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(34) The ^{11}B NMR spectrum was kindly recorded by Professor S. Shore at The Ohio State University employing side band techniques and a BCl_3 standard (−46.8 ppm).
(35) The high-field spectrum beyond ca. δ 4.25 was obscured by solvent signals.
(36) The IR spectrum of the NMR sample (1992 (s), 1951 (m), 1783 (s) cm^{-1}) was identical with that of the final IR sample and with that of a THF solution of $[FeCp(CO)_2]_2$ (ν(CO) 1993 (s), 1952 (m), 1783 (s) cm^{-1}). The singlet Cp resonance of $[FeCp(CO)_2]_2$ in THF was at δ 4.97.
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Molecular Structure of $(\eta^5\text{-}C_5H_5)_2(CO)Nb(\mu\text{-}CO)Co(CO)_3$, a Heterobimetallic Complex with a Semibridging Carbonyl

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The structure of the product of the reaction of $(\eta^5\text{-}C_5H_5)_2NbH_3$ with $Co_2(CO)_8$, $(\eta^5\text{-}C_5H_5)_2(CO)Nb(\mu\text{-}CO)Co(CO)_3$, has been determined by X-ray diffraction techniques. Crystals are orthorhombic, with cell parameters $a = 13.821$ (6) Å, $b = 13.352$ (5) Å, $c = 16.142$ (6) Å, space group *Pbca*, and $Z = 8$. The structure was refined to $R = 0.048$ and $R_w = 0.057$ for 3924 unique observed reflections. The molecule contains a semibridged carbonyl group between the Nb and Co atoms with parameters Nb–Co = 2.992 (1) Å, Nb–C_B = 2.531 (4) Å, C_B–Co = 1.792 (4) Å, and Nb–C_B–Co = 85.8 (1)°. Spectral studies indicate an isomeric mixture in solution.

Introduction

As part of our study on the use of early transition metal hydrides in catalytic CO reduction,[1] we have examined the reaction of Cp_2NbH_3 (Cp = $\eta^5\text{-}C_5H_5$) with $Co_2(CO)_8$. The product of this reaction turned out to have several interesting structural features, and the results of a single-crystal X-ray structural determination are reported here.

Experimental Section

Synthesis and Characterization. All reactions and manipulations were carried out under inert atmosphere with standard techniques[2] or otherwise as noted. Infrared spectra were recorded on Perkin-Elmer Infracord and 457 instruments and ^1H NMR on Varian A-60 and XL-100 instruments. Cp_2NbCl_2 was prepared as described elsewhere;[3] commercially available $Co_2(CO)_8$ was used without further purification; solvents were distilled from benzophenone ketyl under argon prior to use.

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. On addition of a slight excess of $Co_2(CO)_8$ the solution turned dark immediately (room temperature), accompanied by evolution of gas (ca. 1 mol/mol of Cp_2NbH_3). Removal of solvent, followed by extraction with toluene and recrystallization from cold hexane, gave air-sensitive, dark brown to black prisms, in about 70% yield. The ^1H NMR spectrum (C_6D_6) showed three peaks in the Cp region (τ 5.17, 5.34, and 5.47, relative intensities ca. 1:1:2). This pattern was not significantly changed following repeated recrystallization of the sample. No peak in the normal metal hydride region was observed, and no change in the spectrum occurred on adding $CDCl_3$, indicating no metal hydride was present. The IR spectrum proved highly medium-dependent; peaks observed in the CO-stretching region are listed in Table I.

Table I. CO-Stretching Absorptions of $Cp_2(CO)Nb(\mu\text{-}CO)Co(CO)_3$

solvent	ν_{max}, cm^{-1} (intensity)
hexane^a	2060 vs, 2040 m, sh, 1875 s
THF^a	2060 vs, 2020 vs, 1940 s, 1880 s
benzene^a	2080 s, 2040 vs, 1970 s, 1948 m, 1855 m, br
toluene^a	2060 s, 2020 s, 1960 m, sh, 1940 s, 1850 m
Nujol^b	2060 vs, 2020 vs, 1980 m, 1870 vs

^{a} CaF_2 cells. ^{b} Mull, NaCl plates.

