)	0.1064 (4)	−0.0866 (5)
C(6)	−0.1053 (7)	0.0809 (5)	0.1875 (6)
C(7)	−0.0801 (7)	0.1677 (5)	0.1769 (6)
C(8)	0.0186 (7)	0.1722 (5)	0.1741 (5)
C(9)	0.0595 (6)	0.0879 (6)	0.1842 (5)
C(10)	−0.0234 (7)	0.0338 (4)	0.1941 (5)
C(11)	−0.0039 (5)	−0.2528 (4)	0.0386 (6)
C(12)	0.0364 (5)	−0.1800 (4)	0.0874 (5)
C(13)	0.0858 (4)	−0.1348 (4)	0.0098 (6)
C(14)	0.0764 (5)	−0.1779 (4)	−0.0862 (5)
C(15)	0.0184 (5)	−0.2511 (4)	−0.0674 (6)
C(16)	−0.1724 (6)	−0.2015 (5)	−0.1744 (7)
C(17)	−0.1396 (5)	−0.1247 (5)	−0.2161 (5)
C(18)	−0.1847 (5)	−0.0588 (5)	−0.1633 (6)
C(19)	−0.2459 (5)	−0.0920 (6)	−0.0856 (6)
C(20)	−0.2399 (6)	−0.1841 (6)	−0.0934 (7)
C(21)	0.0030 (5)	−0.4855 (4)	−0.0815 (5)
O(1)	0.0825 (3)	−0.4659 (4)	−0.1080 (4)
C(22)	−0.1733 (5)	−0.4525 (5)	0.0635 (5)
O(2)	−0.2099 (4)	−0.4120 (5)	0.1287 (4)
C(23)	−0.1853 (4)	−0.4526 (4)	−0.1349 (5)
O(3)	−0.2305 (4)	−0.4121 (3)	−0.1926 (4)
C(24)	−0.1749 (5)	−0.6111 (4)	−0.0992 (6)
O(4)	−0.2112 (4)	−0.6699 (3)	−0.1359 (5)
C(25)	−0.0665 (7)	−0.5835 (4)	0.0649 (5)
O(5)	−0.0297 (7)	−0.6236 (4)	0.1303 (5)
C(26)	−0.1779 (5)	0.1243 (4)	−0.0072 (7)
O(6)	−0.2611 (3)	0.1399 (4)	−0.0237 (6)
C(27)	−0.1626 (5)	−0.1421 (5)	0.1066 (6)
O(7)	−0.2064 (4)	−0.1502 (4)	0.1829 (5)
H	−0.043 (4)	−0.019 (4)	−0.032 (5)

[a] Estimated standard deviations are given in parentheses.

Table V. Selected Molecular Parameters for 2a

	Bond Lengths, pm		
Nb(1)–Nb(2)	377.4 (1)	Mn–C(21)	179.7 (6)
Nb(1)–H	196 (6)	Mn–C(22)	179.8 (7)
Nb(2)–H	190 (6)	Mn–C(23)	182.4 (7)
Nb(1)–C(26)	202.6 (6)	Mn–C(24)	182.6 (7)
Nb(2)–C(27)	205.6 (7)	Mn–C(25)	180.5 (7)
C(26)–O(6)	117.4 (7)	C(21)–O(1)	117.0 (7)
C(27)–O(7)	114.0 (8)	C(22)–O(2)	114.9 (8)
Nb(1)–P(1)[a]	205.5	C(23)–O(3)	114.2 (7)
Nb(1)–P(2)	205.3	C(24)–O(4)	113.8 (8)
Nb(2)–P(3)	206.0	C(25)–O(5)	114.9 (9)
Nb(2)–P(4)	206.1		
	Bond Angles, deg		
Nb(2)–H–Nb(1)	156.0 (35)	Mn–C(24)–O(4)	179.1 (7)
H–Nb(1)–C(26)	93.5 (17)	Mn–C(25)–O(5)	176.6 (8)
H–Nb(2)–C(27)	101.5 (18)	C(21)–Mn–C(22)	116.5 (3)
C(26)–Nb(1)–Nb(2)	88.3 (2)	C(21)–Mn–C(23)	96.2 (3)
C(27)–Nb(2)–Nb(1)	89.4 (2)	C(21)–Mn–C(24)	118.7 (3)
Nb(1)–C(26)–O(1)	179.2 (6)	C(21)–Mn–C(25)	91.3 (3)
Nb(2)–C(27)–O(2)	176.5 (7)	C(22)–Mn–C(23)	87.7 (3)
P(1)–Nb(1)–P(2)	139.1	C(22)–Mn–C(24)	124.8 (3)
P(3)–Nb(2)–P(4)	139.0	C(22)–Mn–C(25)	88.0 (3)
Mn–C(21)–O(1)	178.7 (6)	C(23)–Mn–C(24)	86.9 (3)
Mn–C(22)–O(2)	179.0 (7)	C(23)–Mn–C(25)	172.4 (3)
Mn–C(23)–O(3)	177.4 (5)	C(24)–Mn–C(25)	90.4 (3)

