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X-Ray and Neutron Diffraction Studies on H₃Nb(C₅H₅)₂ and H₃Ta(C₅H₅)₂[1]

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Abstract: The molecular structures of $H_3Nb(C_5H_5)_2$ and $H_3Ta(C_5H_5)_2$ have been analyzed by x-ray and neutron diffraction techniques, respectively. In both compounds the central H_3M fragment is planar within experimental error and defines a noncrystallographic mirror plane for the molecule. The three hydridic atoms are essentially equidistant from the metal atom and are arranged with the central M–H bond in a bisecting position. From the x-ray diffraction analysis of $H_3Nb(C_5H_5)_2$, Nb–H = 1.65 (6), 1.65 (6), and 1.76 (7) Å, and H–Nb–H = 65 (3) and 61 (3)°. More accurate distances and angles were obtained from the neutron diffraction analysis of $H_3Ta(C_5H_5)_2$: Ta–H = 1.769 (8), 1.775 (9), and 1.777 (9) Å; H–Ta–H = 62.8 (5) and 63.0 (4)°. Other important molecular parameters are as follows: for $H_3Nb(C_5H_5)_2$, Nb–ring(centroid) = 2.059 Å, Nb–C (av) = 2.375 Å, ring–Nb–ring bending angle = 141.6°; for $H_3Ta(C_5H_5)_2$, Ta–ring = 2.065 Å, Ta–C(av) = 2.393 Å, ring–Ta–ring bending angle = 139.9°. The structure of the isoelectronic compound $[H_3W(C_5H_5)_2]^+Cl^-$ has also been examined, and found to be similar to that of $H_3Nb(C_5H_5)_2$ and $H_3Ta(C_5H_5)_2$. Crystallographic details: for $H_3Nb(C_5H_5)_2$, space group $P4_12_12$, a = 11.012 (5) Å, c = 14.960 (5) Å, V = 1814.1 Å³, Z = 8; for $H_3Ta(C_5H_5)_2$, space group $P4_12_12$, a = 10.965 (5) Å, c = 14.817 (7) Å, V = 1781.6 Å³, Z = 8. Final agreement factors (based on F) for data with $I > 3\sigma$: in $H_3Nb(C_5H_5)_2$, R_F = 0.035 and R_{wF} = 0.043 for 1530 reflections (x-ray data collected at room temperature); in $H_3Ta(C_5H_5)_2$, R_F = 0.069 and R_{wF} = 0.051 for 841 reflections (neutron data collected at 90 K).

The bonding in bent metal sandwich complexes has been an actively discussed subject in recent years.[4-7] The original model proposed by Ballhausen and Dahl in 1961[4] involved three hybrid orbitals directed as shown in I, while an alternative model, proposed by Alcock in 1967,[5] essentially replaced the central orbital in the Ballhausen–Dahl scheme (ψ_3 in I) by a two-lobed orbital perpendicular to it (ψ_3' in II).

I II
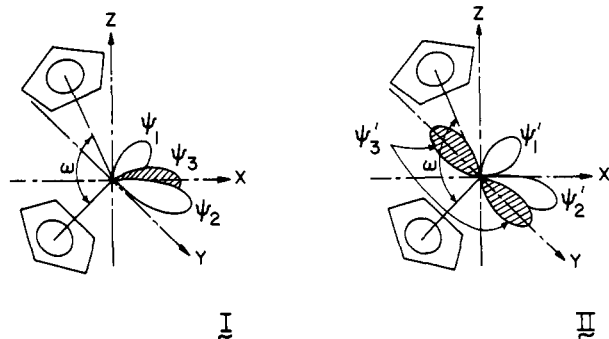
It is now fairly clear that in complexes of the type $(C_5H_5)_2ML_2$ the Alcock model is preferred. Recent x-ray crystallographic[5,6] and EPR studies[7a,b] by Green, Prout, Dahl, and their co-workers have shown that for the series of compounds $(C_5H_5)_2ML_2$ (L = CH_3, F, Cl, Br, I, SC_6H_5), the observed structural features are best explained by the presence or absence of nonbonding electrons in a ψ_3'-type orbital (II). Lauher and Hoffmann recently have systematically studied

the bonding in such complexes, within the framework of extended Hückel (EH) MO theory.[7c] Their EH treatment delineates three frontier orbitals available to bond to the ligands L, quite similar to those deduced on qualitative grounds by Green et al.[6a] and clarifies the relationship between the contrasting hybridization schemes of Ballhausen and Dahl and Alcock models. They point out that these latter schemes are equivalent to taking different linear combinations of the frontier orbitals. In this paper, as part of our continuing investigations of the structures of metal hydride complexes,[8] we report the crystal structure determinations of two of the simplest complexes of the $(C_5H_5)_2ML_3$ type: $(C_5H_5)_2NbH_3$ and $(C_5H_5)_2TaH_3$.