X-ray Crystallographic Data. Suitable crystals were obtained by slow cooling of a solution in hexane. A crystal of dimensions 0.42 × 0.56 × 0.47 mm was selected and mounted in a thin-walled glass capillary. The crystal was found to be orthorhombic, with cell dimensions $a = 13.821$ (6) Å, $b = 13.352$ (5) Å, $c = 16.142$ (6) Å, and $V = 2961$ Å^3. The space group was determined as *Pbca*, with $Z = 8$ and a calculated density of 1.89 g/cm^3.

Diffraction data were collected at 292 K on a Syntex $P\bar{1}$ diffractometer, by 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 $2\theta < 59°$. 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 ($\mu = 19.34$ cm^{-1}) effects. After averaging of equivalent reflections, a total of 3924 independent reflections were used for solution and refinement.

Solution and Refinement of the Structure. The positions of the cobalt and niobium atoms were determined from three-dimensional Patterson functions calculated from intensity data, and the oxygen and carbon atoms were located from a series of difference Fourier maps. Full-matrix least-squares refinement was based on minimization of

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Table II. Atomic Parameters and Their Standard Deviations[a] for $(\eta\text{-}C_5H_5)_2(CO)Nb(\mu\text{-}CO)Co(CO)_3$

	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	0.1143 (0)	0.2580 (0)	0.0962 (0)	2.49 (1)	2.36 (1)	2.45 (1)	0.05 (1)	−0.12 (1)	−0.09 (1)	2.43
Co	0.1250 (0)	0.4025 (0)	0.2376 (0)	3.65 (2)	3.04 (2)	2.76 (2)	−0.28 (1)	0.32 (2)	−0.34 (2)	3.09
O_B	0.2709 (2)	0.2484 (3)	0.2482 (2)	4.6 (2)	6.6 (2)	4.9 (1)	1.2 (1)	−1.7 (1)	−0.4 (1)	4.9
O_1	0.2517 (3)	0.5108 (3)	0.3474 (3)	13.1 (4)	8.3 (3)	7.9 (3)	−2.2 (3)	−6.2 (3)	−1.2 (2)	7.7
O_2	0.0690 (3)	0.5722 (3)	0.1329 (2)	8.9 (2)	4.8 (1)	5.0 (2)	0.8 (1)	−0.3 (2)	0.8 (2)	5.9
O_3	−0.0365 (3)	0.3438 (3)	0.3429 (2)	6.7 (2)	8.8 (3)	7.3 (2)	−0.8 (2)	3.9 (2)	0.2 (2)	6.6
O	−0.0718 (2)	0.3951 (2)	0.0659 (2)	4.1 (2)	5.4 (1)	8.5 (2)	1.2 (1)	−2.3 (2)	−0.0 (2)	5.3
C_B	0.2069 (3)	0.2992 (3)	0.2271 (2)	3.5 (2)	4.2 (1)	3.4 (1)	0.2 (1)	0.0 (1)	−0.2 (2)	3.7
C_1	0.2013 (4)	0.4693 (3)	0.3042 (3)	7.1 (3)	4.3 (2)	4.6 (2)	−0.5 (2)	−1.4 (2)	0.2 (2)	5.1
C_2	0.0897 (3)	0.5040 (3)	0.1722 (2)	5.1 (2)	3.8 (1)	3.3 (1)	−0.2 (1)	−0.2 (2)	−0.5 (2)	3.9
C_3	0.0240 (3)	0.3658 (3)	0.3000 (3)	4.9 (2)	4.2 (2)	4.2 (2)	0.2 (1)	0.9 (2)	−0.2 (2)	4.3
C	−0.0046 (3)	0.3486 (3)	0.0798 (2)	3.2 (2)	3.7 (1)	4.4 (2)	−0.0 (1)	−0.8 (1)	−0.0 (2)	3.7
C_{11}	0.1284 (3)	0.0897 (3)	0.1470 (3)	4.6 (2)	2.7 (1)	6.0 (2)	0.4 (1)	−0.3 (2)	0.8 (2)	4.1
C_{12}	0.0804 (4)	0.0873 (3)	0.0714 (3)	6.4 (2)	2.7 (1)	4.9 (2)	−0.2 (1)	−0.3 (2)	−0.7 (2)	4.3
C_{13}	−0.0077 (3)	0.1369 (3)	0.0807 (3)	4.7 (2)	3.5 (2)	6.8 (2)	−1.2 (1)	−2.1 (2)	0.2 (2)	4.4
C_{14}	−0.0145 (3)	0.1700 (3)	0.1620 (3)	3.7 (2)	3.6 (2)	7.9 (3)	−0.6 (1)	1.9 (2)	0.6 (2)	4.4
C_{15}	0.0697 (3)	0.1387 (3)	0.2038 (3)	5.7 (2)	3.2 (2)	4.4 (2)	−1.1 (1)	0.2 (2)	1.2 (2)	4.0
C_{21}	0.2728 (3)	0.2563 (3)	0.0360 (3)	3.6 (2)	5.1 (2)	5.9 (2)	0.6 (1)	1.9 (2)	1.1 (2)	4.4
C_{22}	0.2558 (3)	0.3542 (3)	0.0565 (2)	4.6 (2)	4.7 (2)	4.2 (2)	−1.4 (1)	1.7 (2)	−0.1 (2)	4.1
C_{23}	0.1777 (3)	0.3875 (3)	0.0103 (3)	6.3 (2)	3.9 (2)	5.1 (2)	0.9 (1)	2.6 (2)	1.9 (2)	4.3
C_{24}	0.1474 (3)	0.3092 (5)	−0.406 (2)	6.1 (2)	10.3 (4)	2.3 (2)	−0.3 (3)	−0.3 (2)	1.0 (2)	5.2
C_{25}	0.2060 (4)	0.2277 (4)	−0.0230 (3)	7.4 (3)	5.4 (2)	4.9 (2)	−1.0 (2)	3.1 (2)	−2.4 (2)	4.9

