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Registry No. $[C_6H_5CH_2N(C_2H_5)_3]_2[Rh_9P(CO)_{21}]\cdot CH_3C(O)CH_3$, 68568-12-7; $Cs_2[Rh_9P(CO)_{21}]$, 68408-40-2; $Rh(CO)_2acac$, 14874-82-9; triphenylphosphine, 603-35-0.

Supplementary Material Available: Complete tables of structural factors, atomic distances and angles, and positional and thermal parameters (34 pages). Ordering information is given on any current masthead page.

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(30) ^1H, ^{13}C, and ^{31}P NMR studies were conducted with a solution of $[C_6H_5CH_2N(C_2H_5)_3][Rh_9P(CO)_{21}]\cdot CH_3C(O)CH_3$ (1.2 g) in acetone-d_6 (3 mL) or acetonitrile-d_3. This solution was enriched with 90% ^{13}C carbon monoxide at 25 °C under 1 atm of pressure. ^1H NMR spectra were studied in a range of −40 to +40 ppm with tetramethylsilane as external standard while ^{13}C NMR experiments were conducted between −40 and +45 °C within a sweep range of 320 ppm downfield from the same standard. ^{31}P NMR spectra were recorded using 12-mm tubes and H_3PO_4 as external standard. The sweeps in this case were extended up to 400 ppm downfield from the standard.
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(34) The noble gas rule requires a number of electrons for $[Rh_9P(CO)_{21}]^{2-}$, $N_3 = 18N_1 - 2N_2$, of $122 = (18 \times 9) - (2 \times 20) = 162 - 40$, but electron counting for this anion shows a number of total electrons of $130 = (9 \times 9) + (2 \times 21) + (1 \times 5) + 2$. Thus, it is concluded that the anion does not follow the noble gas rule. Similar calculation following Wade's rules, $N_3 = 14N_1 + \chi$,[20] $130 = (14 \times 9) + \chi$, results in $\chi = 4$, as required based on these rules for a nido cluster. The open-square basal face present on the anion structure (vide supra) is thus in agreement with Wade's rules predictions.

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Structural Characterization of the Hydrogen-Bridged Heterobimetallic Complex $(\eta^5\text{-}C_5H_5)_2(CO)Nb(\mu\text{-}H)Fe(CO)_4$

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The structure of the product of the reaction of $(\eta^5\text{-}C_5H_5)_2NbH_3$ with $Fe(CO)_5$, $(\eta^5\text{-}C_5H_5)_2(CO)Nb(\mu\text{-}H)Fe(CO)_4$, has been determined by X-ray diffraction techniques. Crystals are monoclinic, space group $P2_1/c$, with cell parameters a = 7.835 (3) Å, b = 13.508 (2) Å, c = 15.165 (2) Å, β = 97.05 (2)°, and Z = 4. The structure was refined to R = 0.033 and R_w = 0.042 for 3063 unique observed data. The molecule contains a triangular Nb–H–Fe group with parameters Nb–Fe = 3.324 (1) Å, Nb–H = 1.91 (3) Å, H–Fe = 1.61 (3) Å, and Nb–H–Fe = 141 (2)°. The geometry about Nb is typical for $(\eta^5\text{-}C_5H_5)_2MX_n$ compounds, with a ring bending angle of 136.3°. The geometry about Fe is a nearly regular trigonal bipyramid (neglecting the bridging hydrogen) with the Nb atom in an axial position. NMR studies suggest a possibly different structure in solution.

Introduction

During the course of an investigation into the potential role of early transition-metal hydride complexes in catalytic CO reduction,[1] a new complex was isolated from the reaction of Cp_2NbH_3 ($Cp = \eta^5\text{-}C_5H_5$) and $Fe(CO)_5$. Since the analytical, spectroscopic, and chemical properties of this species did not permit complete and unequivocal characterization, a single-crystal X-ray structural determination was undertaken. A brief description of this study appeared in an earlier preliminary communication.[1]

Experimental Section

Synthesis and Characterization. All reactions and manipulations were carried out under inert atmosphere using standard techniques.[2] Infrared spectra were obtained on Perkin-Elmer Infracord and 457 instruments, ^1H and ^{13}C NMR spectra were taken on Varian A-60 and XL-100 instruments, and mass spectra were recorded on an AEI-MS9 instrument. Cp_2NbCl_2 was prepared according to a published procedure;[3] commercially available $Fe(CO)_5$ was used without further purification; solvents were distilled from benzophenone ketyl under argon prior to use. Elemental analysis was performed by Spang Microanalytical Laboratory.