$H_3Ta(C_5H_5)_2$ was first prepared by Wilkinson and co-workers in 1961 by the reaction of $TaCl_5$, NaC_5H_5, and $NaBH_4$ in tetrahydrofuran.[9] On the basis of NMR data (which showed an A_2B pattern of signals in the hydridic region) and other spectral evidence, a bent-sandwich structure with three M–H bonds arranged along orbitals ψ_1–ψ_3 in I was proposed. Recent photoelectron studies of the compound support this model by showing three peaks attributable to Ta–H bonding electrons.[6c]

Interest in $H_3Ta(C_5H_5)_2$ was heightened in 1970 when Barefield, Parshall, and Tebbe discovered a remarkable H_2/D_2 exchange reaction catalyzed by it: when a C_6D_6 solution of $H_3Ta(C_5H_5)_2$ is heated under a hydrogen atmosphere, HD and D_2 can be detected in the vapor phase.[10] This exchange reaction, which was also found to take place with other polyhydrido

Table I. Crystal Data for $H_3Nb(C_5H_5)_2$ and $H_3Ta(C_5H_5)_2$

$H_3Nb(C_5H_5)_2$ (x-ray; room temp.)	$H_3Ta(C_5H_5)_2$ (neutron, 90 K)[a]
Space group $P4_12_12$	Space group $P4_12_12$
$a = 11.012$ (5) Å	$a = 10.965$ (5) Å
$c = 14.960$ (5) Å	$c = 14.817$ (7) Å
$V = 1814.1$ Å^3	$V = 1781.6$ Å^3
$Z = 8$	$Z = 8$
Mol wt = 226.1	Mol wt = 314.2
ρ(calcd)[b] = 1.656 g cm^{-3}	ρ(calcd)[b] = 2.342 g cm^{-3}
$\mu = 12.2$ cm^{-1} (for Mo Kα x-rays)	$\mu = 2.38$ cm^{-1} (for 1.02-Å neutrons)
$R_F = 0.035$, $R_{wF} = 0.043$ for 1530 reflections with $I > 3\sigma(I)$	$R_F = 0.069$, $R_{wF} = 0.051$ for 841 reflections with $F > 3\sigma(F)$

[a] For $H_3Ta(C_5H_5)_2$, room temperature measurements of unit cell parameters yielded the following results: $a = 11.026$ (14) Å, $c = 15.018$ (19) Å, $V = 1825.8$ Å^3, ρ(calcd) = 2.284 g cm^{-3}. [b] Experimental densities could not be obtained because of the reactivities of the compounds.

complexes such as H_5IrL_2 (L = PMe$_3$, PEt$_3$, PEt$_2$Ph), provided the impetus for the synthesis of the then unknown niobium analogue.[11a] $H_3Nb(C_5H_5)_2$ was found to exhibit many of the properties of $H_3Ta(C_5H_5)_2$, but turned out to be a much more reactive compound. In particular, it easily loses H_2 in the presence of other ligands L (L = C_2H_4, CO, PR$_3$) to form complexes of the type $(C_5H_5)_2NbH(L)$. Reactions of both $H_3Ta(C_5H_5)_2$ and $H_3Nb(C_5H_5)_2$ with Lewis acids suggest a significantly higher basicity for the unique central M–H bond relative to the other two.[11b]

Experimental Section

The samples of $H_3Nb(C_5H_5)_2$ and $H_3Ta(C_5H_5)_2$ used in this work were generously supplied by Drs. F. N. Tebbe and G. W. Parshall of E. I. duPont de Nemours, Co. The structural analysis was first carried out on crystals of $H_3Nb(C_5H_5)_2$, largely because we felt that the lower x-ray scattering power of Nb relative to Ta would make the detection of the hydridic positions in the Nb compound much easier. The instability of $H_3Nb(C_5H_5)_2$ in solution, however, precluded the growth of large crystals necessary for neutron diffraction work. The more stable $H_3Ta(C_5H_5)_2$ fortunately could be kept for longer periods of time in solution, and after much effort we were able to grow a few large crystals via slow cooling from a concentrated toluene solution. The isomorphous relationship between the crystals of the two compounds simplified the subsequent structure analysis in that it enabled us to use the atomic positions from the x-ray analysis of $H_3Nb(C_5H_5)_2$ to phase the neutron diffraction data of $H_3Ta(C_5H_5)_2$.

X-Ray Diffraction Analysis of $H_3Nb(C_5H_5)_2$. A columnar-shaped crystal of dimensions 0.29 × 0.30 × 0.77 mm was mounted along its long axis in a thin-walled glass capillary in an inert atmosphere chamber. Preliminary precession photographs indicated the tetragonal space group $P4_12_12$, with the unit cell parameters and other crystallographic details given in Table I.