[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 $B_{ij} = 4B_{ij}/a_i{}^*a_j{}^*$. [c] Isotropic thermal parameter calculated from $B = 4[V^2 \det(\beta_{ij})]^{1/3}$.

Table III. Bond Distances (Å)

Nb-Co	2.992 (1)	O_B-C_B	1.165 (4)
Nb-C_B	2.531 (4)	O_1-C_1	1.131 (5)
Nb-C	2.058 (4)	O_2-C_2	1.145 (5)
Nb-C_{11}	2.399 (4)	O_3-C_3	1.124 (5)
Nb-C_{12}	2.362 (2)	O-C	1.140 (4)
Nb-C_{13}	2.351 (4)	C_{11}-C_{12}	1.390 (6)
Nb-C_{14}	2.383 (4)	C_{11}-C_{15}	1.388 (6)
Nb-C_{15}	2.436 (4)	C_{12}-C_{13}	1.394 (7)
Nb-C_{21}	2.397 (4)	C_{13}-C_{14}	1.388 (6)
Nb-C_{22}	2.426 (4)	C_{14}-C_{15}	1.408 (6)
Nb-C_{23}	2.383 (4)	C_{21}-C_{22}	1.369 (6)
Nb-C_{24}	2.356 (4)	C_{21}-C_{25}	1.382 (7)
Nb-C_{25}	2.341 (4)	C_{22}-C_{23}	1.386 (6)
Co-C_B	1.792 (4)	C_{23}-C_{24}	1.394 (7)
Co-C_1	1.749 (5)	C_{24}-C_{25}	1.386 (8)
Co-C_2	1.787 (4)		
Co-C_3	1.790 (4)		

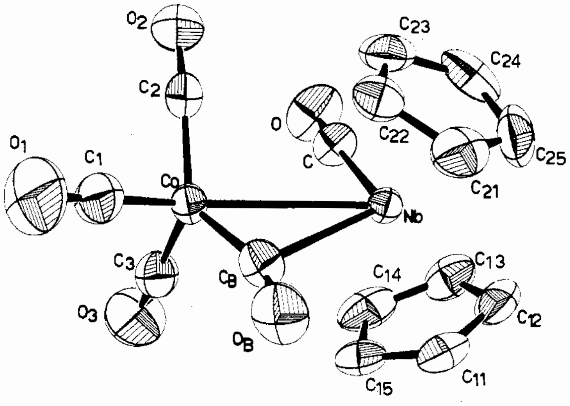

Figure 1.