A benzene solution of Cp_2NbH_3 was prepared by reaction of Cp_2NbCl_2 with $LiAlH_4$ followed by hydrolysis, as previously described,[4] and standardized by quantitative NMR measurement. Addition of a slight excess of $Fe(CO)_5$ results in essentially quantitative (by NMR) conversion to a new complex, formulated as $Cp_2(CO)Nb(\mu\text{-}H)Fe(CO)_4$ (I), accompanied by evolution of 1 mol of H_2/mol of starting niobium complex (determined manometrically). Removal of solvent and

Table I. Atomic Parameters and Their Standard Deviations[a] for $(\eta^5\text{-}C_5H_5)_2(CO)Nb(\mu\text{-}H)Fe(CO)_4$

	coordinates			anisotropic thermal parameters[b]						
atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	B,[c] Å^2
Nb	0.3531 (0)	0.2052 (0)	0.1439 (0)	3.63 (2)	2.95 (0)	2.92 (0)	0.07 (0)	0.07 (0)	0.01 (0)	3.16
Fe	0.0586 (1)	0.3114 (0)	−0.0025 (0)	4.07 (2)	3.54 (0)	3.91 (0)	0.13 (0)	−0.06 (0)	0.03 (0)	3.85
O_1	−0.0232 (4)	0.1188 (2)	−0.0856 (2)	8.9 (2)	4.9 (1)	9.0 (2)	−1.9 (1)	−0.8 (1)	−1.7 (2)	7.0
O_2	−0.2306 (4)	0.3980 (2)	−0.1133 (2)	7.6 (2)	6.6 (1)	8.8 (2)	1.7 (1)	−3.6 (1)	−0.5 (2)	7.0
O_3	0.3043 (4)	0.4485 (2)	−0.0683 (2)	8.4 (2)	6.1 (1)	10.1 (3)	−1.6 (1)	2.7 (2)	1.5 (2)	7.5
O_4	−0.0902 (4)	0.3614 (3)	0.1590 (2)	6.0 (1)	14.2 (3)	6.6 (2)	2.8 (2)	2.4 (1)	−0.3 (2)	7.6
O	0.0238 (5)	0.1079 (3)	0.2162 (2)	7.9 (2)	10.7 (2)	8.8 (2)	−3.8 (2)	2.9 (1)	0.7 (2)	8.0
C_{11}	0.3198 (5)	0.0600 (2)	0.0579 (3)	6.3 (2)	3.0 (1)	5.6 (2)	0.6 (1)	−0.2 (1)	−0.9 (2)	4.7
C_{12}	0.4189 (6)	0.1224 (3)	0.0119 (2)	7.4 (2)	4.2 (1)	4.2 (2)	1.8 (2)	1.5 (1)	−0.6 (1)	4.7
C_{13}	0.5753 (5)	0.1377 (3)	0.0661 (3)	5.7 (2)	5.1 (1)	7.9 (3)	0.5 (2)	2.7 (2)	−1.6 (2)	5.6
C_{14}	0.5692 (6)	0.0833 (3)	0.1443 (3)	6.3 (2)	5.7 (2)	6.4 (2)	2.6 (2)	−0.6 (2)	−1.0 (2)	5.7
C_{15}	0.4153 (7)	0.0348 (3)	0.1389 (3)	8.8 (3)	3.4 (1)	6.0 (2)	1.5 (2)	0.0 (2)	1.0 (2)	5.4
C_{21}	0.2948 (5)	0.3130 (3)	0.2620 (3)	5.0 (2)	6.9 (2)	4.6 (2)	−0.1 (2)	1.1 (2)	−2.7 (2)	4.9
C_{22}	0.4357 (5)	0.2520 (3)	0.2924 (2)	6.6 (2)	6.1 (2)	3.1 (2)	−0.3 (2)	−0.1 (1)	−0.6 (2)	5.0
C_{23}	0.5690 (5)	0.2775 (3)	0.2435 (2)	4.3 (1)	5.2 (2)	4.6 (2)	−0.2 (1)	−0.6 (1)	−0.6 (2)	4.6
C_{24}	0.5129 (5)	0.3527 (2)	0.1830 (2)	5.4 (2)	3.7 (1)	5.3 (2)	−0.9 (1)	0.1 (1)	−0.8 (1)	5.4
C_{25}	0.3435 (5)	0.3747 (3)	0.1959 (3)	6.0 (2)	3.9 (1)	5.3 (2)	0.6 (1)	−1.0 (1)	−1.9 (2)	4.7
C_1	0.0120 (5)	0.1937 (3)	−0.0514 (3)	5.2 (2)	4.5 (1)	5.4 (2)	−0.4 (2)	−0.4 (1)	0.3 (2)	5.0
C_2	−0.1157 (6)	0.3642 (3)	−0.0689 (3)	6.4 (2)	4.3 (1)	5.5 (2)	0.3 (1)	−1.2 (1)	−0.6 (2)	5.3
C_3	0.2073 (5)	0.3957 (3)	−0.0434 (2)	5.7 (2)	4.2 (1)	5.1 (2)	0.3 (1)	0.5 (1)	0.2 (2)	5.0
C_4	−0.0291 (4)	0.3414 (3)	0.0967 (3)	3.8 (1)	6.9 (2)	5.6 (2)	0.8 (2)	0.4 (1)	0.3 (2)	5.2
C	0.1392 (5)	0.1445 (3)	0.1890 (3)	5.4 (2)	6.4 (2)	4.8 (2)	−1.3 (2)	1.0 (1)	0.4 (2)	5.3
H	0.2458 (45)	0.2816 (25)	0.0464 (24)	5.1 (8)						5.1