One octant of data was collected by the $\theta/2\theta$ scan technique on a Nonius CAD-3 diffractometer with Zr-filtered Mo Kα radiation up to a 2θ limit of 50°. For the inner-shell data ($2\theta \leq 36°$), an entire half-sphere of reflections was collected, representing eight asymmetric sets of data. A scan speed of 10°/min was used, with the scan defined as $\Delta\theta = (1.2 + 0.15 \tan \theta)°$. Each reflection was scanned between two and ten times, depending upon its intensity. Background counts were taken at the beginning and the end of each scan, and the takeoff angle was set at 4°. Zirconium foil attenuators were automatically inserted to prevent the counting rate from exceeding 2500 counts/s. As a check on the stability of the experiment, the (6, 0, 0), (0, 6, 0) and (0, 0, 12) reflections were measured at 60-reflection intervals during data collection. No significant variations in these monitored intensities were observed. Subsequent data processing yielded a set of 1530 reflections with $I > 3\sigma$: this represents one complete octant ($2\theta \leq 50°$) and contains two Bijvoet related sets of data.[12] The standard deviation of each intensity reading was estimated using the expression $\sigma(I) =$

$[(\text{peak} + \text{background counts}) + (0.04(\text{net intensity}))^2]^{1/2}$. Observed intensities were corrected for Lorentz and polarization effects. An absorption correction was not applied because of the low absorption coefficient ($\mu = 12.2$ cm^{-1} for Mo Kα radiation), and the observation that the intensity of an axial reflection (at $\chi = 90°$) showed no significant variation with spindle angle ϕ.

The structure was solved with conventional heavy atom methods: the coordinates of the niobium atom were obtained from a Patterson synthesis, and the carbon atoms were located from a series of difference Fourier maps.[13] The hydrogen atom positions were readily located from special difference Fourier syntheses calculated with low-angle data.[14a] Subsequent cycles of least-squares refinement resulted in the successful convergence of all atomic parameters (a total of 112 variables). In the least-squares procedure, the metal-bonded hydrogen atoms were refined isotropically and all other atoms refined anisotropically.[14b] The temperature factors of the three hydridic atoms (H(11), H(12), H(13)) converged to reasonable values during this refinement (3.7, 4.2, and 5.9 Å^2, respectively). The cyclopentadienyl hydrogen atoms were set at calculated positions, given isotropic temperature values of 5.0 Å^2, and were not refined. The final agreement factors[15] are $R_F = 0.0352$ and $R_{wF} = 0.0431$ for data with $I > 3\sigma$ (1530 reflections) and the goodness-of-fit parameter is 0.78.

At this point the possibility that the space group might be the enantiomorphic $P4_32_12$ was checked out. The refinement was repeated with inverted coordinates ($-x, -y, -z$) in space group $P4_32_12$. This refinement converged to values of $R_F = 0.0354$ and $R_{wF} = 0.0438$. According to Hamilton's R factor significance test, the ratio of agreement factors $[R_{wF}(P4_32_12)/R_{wF}(P4_12_12) = 1.016]$ is sufficient to favor $P4_12_12$ as the correct space group at a 99.5% confidence level.[16a]

Neutron Diffraction Analysis of $H_3Ta(C_5H_5)_2$. First Crystal. An initial set of neutron diffraction data was collected on a small octahedral-shaped crystal (volume 1.5 mm^3; dimensions 1.61 × 1.79 × 1.50 mm) which was unfortunately in a partially decomposed state. The crystal was mounted in a quartz capillary in an inert atmosphere chamber. Precession photographs indicated that it was isomorphous with the niobium complex. Data were collected at room temperature on an automated four-circle diffractometer at the Brookhaven High Flux Beam Reactor[16b] with a crystal-monochromated neutron beam of wavelength 1.381 Å. Intensities were measured for 1041 unique reflections having $d^* < 0.831$ Å^{-1}, with a $\theta/2\theta$ step-scan technique. The scan range was varied according to $\Delta2\theta = 1.2(1 + 13.3 \tan \theta)°$ for the high-angle data ($0.50 < d^* < 0.831$) and $\Delta2\theta = 4.0°$ for the low-angle data, and the step size was varied to give approximately 70 steps for each scan.

Background corrections were made by a method which divides the reflection profile in such a way that $\sigma(I)/I$ is minimized.[16c] I is the integrated intensity and $\sigma(I)$ its estimated standard deviation based on counting statistics. The observed intensities were corrected for absorption by numerical integration over a Gaussian grid; calculated transmission coefficients ranged from $t = 0.79$ to 0.86.[17] Squared observed structure factors were obtained as $F_o^2 = (I/t) \sin(2\theta)$ and were averaged for symmetry-related reflections.

The starting parameters for refinement were the final coordinates from the x-ray analysis on the isomorphous compound $H_3Nb(C_5H_5)_2$. Because of the weakness of the data, it was felt that rigid-body refinement[18] would produce the best results. This was carried out using an idealized planar D_{5h} geometry for the cyclopentadienyl groups with distances (C–C = 1.404, C–H = 1.073 Å) derived from an earlier neutron diffraction analysis of $HMo_2(C_5H_5)_2(CO)_4(\mu\text{-PMe}_2)$.[19] The atoms of the H_3Ta fragment of the molecule were refined independently and anisotropically, while the atoms of the rigid groups were given individual isotropic temperature factors. The quantity minimized by the refinement was $\Sigma w|F_o - F_c|^2$; weights were chosen as $w = 1/\sigma^2(F_o)$ with

$$\sigma^2(F_o) = \sigma^2_{count}(F_o) + (0.02F_o)^2$$

and with σ_{count} based on counting statistics. The neutron scattering lengths ($b \times 10^{-12}$ cm) used in the refinements were: $b_H = -0.374$, $b_C = 0.6648$, $b_{Ta} = 0.691$.[20] Only data with $F > 3\sigma$ (610 reflections) were used. The final agreement factors, $R_F = 0.143$ and $R_{wF} = 0.108$,[15] are comparable to those in other neutron diffraction analyses where weak data are limiting factors.[21] Because of the subsequent availability of a much improved data set (vide infra), however, the results of this analysis are simply summarized in a footnote.[22]