Table IV. Bond Angles (deg)

Co-Nb-C	76.0 (1)	C_{21}-Nb-C_{22}	32.9 (1)
Co-Nb-C_B	36.7 (1)	C_{21}-Nb-C_{23}	55.6 (1)
C-Nb-C_B	112.6 (1)	C_{21}-Nb-C_{24}	56.3 (2)
Nb-C_B-O_B	120.1 (3)	C_{21}-Nb-C_{25}	33.9 (2)
Co-C_B-O_B	154.1 (3)	C_{22}-Nb-C_{23}	33.5 (1)
Nb-Co-C_1	145.8 (2)	C_{22}-Nb-C_{24}	56.1 (2)
Nb-Co-C_2	91.4 (1)	C_{22}-Nb-C_{25}	55.8 (2)
Nb-Co-C_3	102.4 (1)	Nb-C_{23}-C_{22}	74.9 (2)
C_B-Co-C_1	92.0 (2)	Nb-C_{23}-C_{24}	71.9 (3)
C_B-Co-C_2	134.5 (2)	Nb-C_{24}-C_{23}	73.9 (2)
C_B-Co-C_3	109.6 (2)	Nb-C_{24}-C_{25}	72.2 (3)
C_1-Co-C_2	98.1 (2)	Nb-C_{25}-C_{24}	73.5 (2)
C_1-Co-C_3	105.3 (2)	Nb-C_{25}-C_{21}	75.3 (2)
C_2-Co-C_3	109.1 (2)	C-Nb-C_{21}	133.1 (2)
Co-C_1-O_1	178.6 (13)	C-Nb-C_{22}	107.4 (2)
Co-C_2-O_2	176.7 (8)	C-Nb-C_{25}	115.4 (2)
Co-C_3-O_3	176.2 (4)	C-Nb-C_{11}	131.2 (1)
Nb-C-O	175.3 (5)	C-Nb-C_{12}	112.7 (2)
C_{12}-C_{11}-C_{15}	108.2 (4)	C-Nb-C_{15}	105.9 (2)
C_{11}-C_{12}-C_{13}	108.1 (4)	C_B-Nb-C_{11}	82.9 (1)
C_{12}-C_{13}-C_{14}	108.2 (4)	C_B-Nb-C_{12}	116.9 (1)
C_{13}-C_{14}-C_{15}	107.7 (4)	C_B-Nb-C_{13}	126.9 (1)
C_{14}-C_{15}-C_{11}	107.8 (4)	C_B-Nb-C_{21}	82.0 (2)
C_{22}-C_{21}-C_{25}	108.4 (4)	C_B-Nb-C_{25}	116.8 (2)
C_{21}-C_{22}-C_{23}	108.1 (4)	C_B-Nb-C_{24}	128.4 (2)
C_{22}-C_{23}-C_{24}	108.1 (4)	C_{11}-Nb-Co	109.8 (1)
C_{23}-C_{24}-C_{25}	107.1 (4)	C_{12}-Nb-Co	139.6 (1)
C_{24}-C_{25}-C_{21}	108.3 (4)	C_{13}-Nb-Co	124.1 (1)
Nb-C_B-Co	85.8 (1)	C_{13}-Nb-C	79.5 (2)
C_{11}-Nb-C_{12}	33.9 (2)	C_{14}-Nb-C	75.5 (2)
C_{11}-Nb-C_{13}	56.6 (1)	C_{14}-Nb-Co	90.9 (1)
C_{11}-Nb-C_{14}	56.4 (1)	C_{14}-Nb-C_B	96.5 (2)
C_{11}-Nb-C_{15}	33.4 (1)	C_{15}-Nb-Co	83.7 (1)
C_{12}-Nb-C_{13}	34.4 (2)	C_{15}-Nb-C_B	71.0 (1)
C_{12}-Nb-C_{14}	56.7 (2)	C_{21}-Nb-Co	105.7 (1)
C_{12}-Nb-C_{15}	55.9 (1)	C_{22}-Nb-Co	79.7 (1)
Nb-C_{13}-C_{12}	73.2 (2)	C_{22}-Nb-C_B	72.4 (1)
Nb-C_{13}-C_{14}	74.2 (2)	C_{23}-Nb-C	78.0 (2)
Nb-C_{14}-C_{13}	71.7 (2)	C_{23}-Nb-Co	87.6 (1)
Nb-C_{14}-C_{15}	75.1 (2)	C_{23}-Nb-C_B	98.2 (2)
Nb-C_{15}-C_{14}	70.9 (2)	C_{24}-Nb-C	82.2 (2)
Nb-C_{15}-C_{11}	71.9 (2)	C_{24}-Nb-Co	121.2 (2)
		C_{25}-Nb-Co	135.4 (1)

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 Cp hydrogens were assigned fixed positions (C–H = 0.95 Å; B_{iso} = 5.0 Å^2).