[a] The number following each datum is the estimated standard deviation in the least significant figure. [b] B_{ij} is related to the dimensionless β_{ij} employed during refinement as $B_{ij} = 4\beta_{ij}/a_i^*a_j^*$. [c] Isotropic thermal parameter calculated from $B = 4[V^2 \det(\beta_{ij})]^{1/3}$.

Table II. Bond Distances (Å)

Nb-Fe	3.324 (1)	Fe-C_3	1.794 (4)
Nb-H	1.91 (3)	Fe-C_4	1.775 (4)
Nb-C	2.057 (4)	O-C	1.150 (5)
Nb-C_{11}	2.352 (3)	O_1-C_1	1.155 (4)
Nb-C_{12}	2.404 (3)	O_2-C_2	1.151 (4)
Nb-C_{13}	2.399 (4)	O_3-C_3	1.140 (4)
Nb-C_{14}	2.362 (4)	O_4-C_4	1.143 (5)
Nb-C_{15}	2.356 (4)	C_{11}-C_{12}	1.390 (6)
Nb-C_{21}	2.396 (3)	C_{11}-C_{15}	1.399 (5)
Nb-C_{22}	2.352 (4)	C_{12}-C_{13}	1.405 (6)
Nb-C_{23}	2.339 (4)	C_{13}-C_{14}	1.401 (6)
Nb-C_{24}	2.389 (3)	C_{14}-C_{15}	1.366 (6)
Nb-C_{25}	2.425 (3)	C_{21}-C_{22}	1.409 (6)
Fe-H	1.61 (3)	C_{21}-C_{25}	1.392 (6)
Fe-C_1	1.773 (4)	C_{22}-C_{23}	1.397 (5)
Fe-C_2	1.747 (4)	C_{23}-C_{24}	1.401 (5)
		C_{24}-C_{25}	1.397 (5)

unreacted $Fe(CO)_5$, followed by recrystallization from cold toluene–heptane, gave I as air-sensitive, dark brown prisms. Anal. Calcd for $C_{15}H_{11}FeO_5Nb$: C, 42.89; H, 2.64. Found: C, 43.27; H, 3.17. The solution infrared spectrum (THF, CaF_2 cells) shows four strong bands in the CO stretching region at 2030, 1990, 1960 and 1920 cm^{-1}. The Nujol mull spectrum shows a more complex pattern in this region, plus a much weaker peak at 1720 cm^{-1} tentatively assigned to metal–hydrogen stretching. Both room-temperature (in benzene) and variable-temperature (in toluene) ^1H and ^{13}C NMR spectra were recorded; a peak attributable to metal-bonded hydride at τ 16.4 was observed only in the latter (see Discussion).

The highest peak observed in the mass spectrum has m/e 252, assigned as $Cp_2NbH(CO)^+$; no parent peak could be seen. I reacts rapidly with $CDCl_3$ to give 1 mol of $CHDCl_2$/mol of I, indicating the presence of a single metal-bonded hydride. The tantalum analogue of I was prepared from Cp_2TaH_3 and characterized by infrared and NMR spectroscopies; the ^1H NMR spectrum shows two peaks at τ 5.40 and 16.70, assigned to Cp and metal-bonded H, respectively.