Table II. Final Atomic Parameters[a] for $H_3Nb(C_5H_5)_2$ (x-ray data)

A. Atomic Positions

Atom	x	y	z
Nb	0.18925 (4)	0.19776 (4)	0.21482 (3)
C(1)	0.0014 (6)	0.2311 (8)	0.2892 (6)
C(2)	0.0677 (9)	0.3415 (8)	0.2923 (6)
C(3)	0.1711 (8)	0.3219 (7)	0.3425 (5)
C(4)	0.1680 (6)	0.2016 (8)	0.3720 (4)
C(5)	0.0649 (6)	0.1478 (7)	0.3408 (4)
C(6)	0.3214 (6)	0.1494 (6)	0.0939 (4)
C(7)	0.3463 (6)	0.2694 (6)	0.1184 (5)
C(8)	0.3915 (6)	0.2682 (6)	0.2044 (5)
C(9)	0.3967 (6)	0.1475 (8)	0.2357 (5)
C(10)	0.3549 (6)	0.0741 (6)	0.1666 (5)
H(11)	0.139 (5)	0.309 (6)	0.150 (4)
H(12)	0.092 (5)	0.155 (6)	0.137 (4)
H(13)	0.135 (7)	0.047 (6)	0.215 (5)

B. Thermal Parameters[b]

Atom	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Nb	45.6 (4)	40.3 (4)	26.8 (2)	4.2 (7)	1.5 (5)	1.1 (5)
C(1)	70 (6)	132 (9)	56 (4)	47 (10)	30 (8)	−17 (10)
C(2)	174 (10)	69 (6)	65 (4)	113 (14)	93 (13)	21 (9)
C(3)	135 (9)	87 (7)	54 (4)	−54 (14)	64 (10)	−73 (9)
C(4)	99 (6)	110 (7)	26 (2)	6 (11)	9 (6)	3 (8)
C(5)	94 (6)	63 (5)	38 (3)	−18 (9)	40 (8)	10 (7)
C(6)	69 (6)	114 (6)	37 (3)	24 (10)	17 (7)	−30 (8)
C(7)	69 (6)	99 (7)	56 (4)	−20 (9)	47 (8)	12 (8)
C(8)	54 (5)	104 (8)	60 (4)	−34 (9)	16 (8)	−16 (9)
C(9)	62 (5)	146 (8)	43 (4)	65 (10)	−13 (7)	−13 (9)
C(10)	64 (5)	81 (6)	62 (4)	44 (10)	22 (8)	−14 (8)
H(11)	3.7 (13)[c]					
H(12)	4.2 (14)[c]					
H(13)	5.9 (17)[c]					

[a] Numbers in parentheses refer to the standard deviation of the least significant digit. Not listed in this table are the calculated positions for the cyclopentadienyl hydrogen atoms, which were included in the least-squares analysis but not refined. [b] The form of the thermal ellipsoid is: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [c] Isotropic temperature factor, in units of Å^2.

Second Crystal. Several months later we were able to grow a much larger, triangular-faced crystal of the Ta complex (volume 7.80 mm^3; dimensions 3.00 × 2.40 × 1.15 mm). As with the first crystal, this one was obtained by slow cooling of a concentrated toluene solution and mounted in a quartz cap under an inert atmosphere. This time the crystal was placed in a specially constructed closed-cycle helium refrigerator for low-temperature data collection.[23] Data were collected as described earlier with a neutron beam of wavelength 1.0194 Å. The temperature of data collection was 90 K. The cell dimensions, refined by a least-squares procedure based on the setting angles of well-centered reflections evenly distributed in reciprocal space, are noticeably smaller than those obtained at room temperature (see Table I, footnote). Intensities were measured in two ways: the inner-shell data (0 < d^* < 0.703; two asymmetric sets) were collected with an ω step-scan mode (scan width = 1.3°) to minimize interference from aluminum diffraction lines of the cryostat, while the outer-shell data (0.671 < d^* < 1.261; one asymmetric set) were collected with a $\theta/2\theta$ step-scan mode [scan formula $\Delta 2\theta = 0.5 (1 + 10.7 \tan \theta)$]. The raw intensity data were processed as described earlier and corrected for absorption effects. Calculated transmission coefficients varied between 0.54 and 0.69. Several dozen reflections had to be rejected because of interference from aluminum diffraction lines. The resulting data set is of vastly better quality than that from the first crystal, and subsequent refinement was carried out without rigid-body constraints, using all reflections (including those with weak or negative F_o^2 values). After exhaustive full-matrix least-squares refinement[13] with anisotropic temperature factors assigned to all atoms, the final agreement factors[15] are as follows: for all data (1054 reflections), $R_{F^2} = 0.096$ and