[a] P(*n*)'s are the Cp ring centroids.

Table VI. Fractional Atomic Coordinates for 3b[a]

atom	*x*	*y*	*z*
Ta	0.22700 (2)	0.15806 (2)	0.32338 (2)
Mn(1)	0.20562 (7)	−0.14458 (8)	0.24609 (7)
Mn(2)	0.30186 (7)	−0.16449 (8)	0.11528 (7)
C(1)	0.3186 (5)	0.2962 (7)	0.2673 (6)
C(2)	0.3319 (6)	0.3352 (7)	0.3579 (7)
C(3)	0.3810 (5)	0.2429 (9)	0.4210 (6)
C(4)	0.3978 (5)	0.1431 (7)	0.3691 (5)
C(5)	0.3607 (5)	0.1795 (6)	0.2760 (5)
C(6)	0.0527 (6)	0.1388 (9)	0.2342 (8)
C(7)	0.0695 (6)	0.1323 (8)	0.3241 (9)
C(8)	0.1070 (6)	0.245 (1)	0.3660 (6)
C(9)	0.1152 (6)	0.3185 (7)	0.3034 (7)
C(10)	0.0820 (6)	0.254 (1)	0.2176 (6)
C(11)	0.0929 (5)	−0.1195 (6)	0.1409 (5)
O(11)	0.0217 (4)	−0.1042 (6)	0.0760 (4)
C(12)	0.3254 (6)	−0.1697 (7)	0.3425 (6)
O(12)	0.3983 (5)	−0.1856 (7)	0.4054 (4)
C(13)	0.1421 (6)	−0.1576 (6)	0.3205 (5)
O(13)	0.1025 (5)	−0.1724 (5)	0.3689 (5)
C(14)	0.1929 (6)	−0.3087 (7)	0.2259 (6)
O(14)	0.1814 (5)	−0.4147 (5)	0.2173 (5)
C(21)	0.4097 (5)	−0.1019 (7)	0.2112 (5)
O(21)	0.4841 (4)	−0.0699 (5)	0.2695 (4)
C(22)	0.3577 (7)	−0.1506 (7)	0.0318 (6)
O(22)	0.3944 (6)	−0.1394 (6)	−0.0191 (5)
C(23)	0.1907 (6)	−0.2407 (7)	0.0309 (5)
O(23)	0.1241 (4)	−0.2873 (6)	−0.0235 (5)
C(24)	0.2398 (5)	−0.0131 (6)	0.0843 (4)
O(24)	0.2000 (4)	0.0782 (5)	0.0596 (3)
C(25)	0.3480 (6)	−0.3208 (7)	0.1599 (5)
O(25)	0.3759 (5)	−0.4174 (5)	0.1869 (5)
C	0.2601 (5)	0.0670 (7)	0.4469 (5)
O	0.2782 (5)	0.0276 (7)	0.5198 (4)
H	0.207 (4)	0.020 (5)	0.241 (4)

[a] Estimated standard deviations are given in parentheses.