The final agreement factors are $R = 0.048$ and $R_w = 0.057$,[6] and the estimated standard deviation of an observation of unit weight is 1.783. The ratio of data to parameters is 19.7. Atomic coordinates and thermal parameters for all atoms are listed in Table II. Interatomic distances, intramolecular angles, and deviations of atoms

Table V. Selected Molecular Planes

atom	deviation, Å	atom	deviation, Å
Plane 1: Cyclopentadienyl Ring (C_{11}–C_{15}) $0.4379X + 0.8633Y - 0.2509Z = 1.2066$			
C_{11}	−0.0089	O	−2.6459
C_{12}	0.0032	C	−2.4596
C_{13}	0.0037	C_B	−2.5741
C_{14}	−0.0092	Nb	−2.0696
C_{15}	0.0112	O_B	−2.2905
Plane 2: Cyclopentadienyl Ring (C_{21}–C_{25}) $0.6293X + 0.2966Y - 0.7184Z = 2.9681$			
C_{21}	−0.0019	O	2.7931
C_{22}	−0.0037	C	2.5541
C_{23}	0.0079	C_B	2.6179
C_{24}	−0.0090	Nb	2.0678
C_{25}	0.0068	O_B	2.5071
Plane 3: Nb, Co, C, O $0.5480X + 0.6209Y - 0.5604Z = 2.1339$			
Nb	−0.0006	C	0.0017
Co	0.0000	O	−0.0011

planes	dihedral angle, deg	planes	dihedral angle, deg
1,2	44.6	2,3	21.3
1,3	23.6		

from selected planes are listed in Tables III–V, respectively.

Results and Discussion

Description of the Structure. Although spectroscopic characterization was not conclusive, the crystallographic study identified the product as $Cp_2(CO)Nb(\mu\text{-}CO)Co(CO)_3$ (I). In terms of electron counting this is a quite reasonable structure, consisting of two 17-electron fragments, $Cp_2Nb(CO)$ and $Co(CO)_4$, joined by a metal–metal bond (Figure 1). I is isoelectronic with the Nb–Fe compound, $Cp_2(CO)Nb(\mu\text{-}H)Fe(CO)_4$ (II), whose structure we recently reported.[7] The most interesting features of I will be discussed largely in terms of its structural relation to II as well as to $[FeCo(CO)_8]^-$ (III),[8] with which it is also isoelectronic.

Bridging Carbonyl. The bridging carbonyl is very far from symmetric bonding to the two metals, in terms of both metal–carbon distance (Nb–C_B = 2.526 (4), Co–C_B = 1.788 (4) Å) and metal–carbon–oxygen angle (Nb–C_B–O_B = 120.1 (3), Co–C_B–O_B = 154.1 (3)°). While a certain degree of asymmetry is to be expected since the two metals are of different size, these discrepancies appear much too large to be thus simply accounted for. It may be noted that the Co–C_B distance falls within the range of values found for Co–C_T distances in I (1.749 (5)–1.790 (4) Å), while Nb–C_B is considerably longer than Nb–C_T (2.054 (4) Å). (Here and elsewhere C_BO_B refers to the bridging CO and C_TO_T to a terminal CO.)

This group is thus best described as a *semibridging* carbonyl and can be understood within the context of the interpretation of such an interaction offered by Cotton.[9] For comparison, consider III, which is strictly isoelectronic to I if viewed as $(CO)_4Fe^-$–$Co(CO)_4$. In Cotton's view, one of the CO ligands from Co moves to a semibridging position to help delocalize the excess negative charge on Fe. In I there is no formal charge on the Nb, but the (formally) Nb(III) center with two strongly electron-donating Cp groups and only one CO can be reasonably expected to be highly electron-rich, thus favoring a similar arrangement with a semibridging CO.

Several parameters of I and III are compared in Table VI; the similarities are rather striking, considering the rather substantial differences in the groups attached to Co. In particular, the Co–C_B–O_B angle and the Co–C_B distance are nearly the same in both compounds. The IR stretching frequency assigned to C_BO_B in I, 1870 cm^{-1}, is considerably higher than in III (1776 cm^{-1});[10] presumably this reflects the presence of a net negative charge in the latter.