X-ray Crystallographic Data. Suitable crystals were obtained by slow cooling of a solution of I in toluene–heptane (2:3). A crystal of dimensions 0.36 × 0.45 × 0.51 mm was selected and mounted along its long axis in a thin-walled glass capillary. The crystal was found to be monoclinic, with cell dimensions a = 7.835 (3) Å, b = 13.508 (2) Å, c = 15.165 (2) Å, β = 97.05 (2)°, and V = 1593 Å^3. The space group was determined as $P2_1/c$, with Z = 4 and a calculated density of 1.75 g/cm^3.

Diffraction data were collected at 292 K on a Syntex $P\bar{1}$ diffractometer, using graphite-monochromated Mo Kα radiation. One octant of data was collected by the θ–2θ scan technique, with scan speeds varying from 2 to 12°/min, to the limit $2\theta < 55°$. The intensities of four standard reflections, monitored at regular intervals, showed no significant fluctuation during the collection procedure. The raw intensity data were corrected for Lorentz polarization and absorption (μ = 16.26 cm^{-1}) effects. After averaging equivalent reflections, a total of 3063 independent reflections were used for solution and refinement.

Solution and Refinement of the Structure. The positions of the iron and niobium atoms were determined from three-dimensional Patterson functions calculated from intensity data, and the oxygen, carbon, and metal-bonded hydrogen atoms were located from a series of difference Fourier maps. Full-matrix least-squares refinement was based on minimization of the function $\sum w(|F_o| - |F_c|)^2$, with the weights w taken as $(2F_o/\sigma(F_o)^2)^2$, where F_o and F_c are the observed and calculated structure factor amplitudes, respectively. Atomic scattering factors for nonhydrogen atoms were taken from Cromer and Waber.[5] Anisotropic temperature factors were introduced for all nonhydrogen atoms. The metal-bonded hydrogen was refined isotropically, and the Cp hydrogens were assigned fixed positions (C–H = 0.95 Å; β_{iso} = 5.0 Å^2).

The final agreement factors are R = 0.033 and R_w = 0.042,[6] and the estimated standard deviation of an observation of unit weight is 1.429. The ratio of data to parameters is 15.1. Atomic coordinates and thermal parameters for all atoms are listed in Table I. Interatomic distances, intramolecular angles, and deviations of atoms from selected planes are listed in Tables II–IV, respectively.

Results and Discussion

Description of the Structure. The molecular structure of I is shown in Figure 1. The bonding may be most easily described in terms of an 18-electron unit, $Cp_2NbH(CO)$, functioning as a two-electron donor to the 16-electron $Fe(CO)_4$ group, by means of both a metal–metal bond and a bridging hydrogen atom. Precedent for this "dative" type of metal–metal interaction may be found in $Cp(CO)Mo(\mu\text{-}C_5H_4)\text{-}Mn(CO)_4$[7] and $Cp_2H_2MM'(CO)_5$ (M, M′ = Cr, Mo, W; no crystal structure has been reported, but a non-hydrogen-bridged structure was inferred from NMR coupling constants).[8] Several aspects of the structure are of interest in light of previously reported related structures, and these will be discussed in turn.

The Nb–H–Fe Grouping. The most notable feature is the length of the metal–metal bond, 3.324 (1) Å. This may be

Table III. Bond Angles (deg)