Table VII. Selected Molecular Parameters for 3b

	Bond Lengths, pm		
Ta–Mn(1)	344.1 (1)	Mn(2)–C(16)	181.2 (8)
Ta–H	191 (5)	Mn(2)–C(17)	183.4 (7)
H–Mn(1)	177 (5)	Mn(2)–C(18)	183.7 (7)
Ta–C	203.5 (7)	Mn(2)–C(19)	184.2 (7)
C–O	113.8 (8)	C(11)–O(1)	114.0 (8)
Ta–P(1)[a]	205.9	C(12)–O(2)	114.0 (9)
Ta–P(2)	205.3	C(13)–O(3)	114.3 (9)
Mn(1)–Mn(2)	293.8 (1)	C(14)–O(4)	115.3 (9)
Mn(1)–C(11)	182.5 (7)	C(15)–O(5)	116.2 (8)
Mn(1)–C(12)	182.3 (8)	C(16)–O(6)	114.0 (10)
Mn(1)–C(13)	177.3 (7)	C(17)–O(7)	112.6 (8)
Mn(1)–C(14)	178.9 (8)	C(18)–O(8)	113.0 (7)
Mn(2)–C(15)	181.8 (8)	C(19)–O(9)	113.5 (8)
	Bond Angles, deg		
Mn(1)–H–Ta	138.2 (3)	Mn(1)–Mn(2)–C(16)	170.9 (2)
H–Ta–C	100.2 (16)	Mn(1)–Mn(2)–C(17)	88.8 (2)
C–Ta–Mn(1)	80.1 (2)	Mn(1)–Mn(2)–C(18)	77.5 (2)
Ta–C–O	173.0 (7)	Mn(1)–Mn(2)–C(19)	90.0 (2)
P(1)–Ta–P(2)	135.4	C(15)–Mn(2)–C(16)	92.9 (4)
Ta–Mn(1)–Mn(2)	108.09 (3)	C(15)–Mn(2)–C(17)	172.1 (4)
Ta–Mn(1)–C(11)	95.4 (2)	C(16)–Mn(2)–C(17)	93.7 (4)
Ta–Mn(1)–C(12)	86.1 (2)	C(16)–Mn(2)–C(18)	93.8 (3)
Ta–Mn(1)–C(13)	81.0 (2)	C(16)–Mn(2)–C(19)	97.9 (3)
Ta–Mn(1)–C(14)	169.4 (2)	C(17)–Mn(2)–C(18)	90.0 (3)
Mn(2)–Mn(1)–C(11)	85.2 (2)	C(18)–Mn(2)–C(19)	168.1 (3)
Mn(2)–Mn(1)–C(12)	88.4 (3)	Mn(1)–C(11)–O(1)	179.0 (6)
Mn(2)–Mn(1)–C(13)	170.9 (2)	Mn(1)–C(12)–O(2)	177.0 (8)
Mn(2)–Mn(1)–C(14)	81.5 (2)	Mn(1)–C(13)–O(3)	176.5 (6)
C(11)–Mn(1)–C(12)	173.6 (3)	Mn(1)–C(14)–O(4)	175.0 (7)
C(11)–Mn(1)–C(13)	93.5 (3)	Mn(2)–C(15)–O(5)	173.1 (6)
C(12)–Mn(1)–C(14)	89.8 (4)	Mn(2)–C(16)–O(6)	178.2 (8)
C(13)–Mn(1)–C(14)	89.5 (3)	Mn(2)–C(17)–O(7)	177.2 (8)
Mn(1)–Mn(2)–C(15)	85.3 (2)	Mn(2)–C(18)–O(8)	175.7 (6)
		Mn(2)–C(19)–O(9)	179.5 (7)

[a] P(*n*)'s are the Cp ring centroids.

presented in Tables II–VII. Other data are available as supplementary material.

Results and Discussion

The $(\eta\text{-}C_5H_5)_2NbH_3$–$M(CO)_6$ (M = Cr, Mo, W) System. Photochemical reaction of $(\eta\text{-}C_5H_5)_2NbH_3$ (**4a**) with $M(CO)_6$ proceeds analogously, both in stoichiometry and presumably in mechanism (vide infra), to the previously-demonstrated reactions of **4a** with $(\eta\text{-}C_5H_5)M(CO)_4$ (M = V, Nb, Ta)[8,9] and $(\eta\text{-}C_5H_5)Mn(CO)_3$.[10] The hydrogen-bridged bimetallic compounds $(\eta\text{-}C_5H_5)_2(CO)Nb(\mu\text{-}H)M(CO)_5$ (**1a–c**) are obtained in 25–50% yields. (**1b** and **1c** have also been prepared by a thermal reaction;[11] the tantalum analogs have also been reported.[12] All three are quite air-sensitive in solution but briefly stable to air as solids, although on prolonged storage even under N_2 they show some decomposition (especially **1b**). IR, NMR, and MS properties are all unexceptional (see Experimental Section). Only four IR peaks are observed in solution, although the low symmetry of the molecules could result in up to six; the appearance of nine bands in KBr is presumably due to solid-state effects. Ions corresponding to both CO loss and metal–metal bond cleavage are observed, along with the parent ions, in the MS.