Table III. Final Atomic Parameters for $H_3Ta(C_5H_5)_2$ (neutron data)

A. Atomic Positions

Atom	x	y	z
Ta	0.1878 (3)	0.1987 (3)	0.2132 (2)
C(1)	−0.0004 (4)	0.2326 (4)	0.2902 (3)
C(2)	0.0659 (5)	0.3440 (4)	0.2924 (3)
C(3)	0.1729 (5)	0.3244 (4)	0.3438 (3)
C(4)	0.1716 (4)	0.2003 (4)	0.3733 (3)
C(5)	0.0636 (4)	0.1450 (4)	0.3410 (3)
C(6)	0.3230 (3)	0.1529 (4)	0.0910 (3)
C(7)	0.3458 (4)	0.2773 (4)	0.1159 (3)
C(8)	0.3917 (4)	0.2763 (4)	0.2058 (3)
C(9)	0.3982 (3)	0.1530 (4)	0.2359 (3)
C(10)	0.3578 (4)	0.0771 (4)	0.1644 (3)
H(1)	−0.0858 (9)	0.2218 (10)	0.2559 (6)
H(2)	0.0387 (10)	0.4285 (9)	0.2605 (7)
H(3)	0.2433 (10)	0.3928 (10)	0.3556 (7)
H(4)	0.2404 (9)	0.1561 (11)	0.4129 (6)
H(5)	0.0349 (9)	0.0488 (8)	0.3526 (5)
H(6)	0.2892 (8)	0.1232 (8)	0.0270 (5)
H(7)	0.3318 (8)	0.3581 (9)	0.0750 (6)
H(8)	0.4164 (9)	0.3565 (10)	0.2439 (6)
H(9)	0.4295 (9)	0.1228 (9)	0.3014 (5)
H(10)	0.3555 (9)	−0.0232 (7)	0.1658 (6)
H(11)	0.1289 (8)	0.3109 (8)	0.1393 (5)
H(12)	0.0814 (8)	0.1497 (9)	0.1306 (6)
H(13)	0.1496 (8)	0.0413 (7)	0.2124 (6)

B. Thermal Parameters[a]

Atom	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Ta	20 (3)	25 (3)	8 (1)	2 (2)	2 (2)	2 (2)
C(1)	34 (4)	54 (4)	18 (2)	13 (3)	11 (3)	6 (2)
C(2)	73 (5)	33 (4)	27 (2)	18 (4)	18 (3)	5 (3)
C(3)	75 (5)	43 (4)	15 (2)	−12 (4)	15 (3)	−14 (2)
C(4)	50 (4)	47 (4)	13 (2)	2 (4)	2 (2)	−4 (2)
C(5)	33 (3)	33 (4)	18 (2)	−5 (3)	10 (2)	2 (2)
C(6)	33 (4)	33 (3)	11 (2)	4 (3)	4 (2)	−1 (2)
C(7)	32 (4)	36 (4)	15 (2)	−1 (3)	5 (2)	2 (2)
C(8)	26 (4)	45 (4)	20 (2)	−10 (3)	0 (2)	2 (3)
C(9)	31 (4)	47 (4)	14 (2)	5 (3)	−5 (2)	1 (2)
C(10)	35 (4)	33 (4)	19 (2)	9 (3)	3 (2)	−4 (2)
H(1)	47 (9)	126 (12)	42 (5)	−1 (9)	11 (6)	9 (7)
H(2)	127 (13)	55 (9)	53 (5)	51 (9)	39 (7)	29 (6)
H(3)	119 (14)	113 (13)	46 (5)	−59 (11)	35 (7)	−44 (7)
H(4)	74 (10)	123 (12)	25 (4)	3 (9)	−9 (5)	21 (7)
H(5)	106 (11)	39 (8)	33 (4)	−21 (7)	21 (6)	2 (5)
H(6)	75 (8)	85 (9)	14 (3)	−1 (8)	−2 (5)	−13 (5)
H(7)	71 (10)	67 (9)	34 (5)	−3 (8)	14 (5)	20 (6)
H(8)	74 (9)	86 (10)	40 (5)	−27 (8)	−2 (6)	−14 (7)
H(9)	84 (9)	100 (11)	24 (4)	18 (8)	−13 (5)	7 (6)
H(10)	92 (10)	27 (8)	49 (5)	6 (7)	−1 (6)	−13 (5)
H(11)	77 (9)	63 (9)	27 (4)	30 (7)	−1 (4)	18 (5)
H(12)	67 (9)	83 (9)	37 (4)	−19 (8)	−17 (5)	−8 (6)
H(13)	63 (8)	45 (8)	43 (4)	−18 (7)	14 (6)	−11 (5)

[a] The form of the thermal ellipsoid is: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

$R_{wF^2} = 0.096$; for "significant" data ($I > 3\sigma$) (841 reflections), $R_F = 0.069$ and $R_{wF} = 0.051$. Extinction effects[24] are very small, with only six reflections having E^2 values less than 0.995. The goodness-of-fit parameter, $S = [\Sigma w(F_o^2 - |F_c|^2)^2/(N_o - N_v)]^{1/2}$, is 1.76.