Fe-Nb-C	82.4 (1)	Nb-C_{15}-C_{11}	72.6 (2)
Fe-Nb-H	17.6 (11)	C_{21}-Nb-C_{22}	34.5 (1)
C-Nb-H	100.0 (11)	C_{21}-Nb-C_{23}	56.8 (1)
Nb-Fe-C_1	89.0 (1)	C_{21}-Nb-C_{24}	56.6 (1)
Nb-Fe-C_2	172.2 (2)	C_{21}-Nb-C_{25}	33.6 (1)
Nb-Fe-C_3	94.5 (1)	C_{22}-Nb-C_{23}	34.7 (1)
Nb-Fe-C_4	80.9 (1)	C_{22}-Nb-C_{24}	57.6 (1)
H-Fe-C_1	95.6 (12)	C_{22}-Nb-C_{25}	56.7 (1)
H-Fe-C_2	166.1 (13)	Nb-C_{23}-C_{22}	73.2 (2)
H-Fe-C_3	74.0 (13)	Nb-C_{23}-C_{24}	74.7 (2)
H-Fe-C_4	95.3 (13)	Nb-C_{24}-C_{23}	70.8 (2)
C_1-Fe-C_2	91.0 (2)	Nb-C_{24}-C_{25}	74.6 (2)
C_1-Fe-C_3	122.3 (2)	Nb-C_{25}-C_{24}	71.7 (2)
C_1-Fe-C_4	118.5 (2)	Nb-C_{25}-C_{21}	72.0 (2)
C_2-Fe-C_3	92.1 (2)	C-Nb-C_{21}	75.8 (1)
C_2-Fe-C_4	92.2 (2)	C-Nb-C_{22}	85.9 (1)
C_3-Fe-C_4	118.9 (2)	C-Nb-C_{25}	102.1 (2)
Fe-C_1-O_1	177.4 (9)	C-Nb-C_{11}	79.2 (2)
Fe-C_2-O_2	179.1 (28)	C-Nb-C_{12}	111.0 (2)
Fe-C_3-O_3	178.7 (14)	C-Nb-C_{15}	78.6 (2)
Fe-C_4-O_4	177.9 (6)	H-Nb-C_{11}	90.7 (10)
Nb-C-O	177.3 (5)	H-Nb-C_{12}	74.1 (11)
C_{12}-C_{11}-C_{15}	108.5 (4)	H-Nb-C_{13}	95.8 (11)
C_{11}-C_{12}-C_{13}	107.2 (3)	H-Nb-C_{21}	98.3 (10)
C_{12}-C_{13}-C_{14}	107.5 (4)	H-Nb-C_{25}	73.4 (10)
C_{13}-C_{14}-C_{15}	108.8 (4)	H-Nb-C_{24}	84.8 (10)
C_{14}-C_{15}-C_{11}	108.0 (4)	C_{11}-Nb-Fe	88.2 (1)
C_{22}-C_{21}-C_{25}	108.2 (3)	C_{12}-Nb-Fe	81.2 (1)
C_{21}-C_{22}-C_{23}	106.7 (4)	C_{13}-Nb-Fe	108.8 (1)
C_{22}-C_{23}-C_{24}	109.4 (3)	C_{13}-Nb-C	133.0 (2)
C_{23}-C_{24}-C_{25}	106.8 (4)	C_{14}-Nb-C	109.5 (2)
C_{24}-C_{25}-C_{21}	108.8 (3)	C_{14}-Nb-Fe	137.8 (1)
Nb-H-Fe	141.3 (23)	C_{14}-Nb-H	128.7 (11)
C_{11}-Nb-C_{12}	34.0 (1)	C_{15}-Nb-Fe	122.0 (1)
C_{11}-Nb-C_{13}	56.5 (1)	C_{15}-Nb-H	125.1 (10)
C_{11}-Nb-C_{14}	56.7 (1)	C_{21}-Nb-Fe	93.2 (1)
C_{11}-Nb-C_{15}	34.6 (1)	C_{22}-Nb-Fe	127.6 (1)
C_{12}-Nb-C_{13}	34.0 (1)	C_{22}-Nb-H	129.7 (10)
C_{12}-Nb-C_{14}	56.7 (1)	C_{23}-Nb-C	120.4 (1)
C_{12}-Nb-C_{15}	56.8 (1)	C_{23}-Nb-Fe	129.7 (1)
Nb-C_{13}-C_{12}	73.2 (2)	C_{23}-Nb-H	119.2 (10)
Nb-C_{13}-C_{14}	71.4 (2)	C_{24}-Nb-C	132.3 (1)
Nb-C_{14}-C_{13}	74.4 (2)	C_{24}-Nb-Fe	96.1 (1)
Nb-C_{14}-C_{15}	72.9 (2)	C_{25}-Nb-Fe	76.3 (1)
Nb-C_{15}-C_{14}	73.4 (2)		

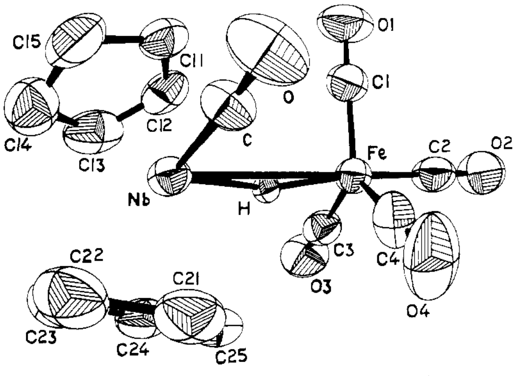

Figure 1. Molecular structure of $(\eta^5\text{-}C_5H_5)_2(CO)Nb(\mu\text{-}H)Fe(CO)_4$. Cp ring hydrogens are not shown.