The crystallographic structure determination for **1a** verifies that these compounds are indeed of the class $(\eta\text{-}C_5H_5)_2(CO)M(\mu\text{-}H)M'L_n$. The structure is shown in Figure 1 and is completely typical of structures determined previously for other members of this class; features of particular interest will be discussed in the context of the general class, below.

The $(\eta\text{-}C_5H_5)_2MH_3$–$Mn_2(CO)_{10}$ (M = Nb, Ta) System. **4a** reacts readily with $Co_2(CO)_8$ at room temperature to

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produce $(\eta\text{-}C_5H_5)_2(CO)Nb(\mu\text{-}CO)Co(CO)_3$.[13,14] We anticipated that the isoelectronic Mn analogue, $(\eta\text{-}C_5H_5)_2(CO)Nb(\mu\text{-}CO)Mn(CO)_4$, should form similarly (it has since been prepared by an alternate route[15]). However, the thermal reaction between **4a** and $Mn_2(CO)_{10}$ proceeds relatively slowly (ca. 30 min at 40 °C for completion) and gives only the monometallic $(\eta\text{-}C_5H_5)_2NbH(CO)$ (**5a**).[11] To test the possibility that the desired bimetallic complex does form but is not stable at elevated temperature, we attempted a photochemical synthesis; however, this led to unexpected and highly complex behavior.

Irradiation of a toluene solution of **4a** and $Mn_2(CO)_{10}$ produces a yellow-brown solution from which no characterizable product could be isolated. On standing *in the dark*, though, the solution turns dark red and precipitates **2a** as plates (or, occasionally, as an oil).[16] The solubility properties of **2a** suggest that it is an ionic compound; this is confirmed by the crystal structure (Figure 2) which shows it to be $[((\eta\text{-}C_5H_5)_2Nb(CO))_2(\mu\text{-}H)]^+[Mn(CO)_5]^-$. At first sight it is not clear that the cation should be included in the general class of structures $(\eta\text{-}C_5H_5)_2(CO)M(\mu\text{-}H)\text{-}M'L_n$; a more logical description would be based upon the (unknown) simple dimer of two 17-electron fragments, $(\eta\text{-}C_5H_5)_2(CO)Nb\text{-}Nb(CO)(\eta\text{-}C_5H_5)_2$, protonated at the Nb–Nb bond. However, several considerations suggest that the alternative formulation is in fact a better representation of the bonding in **2a**. In particular, the bridging hydrogen is asymmetrically placed with respect to the two Nb atoms. The difference in Nb–H bond lengths (Nb(2)–H = 190 (6) pm; Nb(1)–H = 196 (6) pm) is not really statistically significant, but the bridging H lies essentially *within* the equatorial plane (defined by the two Nb atoms and the CO group attached to the Nb) of Nb(2) and well *outside* the corresponding plane of Nb(1). (The displacements of the H atom from the two planes are respectively 5 (2) and 36 (2) pm.) In all previous examples of this class (see below), the Nb, H, and CO of the "donor" group are coplanar with the metal atom of the "acceptor". The Nb–C(O) distances are also unequal (Nb(1)–C = 202.6 (7) pm; Nb(2)–C = 205.6 (7) pm), again supporting an asymmetric bonding picture.