Table VI. Comparison of Some Structural Parameters[d]

	$Cp_2(CO)$-$Nb(\mu\text{-}H)$-$Fe(CO)_4$[a]	$Cp_2(CO)$-$Nb(\mu\text{-}CO)$-$Co(CO)_3$	$[(CO)_4Fe$-$(\mu\text{-}CO)Co$-$(CO)_3]^-$[b]
M–M′	3.324 (1)	2.992 (1)	2.585 (3)
Cp–Cp	43.7	44.6	
C–Nb–M′	82.4 (1)	76.0 (1)	
Co–C_B–O_B		154.1 (3)	151 (2)
M–C_B–O_B		120.1 (3)	129 (1)
M–C_T	2.057 (4)	2.058 (4)	1.687 (9)[c]
M–C_B		2.531 (4)	2.21 (2)
Co–C_T		1.775 (4)[c]	1.74 (2)[c]
Co–C_B		1.792 (4)	1.77 (2)
C_B–O_B		1.165 (4)	1.18 (2)
C_T–O_T		1.135 (5)[c]	1.18 (1)[c]

[a] Reference 7. [b] Reference 8. [c] Averaged value. [d] Distances are in angstroms and angles in degrees.

Metal–Metal Bond Length. In our previous paper[7] we suggested that the Nb–Fe distance in II, 3.318 (1) Å, was unusually long and attributed this lengthening to the effect of the bridging hydrogen. The structure of I gives us a much better standard for direct comparison to II, and indeed, the Nb–Co distance (2.986 (1) Å) is over 0.3 Å shorter, a change which cannot be attributed to any sizable difference in metal size. Of course I does possess the semibridging CO, which might be expected to favor some shortening of the metal–metal distance; it is difficult to decide how much weight to give to these two effects in interpreting the different bond lengths in I and II. However, the results are at least consistent with the hypothesis that a bridging hydrogen atom causes longer, not shorter, metal–metal bond lengths.[11]

The bond length in I might also be compared to that in $Cp(CO)_3MoMn(CO)_5$ (3.083 Å),[12] which also involves a bond between a first- and second-row transition metal and would be expected to have a similar M–M distance on the basis of metallic radii; the shorter (0.1 Å) distance in I *may* be attributable to the effect of the semibridging CO.

Geometry about Niobium. The parameters of the $Cp_2Nb(CO)$ group in I are very similar to those in II (Table VI). The only notable difference is in the C_T–Nb–M angle, which is considerably smaller in I (76.0 (1)°) than in II (82.4 (1)°). From a steric viewpoint, this may indicate less interaction with the $Co(CO)_3$ group in I than the $Fe(CO)_4$ group in II. Electronic interpretations of structural trends in bent-sandwich systems have been proposed,[13] but it is not clear how they should be applied here, especially in light of the added constraints placed on geometry by bridging ligands.

Geometry about Cobalt. The basic arrangement of ligands is similar to that found in III, with the four CO's (including the bridging one) forming a very distorted tetrahedron, with C–Co–C angles varying from 92.0 (2) to 134.5 (2)° (cf. in III, 97.4 (9)–136.4 (9)°[8]). If the Nb is included as a fifth ligand, the geometry is not readily describable in terms of normal five-coordination structures; because one ligand is bridging, however, this could have been expected. The average Co–C_T distance in I is longer and the average C_T–O_T distance shorter than in III (Table VI), although the differences are just within one standard deviation. This trend is consistent with the greater degree of back-bonding in III due to the negative charge, which was also suggested by the lower C_B–O_B stretching frequency.

Spectral Behavior. Both ^1H NMR and IR spectral results suggest that I can exist as more than one isomer in solution. The IR spectrum in the solid state (Nujol mull) shows a very strong peak at 1870 cm^{-1}, assigned to the bridging CO, as well as a relatively simple pattern at higher wavenumbers for the terminal CO's. In contrast, in benzene or toluene the bridging CO peak is substantially weaker, and the terminal CO region is more complex, indicating an equilibrium between the bridged structure found in the solid state and at least one other structure is present in these solvents. This is supported by the ^{1}H NMR, which shows three peaks in the normal Cp region. The two Cp ligands in I are nearly equivalent[14] and should give only a single peak. Analogous behavior has been observed for $Co_2(CO)_8$, which in solution is an equilibrium mixture of doubly CO-bridged (the solid-state structure) and nonbridged isomers.[15] Because of the low overall symmetry of I, it is not possible to use the total CO-stretching absorption pattern to reach any firm conclusions about the other structures in solution, although the relative intensity of the peak assigned to C_B–O_B suggests that they may well be nonbridged too.