Discussion

The final atomic parameters for $H_3Nb(C_5H_5)_2$ and $H_3Ta(C_5H_5)_2$ are listed in Tables II and III, and distances and angles for both molecules are given in Table IV. Listings of the observed and calculated structure factors for the two structures are available.[27] Except for footnote 22, all the results of

Table IV. Distances and Angles in $H_3Nb(C_5H_5)_2$ and $H_3Ta(C_5H_5)_2$

	$H_3Nb(C_5H_5)_2$ (x-ray)	$H_3Ta(C_5H_5)_2$ (neutron)		$H_3Nb(C_5H_5)_2$ (x-ray)	$H_3Ta(C_5H_5)_2$ (neutron)
M-H(11)	1.65 (6)	1.769 (8)	H(11)-M-H(12)	65 (3)°	62.8 (5)°
M-H(12)	1.65 (6)	1.775 (9)	H(11)-H-H(13)	126 (3)°	125.8 (5)°
M-H(13)	1.76 (7)	1.777 (9)	H(12)-M-H(13)	61 (3)°	63.0 (4)°
Av	1.69 (4) Å	1.774 (3) Å			
M-C(1)	2.377 (7)	2.387 (6)	C(1)-H(1)		1.072 (13)
M-C(2)	2.374 (8)	2.388 (6)	C(2)-H(2)		1.082 (11)
M-C(3)	2.357 (8)	2.381 (5)	C(3)-H(3)		1.090 (13)
M-C(4)	2.363 (6)	2.378 (5)	C(4)-H(4)		1.073 (12)
M-C(5)	2.393 (6)	2.406 (5)	C(5)-H(5)		1.115 (10)
M-C(6)	2.381 (7)	2.393 (5)	C(6)-H(6)		1.069 (10)
M-C(7)	2.386 (7)	2.413 (5)	C(7)-H(7)		1.084 (11)
M-C(8)	2.364 (6)	2.395 (5)	C(8)-H(8)		1.079 (12)
M-C(9)	2.370 (6)	2.384 (5)	C(9)-H(9)		1.080 (9)
M-C(10)	2.387 (7)	2.403 (5)	C(10)-H(10)		1.100 (10)
Av[a]	2.375 (4) Å	2.393 (3) Å	Av[a]		1.084 (4) Å
C(1)-C(2)	1.418 (11)	1.422 (6)	H(1)-C(1)-C(2)		123.5 (7)
C(2)-C(3)	1.381 (12)	1.415 (7)	H(1)-C(1)-C(5)		127.9 (7)
C(3)-C(4)	1.396 (10)	1.429 (6)	H(2)-C(2)-C(1)		125.8 (8)
C(4)-C(5)	1.363 (9)	1.414 (6)	H(2)-C(2)-C(3)		126.4 (8)
C(5)-C(1)	1.388 (10)	1.408 (6)	H(3)-C(3)-C(2)		124.7 (8)
C(6)-C(7)	1.398 (10)	1.435 (6)	H(3)-C(3)-C(4)		127.8 (8)
C(7)-C(8)	1.380 (10)	1.425 (6)	H(4)-C(4)-C(3)		126.2 (7)
C(8)-C(9)	1.411 (11)	1.425 (6)	H(4)-C(4)-C(5)		125.5 (7)
C(9)-C(10)	1.389 (10)	1.419 (6)	H(5)-C(5)-C(4)		126.3 (6)
C(10)-C(6)	1.416 (10)	1.421 (6)	H(5)-C(5)-C(1)		125.9 (6)
Av[a]	1.394 (6) Å	1.421 (3) Å	H(6)-C(6)-C(7)		125.3 (6)
			H(6)-C(6)-C(10)		126.5 (6)
C(1)-C(2)-C(3)	108.0 (6)°	107.8 (4)°	H(7)-C(7)-C(6)		127.5 (6)
C(2)-C(3)-C(4)	107.4 (7)°	107.5 (4)°	H(7)-C(7)-C(8)		125.3 (6)
C(3)-C(4)-C(5)	109.0 (6)°	108.3 (4)°	H(8)-C(8)-C(7)		124.8 (7)
C(4)-C(5)-C(1)	108.8 (6)°	107.8 (4)°	H(8)-C(8)-C(9)		126.6 (7)
C(5)-C(1)-C(2)	106.8 (6)°	108.6 (4)°	H(9)-C(9)-C(8)		126.0 (6)
C(6)-C(7)-C(8)	107.8 (6)°	107.1 (4)°	H(9)-C(9)-C(10)		126.1 (6)
C(7)-C(8)-C(9)	109.4 (6)°	108.5 (4)°	H(10)-C(10)-C(9)		125.5 (6)
C(8)-C(9)-C(10)	106.8 (6)°	107.9 (4)°	H(10)-C(10)-C(6)		126.3 (6)
C(9)-C(10)-C(6)	108.4 (6)°	108.2 (3)°	Av[a]		126.0 (2)°
C(10)-C(6)-C(7)	107.6 (6)°	108.2 (4)°			
Av[a]	108.0 (3)°	108.0 (1)°			

[a] The esd's for the mean values are calculated according to $[\Sigma(x_i - \bar{x})^2/n(n - 1)]^{1/2}$; where x represents the mean value of an observation x_i.