We thus describe the molecule, in analogy to the others of this class, as consisting of the 18-electron group **5a** (Nb(2)) acting as a two-electron donor, via the Nb–H bonding pair, to the 16-electron fragment $[(\eta\text{-}C_5H_5)_2Nb(CO)]^+$ (Nb(1)); the latter has previously been generated as an unstable intermediate.[17] It should be noted that the asymmetry observed in the solid-state structure does not persist in solution, at least on the NMR time scale: a single signal for the Cp hydrogens is observed. One might argue that the asymmetry is in fact a consequence of crystal packing forces rather than any inherent bonding preference. A useful analogy can be drawn to the trihalide ions, X_3^-, which can be given a similar asymmetric description (X^- as donor to X_2); both symmetric and asymmetric structures are observed depending upon the counterion.[18] In any case, since the structure of **2a** *can* be described within the general framework, further details will be reserved for the general discussion below.

The geometry of the $[Mn(CO)_5]^-$ anion is unexceptional: there are no close interactions with the cation, and parameters are fairly similar to those previously found with other counterions,[19] except that there is somewhat more distortion from regular trigonal-bipyramidal geometry.

Similar treatment of a solution $(\eta\text{-}C_5H_5)_2TaH_3$ (**4b**) and $Mn_2(CO)_{10}$—photolysis followed by storage in the dark at reduced temperature—gave no ionic precipitate. Instead purple crystals of a compound with quite different solubility and spectral properties were precipitated by addition of hexane and prolonged cooling. The structure of this compound, **3b**,[20] is shown in Figure 3; it is also a member of the general structure class but with the bimetallic, 34-electron fragment $Mn_2(CO)_9$ functioning as the "acceptor" group. The donor group **5b** effectively occupies an equatorial position of the resulting $Mn_2(CO)_9L$ moiety, analogous to the previously known, isoelectronic $HRe_2Mn(CO)_{14}$[21] and $HRe_3(CO)_{14}$[22] which with the present molecule provide examples of the relatively rare *bent*, open trimetallic structure.

Details of the TaHMn grouping will be discussed later; the remaining features of the molecule are rather unexceptional. The equatorial CO groups of the Mn_2 unit are staggered and bent somewhat towards each other (average $C_{ax}\text{-}Mn(2)\text{-}C_{eq}$ angle = 94.6°), as is typical for related species.[21-23] The Ta–Mn–Mn angle is fairly obtuse, 108.09 (3)°, presumably for steric reasons, while the Mn–Mn distance of 239.8 (1) pm is slightly longer than that in $Mn_2(CO)_{10}$[23] or $[Mn_3(CO)_{14}]^-$.[22] The average Mn–C distance for CO's trans to another CO (183.0 pm) is longer than for those trans to a metal atom (179.1 pm), as would be expected considering relative competition for back-bonding electron density.

For both Nb and Ta, a red compound with spectroscopic and analytical similarities to **3b** could be precipitated from the reaction mixtures by addition of hexane, but large crystals could not be obtained. An attractive possibility is that these are the *linear* isomer of **3b**; note that $[Mn_3(CO)_{14}]^-$ is linear, and it has been suggested that the relative stability of these two forms depends upon a delicate balance of steric and electronic factors.[22] Furthermore, a purple Nb compound was obtained during attempted recrystallization of the above red compound from ether; this was thought to be **3a**, the Nb analogue of **3b**; however, on dissolution in acetone it rapidly changed color and produced ionic compound **2a**. Under no conditions could **3b** be converted to an ionic species. Additional work will be needed for conclusive structural identification of these species.

Bonding in the M–H–M Unit. As discussed previously,[9,10,15,24] all structural parameters support the description of the bonding in these complexes in terms of a three-center, two-electron Nb–H–M′ bond, rather than as a metal–metal bond "supported by" a bridging hydrogen

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Table VIII. MHM′ Parameters for $(\eta\text{-}C_5H_5)_2(CO)Nb(\mu\text{-}H)M'L_n$

$M'L_n$	Nb–H[a]	M′–H[a]	NbHM′[b]	M–M[a]	Σr[c]	Δl[d]	ref
$CpV(CO)_3$[e]	196 (16)	166 (18)	164 (8)	371.3 (4)	315	56	7
$CpNb(CO)_3$[e]	186 (20)	190 (20)	166 (10)	373.3 (3)	332	41	7
$Cp_2Nb(CO)^+$ (**2a**)	190 (6)	196 (6)	156 (4)	377.4 (1)	332	45	this work
$Cr(CO)_5$ (**1a**)	182 (10)	188 (10)	137 (5)	345.3 (2)	312	33	this work
$Mo(CO)_4$[f]	179	205	137	357.2 (2)	324	33	13
$CpMn(CO)_2$	198 (8)	156 (8)	141 (5)	333.0 (2)	304	29	8
$Mn_2(CO)_9$ (**3b**)[g]	191 (5)	177 (5)	138 (3)	344.1 (1)	305	39	this work
$Fe(CO)_4$	191 (3)	161 (3)	141 (2)	332.4 (1)	300	32	22
$Ni(CO)_3$	183	168	133	321.8	301	21	13