Table IV. Selected Molecular Planes

atom	devn, Å	atom	devn, Å
Plane 1: Cyclopentadienyl Ring (C_{11}–C_{15})			
$0.4472X - 0.7877Y - 0.4238Z = 0.0742$			
C_{11}	0.0095	C_{15}	−0.0094
C_{12}	−0.0060	C	2.4871
C_{13}	0.0003	H	2.5433
C_{14}	0.0056	Nb	2.0577
Plane 2: Cyclopentadienyl Ring (C_{21}–C_{25})			
$-0.2414X - 0.6850Y - 0.6874Z = -6.0499$			
C_{21}	−0.0031	C_{25}	0.0053
C_{22}	−0.0004	C	−2.5787
C_{23}	0.0037	H	−2.5204
C_{24}	−0.0055	Nb	−2.0593
Plane 3: Fe, H, Nb, C, O			
$0.1224X - 0.7766Y - 0.6180Z = -3.1770$			
Fe	0.0096	C	0.0068
H	−0.0170	O	−0.0074
Nb	0.0080		
Plane 4: C_1, C_3, C_4			
$-0.7100X + 0.4196Y - 0.5655Z = 1.4010$			
C_2	−1.8021	Fe	−0.0553
		Nb	3.2372
Plane 5: Nb, Fe, C_1, O_1			
$0.7734X + 0.1516Y - 0.6156Z = 1.0196$			
Plane 6: Nb, Fe, C_4, O_4			
$-0.5189X - 0.8515Y - 0.0759Z = -3.8210$			
Plane 7: Nb, Fe, C_3, O_3			
$0.2734X - 0.6708Y - 0.6894Z = -2.6693$			

planes	dihedral angle, deg	planes	dihedral angle, deg
1, 2	43.7	3. 5	69.1
1, 3	21.8	3, 6	49.9
2, 3	22.0	3, 7	11.3
3, 4	86.4		

Table V. Structural Parameters of Some HM_2 Complexes

compd	M–M, Å	M–H–M, deg	method[a]	ref
$HCr_2(CO)_{10}^-$	3.386 (6)	158.9 (6)	N	15
$HFeNbCp_2(CO)_5$	3.324 (1)	141.3 (23)	X	this work
$HCrRe(CO)_{10}$	3.435 (1)	"linear"[b]	X	16
$HW_2(CO)_{10}^-$ (PPN^+ salt)	3.391 (1)	bent[b]	X	17
$HW_2(CO)_{10}^-$ (Et_4N^+ salt)	3.504 (1)	"linear"[b]	X	17
$HW_2(CO)_9(NO)$	3.329 (3)[c]	125.5 (5)[c]	N	13
$HW_2(CO)_8(NO)$-$(P(OMe)_3)$	3.393 (4)	129.4 (3)	N	18

[a] N, neutron diffraction; X, X-ray diffraction. [b] H not located; geometry assigned from carbonyl positions. It should be noted, however, that $HCr_2(CO)_{10}^-$ had been considered linear, on the same grounds, before the neutron diffraction study showed that the hydrogen is located *off* the M–M axis; a similar result for these cases would not be surprising. [c] Average of results for two different crystalline modifications.

compared to the metal–metal bond in $Cp(CO)_3MoMn(CO)_5$, which also involves a bond between a first- and second-row transition metal but has no bridging hydrogen; the Mo–Mn bond distance is 3.083 Å.[9] Comparison of the respective metallic radii[10] suggests that an Nb–Fe bond should be about the same length or perhaps slightly shorter. Aside from steric factors,[11] the only obvious possible cause for this lengthening is the presence of the bridging hydrogen. It has been suggested that a bridging hydrogen does cause such lengthening, with the magnitude of lengthening increasing as the M–H–M angle becomes more obtuse.[12] This is in accord with a picture of the bonding in such species as a closed, three-center, two-electron bond,[13] rather than a metal–metal bond supported by a bridging hydrogen. A listing of results for several HM_2 systems which contain no other bridging ligand[14] is given in Table V; the relative constancy of the metal–metal distance, in spite of the fact that first- through third-row metals are involved, is striking. The complexes with near-linear M–H–M groups have somewhat longer M–M distances, which increase as expected for heavier metals.