$H_3Ta(C_5H_5)_2$ quoted in this paper are derived from the low-temperature neutron data (collected from the second crystal). Corrections to bond lengths and angles due to thermal motion were found to be quite small and have not been included.

$H_3Nb(C_5H_5)_2$. The molecular plot of $H_3Nb(C_5H_5)_2$ is shown in Figure 1. The feature of main interest is the fact that the three hydridic hydrogens are arranged as the lobes of the Ballhausen-Dahl model (I). The H_3Nb fragment is planar within ±0.03 Å and defines a noncrystallographic mirror plane for the molecule. The central H atom is situated in a bisecting position [H(11)-Nb-H(12) = 65 (3), H(12)-Nb-H(13) = 61 (3), H(11)-Nb-H(13) = 126 (3)°], and the Nb-H bond lengths are essentially equal [Nb-H(11) = 1.65 (6), Nb-H(12) = 1.65 (6), Nb-H(13) = 1.76 (7) Å]. The difference between the Nb-H(13) distance and the other two is less than two standard deviations and is not considered to be significant.

The rest of the structure is very similar to the geometries of other bent sandwich complexes.[6] The metal-ring perpendicular distances [2.057 (10), 2.061 (11) Å], average Nb-C and C-C distances [2.375 (4) and 1.394 (6) Å, respectively], and bending angle[28] (141.6°) are all very close to corresponding values in $HNb(C_5H_5)_2(CO)$,[29] $Nb(C_5H_5)_2(C_2H_4)(C_2H_5)$,[30] and $[HNb(C_5H_5)(C_5H_4)]_2$.[31] The average Nb-H distance (1.69 Å) also agrees very well with that found in $[HNb(C_5H_5)(C_5H_4)]_2$ (1.70 Å).[31] These comparisons are summarized in Table V.

$H_3Ta(C_5H_5)_2$. In the neutron diffraction analysis of $H_3Ta(C_5H_5)_2$ most of the important molecular parameters found in $H_3Nb(C_5H_5)_2$ are again observed: the bent C_{2v} structure (Figures 2 and 3), and the planarity of the central MH_3 fragment. The three Ta-H distances are essentially equal [Ta-H(11) = 1.769 (8), Ta-H(12) = 1.775 (9), Ta-H(13) = 1.777 (9) Å], the central M-H bond is again found in a bisecting position [H(11)-Ta-H(12) = 62.8 (5), H(12)-Ta-H(13) = 63.0 (4), H(11)-Ta-H(13) = 125.8 (5)°], and the H_3Ta fragment is planar within ±0.002 Å. Metal-ring perpendicular distances are 2.061 and 2.069 Å, the average metal-carbon distance is 2.393 Å, and the bending angle (ω)[28] is 139.9°. The hydrogen atoms in $(C_6H_6)Cr(CO)_3$ are bent slightly, but significantly, toward the metal,[32] while the cyclopentadienyl hydrogen atoms in $HMo_2(C_5H_5)_2(CO)_4(\mu\text{-}PMe_2)$ are bent slightly away from the metal.[19] In Cp_2TaH_3, however, neither of these trends is seen (Table VI). Although electronic effects may be responsible for forcing hydrogens out of the C_5 plane,[40] intermolecular crowding seems to dominate in this case. There are two very short H⋯H interactions that are considerably less than the usual 2.2-2.4 Å van der Waals distance (Table VII).

The energy barrier to rotation of the $\pi\text{-}C_5H_5$ rings is low and

Table V. A Comparison of Molecular Parameters of $H_3Nb(C_5H_5)_2$, $H_3Ta(C_5H_5)_2$, and Related Compounds

Compound	ω, deg[a]	M–ring, Å[b]	M–C(av), Å	M–H(av), Å	Ref
$H_3Nb(C_5H_5)_2$	141.6	2.059	2.375	1.69	This work
$HNb(C_5H_5)_2(CO)$	143	2.04	2.36		29
$Nb(C_5H_5)_2(C_2H_4)(C_2H_5)$	132.4	2.096	2.402		30
$[HNb(C_5H_5)(C_5H_4)]_2$	140.4	2.058	2.398	1.70	31
$H_3Ta(C_5H_5)_2$	139.9	2.065	2.393	1.774	This work
$[H_3W(C_5H_5)_2]^+Cl^-$	148.2	1.873	2.261		This work[c]
$D_2Mo(C_5H_5)_2$	148.2	1.96	2.32	1.96	39

[a] Bending angle; see ref 28. [b] Average perpendicular distance between the metal atom and the cyclopentadienyl rings. [c] See ref 33.