[a] Bond lengths in pm. [b] Bond angles in deg. [c] Sum of covalent radii of Nb (Ta) and M′ from M–Cp distances: Andrianov, V. G.; Biryukov, B. P.; Struchkov, Yu. T. *Zh. Strukt. Khim.* **1969**, *10*, 1129. [d] Difference between sum of radii and measured bond lengths. [e] Two crystallographically independent molecules in structure; values are averaged. [f] Two Nb–H groups per Mo; values are averaged. [g] Ta complex.

Table IX. Hydrogen Displacements in $(\eta\text{-}C_5H_5)_2(CO)Nb(\mu\text{-}H)M'L_n$

$M'L_n$	$(NbH\text{–}M'H)_{exptl}$[a]	$(NbH\text{–}M'H)_{calcd}$[b]	Δ(H)[c]
$CpV(CO)_3$	30	17	−13
$CpNb(CO)_3$	−4	0	4
$[Cp_2Nb(CO)]^+$	−6	0	6
$Cr(CO)_5$	−6	20	26
$Mo(CO)_4$	−26	8	34
$CpMn(CO)_2$	42	28	−14
$Mn_2(CO)_9$	14	28	14
$Fe(CO)_4$	30	32	2
$Ni(CO)_3$	15	36	21

[a] See Table VIII for data and explanatory footnotes. [b] Based on covalent radii from references cited in Table VIII. [c] Displacement of H *toward* Nb of $(\eta\text{-}C_5H_5)_2NbH(CO)$ group.

(i.e., a three-center, four-electron bond). The clearest evidence is that of the Nb–M′ bond lengths, which are systematically longer by 20–50 pm than single-bonded M–M bond lengths predicted from covalent radii (Table VIII). By way of contrast, in two heterobimetallic complexes involving similar metal environments but containing a semibridging CO instead of a bridging hydrogen, observed bond lengths are *greater* by 4 pm in $(\eta\text{-}C_5H_5)_2(CO)Nb(\mu\text{-}CO)Co(CO)_3$[13] and 13 pm in $(\eta\text{-}C_5H_5)_2(CO)Nb(\mu\text{-}CO)Mn(CO)_4$[15] than the sums of the covalent radii. This picture is also consistent with electronic structure, in that each of these molecules may be hypothetically decomposed into the 18-electron $(\eta\text{-}C_5H_5)_2NbH(CO)$ unit plus a 16-electron fragment $M'L_n$; there is thus only one low-lying empty orbital available for the intermetallic bonding and only a two-electron bond is thus possible. The same situation appears to apply to all such compounds containing a single bridging hydrogen and no other bridging ligand.[25]

Can one conceive of a structure in which the bridging hydrogen would be "in addition to" the metal–metal bond? Consider the structure of "titanocene", $(CpTiH)_2(\mu\text{-}C_{10}H_8)$. Ignoring the C–C bond in the fulvalenide unit, this is equivalent to $(Cp_2TiH)_2$, a dimer of two 15-electron fragments. A simple Ti–Ti bonded structure would thus have a vacant orbital in addition to the filled Ti–H bonding orbital on each Ti, and the doubly H-bridged structure should result, as is the case.[26] In contrast, the analogous molybdenum compound combines two 17-electron fragments; there are no available vacant orbitals, explaining the observed nonbridged structure.[27] If one could make the mixed compound $(CpTiH)(CpMoH)(\mu\text{-}C_{10}H_8)$, then it should contain a three-center, four-electron TiHMo unit. The crystal structure of $(CpTiH)_2(\mu\text{-}C_{10}H_8)$ has never been obtained.