Comparison of the M–H–M angle for I with the values determined by neutron diffraction is of questionable validity. A comparative study of X-ray and neutron results for $(CpMo(CO)_2)_2(\mu\text{-}H)(\mu\text{-}PMe_2)$ shows that the X-ray determination shortens metal–hydrogen distances, resulting in an increase of the Mo–H–Mo angle from 122.9 (2)° (neutron) to 133 (3)° (X-ray).[19] Applying a similar correction here would imply that the "actual" Nb–H–Fe angle is not very different from that found for the tungsten compounds $HW_2(CO)_9(NO)$ and $HW_2(CO)_8(NO)(P(OMe_3))$ (see Table V).

Comparison might also be made with the Nb–Nb bond distance of 3.105 (6) Å[20] in the niobocene dimer $(CpNbH)_2(\mu\text{-}C_5H_4)_2$; this value is much shorter than the Nb–Fe bond in I. However, this difference may represent effects due to the bridging ligands in niobocene dimer as well as the bridging hydrogen in I.

The metal–hydrogen distances are not equal; this is also not surprising since the metals will have different radii. However, the hydrogen appears to be somewhat closer to the iron atom than might have been expected. The metallic radii[21] of Nb and Fe (1.47 and 1.26 Å, respectively[10]) suggest that Nb–H would be about 0.2 Å longer than Fe–H, while examination of terminal metal–hydride distances (Nb–H = 1.69 (4) Å in Cp_2NbH_3 (neutron);[22] Fe–H = 1.51 (4) Å in $FeH_2(PPh(OEt)_2)_4$[23] and 1.57 (12) Å in $HFe(CO)_4^-$[24]) suggests an even smaller difference. The observed difference is 0.30 Å. An analogous asymmetry was found in $HW_2(CO)_8(NO)(P(OMe)_3)$, wherein the hydrogen is closer to the $W(CO)_5$ group (1.859 (7) Å) than to the $W(CO)_3(NO)L$ group (1.894 (6) Å).[18] It was noted that, ignoring the hydrogen– and metal–metal bonds, the electron count of these two groups is 16 and 17, respectively; thus the bridging hydrogen is closer to the more electron-deficient center.[18] The same situation appears to be present in I, with the hydrogen displaced toward the 16-electron $Fe(CO)_4$ group from the 17-electron $Cp_2Nb(CO)$ group. It should be noted, however, that this does not take into account the tendency of X-ray methods to give shortened M–H bonds, as mentioned earlier; for a system with two different metals, it is not unlikely that this effect would distort the *relative*, as well as absolute, M–H distances. Also, the differences involved are not significantly greater than the estimated standard deviations, so it is not clear that this apparent effect is real. It also might be noted that $HW_2(CO)_9(NO)$, which has a similar asymmetric electron count, has equal W–H distances.[13]

Geometry about Niobium. As noted earlier, one way to view the bonding in I is as a Lewis acid–base adduct of $Cp_2NbH(CO)$, with $Fe(CO)_4$ behaving as a Lewis acid. A model for this type of compound is the recently reported cation $Cp_2NbH_2(CO)^+$.[25] The crystal structure of free $Cp_2NbH(CO)$ has been reported[26] and is quite similar in terms of Nb–C and C–O distances; the niobium-bonded hydrogen was not located. The ring bending angle (the angle between lines drawn from the metal normal to the rings, variously defined as θ[27] or ω[26]) is 143° in $Cp_2NbH(CO)$ and 136.3° in I. This may well be due to greater steric repulsion in I, although electronic effects upon this angle have also been considered.[27]

Alternatively, I may be viewed as a Cp_2MX_3 bent-sandwich system. The geometry fits well within this framework, with the niobium atom and the three X ligands (H, Fe, CO) coplanar (see Table IV). The metal–ring distances are quite similar to those in Cp_2NbH_3 as well as other Cp_2NbX_n complexes.[22] It is interesting that the angle made by the outer ligands, H–Nb–CO, is substantially smaller (100 (2)°) than the value found for Cp_2NbH_3 (126 (3)°)[22] or the value calculated for hypothetical $Cp_2TiH_3^-$ (129°),[27] in spite of the greater steric repulsion probable in I. However, the fact that the hydrogen in I is a bridging ligand might well be responsible for this decrease.