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Registry No. I, 69927-38-4; Cp_2NbH_3, 11105-67-2; $Co_2(CO)_8$, 10210-68-1.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes (17 pages). Ordering information is given on any current masthead page.

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Some Reactions of the Octahalodirhenate(III) Ions. 10. Further Study of the Tetrakis(pivalato)dirhenium Dihalides[†]

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The previously known compounds $Re_2(O_2CCMe_3)_4Cl_2$ and $Re_2(O_2CCMe_3)_4Br_2$ have been further studied structurally and spectroscopically. The two compounds are isomorphous, crystallizing in the space group $I4/m$ with $Z = 2$ and the following cell dimensions, where those for the bromide follow those for the chloride in each case: $a = 11.469$ (4), 11.601 (3) Å, $c = 10.733$ (1), 11.154 (3) Å, $V = 1411.8$ (2), 1501.1 (2) Å^3. The molecules have crystallographically imposed $4/m$ (C_{4h}) symmetry and, neglecting the rotational orientations of the CMe_3 groups, approximate very closely to D_{4h} symmetry. The XReReX groups are perfectly linear and parallel to the crystal c axis. The most important molecular dimensions are as follows: for the chloride Re–Re = 2.236 (1) Å, Re–Cl = 2.477 (3) Å, Re–O = 2.025 (4) Å, Re–Re–O = 89.82 (9)°; for the bromide Re–Re = 2.234 (1) Å, Re–Br = 2.603 (1) Å, Re–O = 2.029 (5) Å, Re–Re–O = 89.54 (10)°. The visible spectra are also reported and discussed in a preliminary way.

Introduction

Considerable effort, in several laboratories, has now been devoted to understanding the electronic structures and electronic spectra of compounds with quadruple,[1] triple,[2] and other high-order bonds[3] between transition-metal atoms. With regard to the $M_2X_8^{n-}$ species such as $Re_2Cl_8^{2-}$, $Tc_2Cl_8^{3-}$, and $Mo_2Cl_8^{4-}$ the picture seems reasonably clear. The theoretical descriptions are fairly detailed and the interpretation of spectra is rather complete.[1,3] The bonding in the $Mo_2(NR_2)_6$ and $Mo_2(OR)_6$ species is also understood.[2] For the carboxylato-bridged molecules, as exemplified particularly by the $Mo_2(O_2CR)_4$ compounds, the spectra are replete with subtle details[4] which are not yet fully understood and it cannot yet be said that there is a completely straightforward assignment of the electronic absorption spectra, although a recent study[5] has clarified many points.

For the somewhat more complicated $Re_2(O_2CR)_4X_2$ systems there has not as yet been any serious attempt to study and assign the electronic absorption spectra or to provide a detailed, quantitative description of their electronic structures. It is our intention to undertake both of these tasks by using single-crystal spectroscopy for the former and SCF–Xα–SW calculations, including relativistic corrections, for the latter. Our first step has been to find crystalline compounds well adapted to the spectroscopic studies. The principal requirements are to have favorable orientations of the molecules in the unit cell, crystal symmetry sufficient to define uniquely a set of optic axes, and only one crystallographic type of molecule.

We report here that the pivalates, $Re_2(O_2CCMe_3)_4X_2$, with X = Cl and Br, not only fulfill these minimal requirements but also have structures that are ideal for the purpose of spectroscopic study. The unit cell for these two isomorphous substances (1) contains only molecules related by translation (thus eliminating Davydov splittings), (2) has all molecules rigorously parallel to one another and to one crystallographic axis, and (3) has each molecule at a site of $4/m$ symmetry. An additional favorable property of these substances is that they appear to be sufficiently volatile to allow the measurement of their valence shell ionization spectra in the vapor phase.

Experimental Section

Microanalyses were performed by the Center for Trace Characterization, Texas A&M University. The solution UV–visible spectra were recorded on a Beckman Acta III spectrophotometer in dichloromethane. The pellet spectra were recorded on a Cary 14

[†] Part 9: Cotton, F. A.; DeBoer, B. G.; Jeremic, M. *Inorg. Chem.* **1970**, *9*, 2143. This paper is erroneously numbered part 8.

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