$(\eta\text{-}C_5H_5)_2(CO)Nb\text{–}H$ as a Ligand. We have repeatedly described these compounds as a sort of adduct, with the $(\eta\text{-}C_5H_5)_2NbH(CO)$ unit acting as a two-electron donor toward the coordinatively unsaturated fragment $M'L_n$. Is this a meaningful picture? Several common structural features suggest that it is:

i. The geometry about Nb is quite similar to that in the parent **5a**;[28] in particular, the grouping Nb–H–CO remains a plane of local symmetry, bisecting the angle made by the two ring centroids and Nb. The M′ atom occupies a position within this plane, where it is best placed to accept electron density from the Nb–H bonding orbital. In principle M′ could have been located either between the H and CO, as is found in all cases, or *outside* the H; besides any orbital reasons for favoring the former, the latter is much more sterically hindered because of the wedge-shaped Cp_2M arrangement.

ii. The bridging hydrogen atom is systematically closer to the Nb, relative to M′, than covalent radii would predict (Table IX). This is not as strong an argument for several reasons: the uncertainties in M–H distances are generally larger than the calculated displacement; the validity of the set of covalent radii used may be open to question (the two Nb–Nb dimers are not subject to this problem, however); and the general propensity of X-ray methods to distort *absolute* M–H distances[29] may well have a systematic effect on *relative* distances as well. Nonetheless, with only two exceptions, the bridging H appears to reside closer to the Nb than would be expected for a "symmetric" M–H–M′ bonding picture.

iii. The geometry about M′ is just what one would expect for $XM'L_n$ if **5a** is taken to be a monodentate ligand ("X") located at the midpoint of the Nb–H bond, as shown by comparisons to the corresponding carbonyl complexes. With the exception of the X–Mn–Mn angle in **3b** (which should be the one most affected by steric crowding), all angles are quite close to those observed in the appropriate model complexes (Table X).

Viewing **5a** as an η^2(Nb–H)-ligand, these complexes might be considered as models for the so-called agostic interaction[30] M–(η^2-R_3C-H) which has been proposed for intermediates leading to intermolecular activation of alkanes,[31] although direct observation has only been possible for intramolecular situations. It will be interesting to see

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Table X. Some Geometrical Parameters in Complexes "$XM'L_n$"

$M'L_n$ [a]	X–M′ [b]	bond angles,[c] deg		model	angles,[d] deg
$CpV(CO)_3$	279.7				
$CpNb(CO)_3$	281.5				
$[Cp_2Nb(CO)]^+$	285.5	X–Nb–C	93.5	$[Cp_2V(CO)_2]^+$ [e]	92
$Cr(CO)_5$	262.7	X–Cr–C_t	180	$Cr(CO)_6$	180
		X–Cr–C_c	87.9		90
			88.2		
			88.8		
			92.9		
$Mo(CO)_4$	291.2				
	279.0				
$CpMn(CO)_2$	240.5	X–Mn–C	89.1	$CpMn(CO)_3$	91
			89.8		94
					91
$Mn_2(CO)_9$	256.5	X–Mn–Mn	102.5	$Mn_2(CO)_{10}$ [g]	86.4
		X–Mn–C_t	176.5		172.6
		X–Mn–$C_{c,a}$	86.5		93.6
		X–Mn–$C_{c,e}$	90.5		89.8
			90.4		
$Fe(CO)_4$	243.1	X–Fe–C_a	177.5	$Fe(CO)_5$	180
		X–Fe–C_e	85.6		90
			87.8		
			91.2		

[a] See Table VIII for references. Missing entries indicate insufficient information for ready calculation of parameters. [b] Distance from Nb–H midpoint to M′ in pm. [c] Subscripts: t, trans; c, cis; a, axial; e, equatorial carbonyl. [d] C–M–C angle in model corresponding to X–M′–C cited. [e] Atwood, J. L.; Rogers, R. D.; Hunter, W. E.; Floriani, C.; Fachinetti, G.; Chiesi-Villa, A. *Inorg. Chem.* **1980**, *19*, 3812-7. [f] Berndt, A. F.; Marsh, R. E. *Acta Crystallogr.* **1973**, *16*, 118–23. [g] Reference 21.

whether this analogy has any utility.