Geometry about Iron. If hydrogen is neglected, the coordination geometry about iron is very nearly a regular trigonal bipyramid with the niobium atom occupying an axial position; the bridging hydride thus appears to have virtually no influence on the iron geometry. The axial Fe–C distance is about 0.03 Å shorter than the average equatorial distance (1.747 (4) vs. 1.780 (6) Å), a result also found in $Fe(CO)_5$ (1.806 (5) vs. 1.833 (4) Å, by electron diffraction),[28] $Fe(CO)_4(py)$ (1.772 (7) vs. 1.805 (8) Å),[29] and $Fe(CO)_4(pyz)$ (1.774 (4) vs. 1.810 (4) Å).[29] The overall relative shortness of the Fe–C distances in I compared to those of the other compounds cited suggests that the $Cp_2NbH(CO)$ is acting as a very strong donor and weak acceptor ligand toward iron.

The equatorial carbonyls are oriented such that one of them (C_3–O_3) lies only 11° out of the Nb–H–Fe plane, nearly eclipsing the Nb–H bond. Presumably this orientation minimizes interactions between these carbonyls and the carbonyl on niobium. The nonbonded distance between C_3 and the bridging hydrogen is quite short, 2.05 Å, but the structural parameters of that CO show no evidence for any bonding interaction.

NMR Spectra. The NMR spectra of I show some unexpected and interesting behavior. First, no peak attributable to a metal hydride was observed at ambient temperature in benzene solution. However, on switching to toluene to permit variable-temperature studies, we observed a very weak and broad signal at τ 16.4. When the temperature was lowered, this peak became sharper and stronger. This appears to be a manifestation of "thermal decoupling"[30] which occurs when signals are broadened due to coupling with a quadrupolar nucleus (^{93}Nb, spin $^9/_2$, 100%): lowering the temperature (or increasing the viscosity) increases the correlation time and thus decreases the relaxation time for the quadrupolar nucleus.[31] This technique was previously proven highly useful for ^{13}C NMR spectroscopy of metal carbonyls with quadrupolar nuclei.[30] The appearance of the peak (albeit very broad) in toluene but not benzene at ambient temperature is not readily explicable; the viscosities of the two solvents are very nearly equal.[32] It may be noted that the corresponding peak in the tantalum analogue is sharp even at room temperature.

The signals due to the Cp groups are also unexpected: *two* singlets are observed, both in the ^1H (τ 5.33, 5.38) and in the ^{13}C (85.9 and 93.2 ppm downfield from Me_4Si) NMR spectra. This would appear to indicate that the two rings are nonequivalent. However, the structure shows no likely source for such nonequivalence. The two rings are symmetrically disposed with respect to the H–Nb–Fe plane and differ (in the solid state) only by virtue of the 11° rotation of the group of equatorial carbonyls on iron out of that plane, a difference which would not be expected to be observable on the NMR time scale in solution. This is easily tested by examining the CO region of the ^{13}C NMR: a single peak at 223.9 ppm is observed at temperatures down to −80 °C, assigned to the four iron carbonyls which are rapidly exchanging even at low temperatures. (Iron carbonyl shifts are typically found in the range of 210–220 ppm;[33] the inability to slow the fluxional rearrangement of substituted iron carbonyls is common.[29]) No other peak could be detected in this region, suggesting that the niobium carbonyl signal is broadened by interaction with Nb even at low temperatures. The carbonyl peak in free $Cp_2NbH(CO)$ could not be observed under our conditions either, even in the presence of $Cr(acac)_3$.

Since the ready exchange of CO's rules out the possibility that the rings in I (with the solid-state structure) would be nonequivalent by NMR, the remaining possibilities are that

(i) splitting by interaction with the Nb nucleus is being observed or (ii) the structure in solution differs from that in the solid state. Unusual behavior in other organoniobium systems has been reported. For example, the Cp signal in $CpNb(CO)_4$ is quite broad,[34] in contrast to most Cp–Nb complexes; also, the fine structure of the hydride signals in Cp_2NbH_3 and $Cp_2NbH_3{\cdot}AlEt_3$ shows unexplained temperature dependence.[35] However, in I the two ^1H signals are of different width (half-widths are 2 and 6 Hz, respectively, although the peak areas are equal to experimental accuracy) and their relative shift changes as a function of temperature. These observations appear more in accord with explanation (ii), although the possible nature of any structural change is far from obvious.[36] Again, it is notable that the tantalum analogue shows only one singlet for the Cp protons. Chemical and structural studies on analogous systems with different metals are now in progress in hopes of resolving this problem.

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Registry No. I, 68367-46-4; Cp_2NbH_3, 11105-67-2; $Fe(CO)_5$, 13463-40-6.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes (~13 pages). Ordering information is given on any current masthead page.

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