Mechanistic Aspects. Three basic routes have been found to lead to this class of complex: photochemical reaction of $(\eta\text{-}C_5H_5)_2MH_3$ (**4**) with $M'L_n(CO)$ (generally in THF solution);[8–10] thermal reaction of the same reagents;[11,24] and reactions of $(\eta\text{-}C_5H_5)_2NbBH_4$ with metal carbonyls.[15] For the first, there seems to be little doubt that the photoreactions involve the following steps: i, photogeneration of the solvent-stabilized coordinatively unsaturated fragment $M'L_n(THF)$; ii, photoreaction of **4** with liberated CO to give **5**; iii, thermal reaction of **5** with highly labile $M'L_n(THF)$ to give the bimetallic product. This was shown most clearly by the fact that **5** reacts *in the dark* with pregenerated $M'L_n(THF)$ to give the same products.[9,10,12]

The photoreactions of **4** with $Mn_2(CO)_{10}$ are clearly quite different in nature, as the bimetallic products are not formed during photolysis but only after prolonged subsequent storage in the dark. A key difference, obviously, is that these studies were carried out in noncoordinating solvents; quite possibly in THF a pathway analogous to that above might have been followed. The details of the sequence leading to **2** and/or **3** are still unclear. When monitored by NMR, the reaction of **4a** with $Mn_2(CO)_{10}$ shows $HMn(CO)_5$ as the only detectable new species present immediately after photolysis; the first product arising during the subsequent thermal reaction is **5a**; an as yet unidentified intermediate then grows in before evidence for the presence of **3a** and eventual precipitation of **2a** occurs.[20,32] However, addition of $HMn(CO)_5$ and/or **5a** to the reaction mixture does not lead to any reaction in the absence of irradiation, so there must be at least one other intermediate or catalyst generated during photolysis but not detected by NMR. Further investigation will be needed to fully understand this interesting system.

In the case of the thermal reactions, any simple mechanism based only on ligand substitution reactions seems unlikely, as both **4** and the various $M'L_n(CO)$ are quite inert under the reaction conditions employed. For the cases of $Fe(CO)_5$ and $Cr(CO)_6$ nucleophilic attack of Nb–H upon M′(CO) has been demonstrated, in the former by observation of a formyl- or alkylidene-like intermediate[24] and in the latter by formation of CO-derived hydrocarbons.[33] The Nb–Fe product has also been obtained by the thermal reaction of **4a** with $Fe_2(CO)_9$, and **5a** was detected as an intermediate; this was offered as evidence that hydride transfer is not involved in the $Fe(CO)_5$ reaction above.[34] However, $Fe_2(CO)_9$ is well-known to be *much* more labile toward CO substitution than $Fe(CO)_5$ and undergoes reaction under conditions where the latter is completely inert. In any case, it is not clear that the mechanism for the $Fe_2(CO)_9$ reaction need have any bearing whatsoever on that for $Fe(CO)_5$. Little mechanistic information on the reactions of $(\eta\text{-}C_5H_5)_2NbBH_4$ is available; many (not all) were carried out in the presence of NEt_3, and the preliminary formation of $(\eta\text{-}C_5H_5)_2NbH$ was suggested,[15] but a more complex pathway is not excluded.

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Registry No. **1a**, 111267-11-9; **1b**, 111267-12-0; **1c**, 111267-13-1; **2a**, 79359-07-2; **3b**, 84720-40-1; Cr(CO)6, 13007-92-6; $(\eta\text{-}C_5H_5)_2NbH_3$, 11105-67-2; $Mo(CO)_6$, 13939-06-5; $W(CO)_6$, 14040-11-0; $Mn_2(CO)_{10}$, 10170-69-1; $(\eta\text{-}C_5H_5)_2TaH_3$, 12117-02-1.

Supplementary Material Available: Listings of complete bond lengths and angles, fractional coordinates, thermal parameters, and least-squares planes (12 pages); listings of observed and calculated structure factors for **2a** and **3b** (27 pages). Ordering information is given on any current masthead page. Further details of the X-ray structural analysis of **1a** are available from the Fachinformationszentrum Energie, Physik, Mathematik, D-7514 Eggenstein/Leopoldshafen 2, West Germany, and can be obtained by quoting the depository number CSD 52111, the authors, and the journal citation.

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