Table VI. Displacements[a] of the Atoms of the $H_3Ta(C_5H_5)_2$ Cyclopentadienyl Rings from the Planes of the Five Carbon Atoms

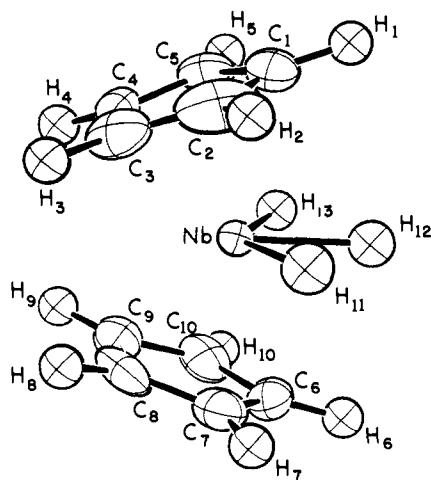Ring 1: Least-Squares Plane of Atoms C(1), C(2), C(3), C(4), C(5)
(direction cosines −0.4480, 0.2767, 0.8278)

C(1)	−0.007	H(1)	−0.004
C(2)	0.003	H(2)	0.014
C(3)	0.002	H(3)	−0.022
C(4)	−0.006	H(4)	−0.022
C(5)	0.008	H(5)	0.012

Ring 2: Least-Squares Plane of Atoms C(6), C(7), C(8), C(9), C(10)
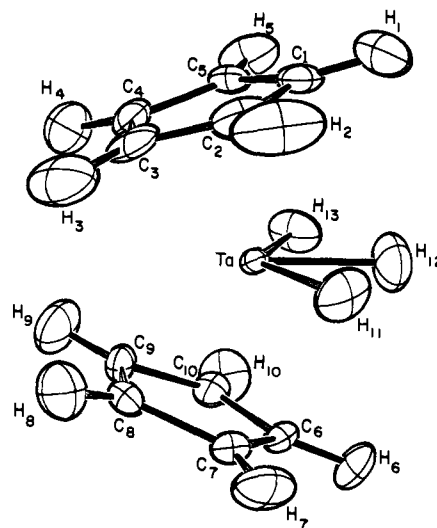(direction cosines 0.9321, −0.0630, −0.3567)

C(6)	−0.010	H(6)	0.003
C(7)	0.006	H(7)	0.023
C(8)	0.001	H(8)	−0.003
C(9)	−0.007	H(9)	−0.012
C(10)	0.011	H(10)	0.048

[a] Displacements are expressed in angstroms. A negative value means that the atom is displaced toward the Ta atom.

Figure 2. The molecular structure of $H_3Ta(C_5H_5)_2$, based on neutron data. 50% probability ellipsoids are shown.

Figure 1. The molecular structure of $H_3Nb(C_5H_5)_2$, based on x-ray data. 40% probability ellipsoids are shown.
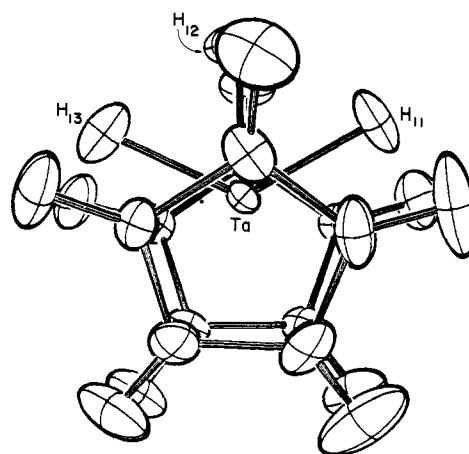
Figure 3. A view of the $H_3Ta(C_5H_5)_2$ molecule normal to the H_3Ta plane. Note the "slipped" position of the tantalum atom.

the conformation of the rings in the solid state is governed by crystal packing forces. Ring motion is seen in the shape of the thermal ellipsoids of the ring hydrogens (Figure 3). In both $H_3Nb(C_5H_5)_2$ and $H_3Ta(C_5H_5)_2$ the rings are eclipsed, giving the molecule two noncrystallographic mirror planes. The metal–ring–metal bending angle is more influenced by the electronic requirements of the metal and by intramolecular nonbonding contacts than by packing forces. The bending angle in $H_3Ta(C_5H_5)_2$ is over 8° smaller than that found in the isoelectronic $[H_3W(C_5H_5)_2]^+Cl^-$,[33] perhaps reflecting a smaller M–ring distance in the W complex (Table V).

A rather interesting result in both structures is the relative closeness of H···H nonbonding contacts. These distances [in $H_3Nb(C_5H_5)_2$, H(11)···h(12) = 1.78 (9) and H(12)···H(13) = 1.74 (9) Å; in $H_3Ta(C_5H_5)_2$, H(11)···H(12) = 1.846 (9) and H(12)···H(13) = 1.856 (9) Å] are much shorter than corresponding distances in $H_2Fe[PPh(OEt)_2]_4$ [2.05 (7) Å][34] and in the $[ReH_9]^{2-}$ anion [1.96 (4) Å];[35] and are comparable to those in other crowded polyhydrido molecules such as $H_4Mo[PMePh_2]_4$ [1.72 (13) Å][36] and $H_4Os(PMe_2Ph)_3$ [1.883 (3), 1.838 (3), 1.910 (3) Å].[37] The corresponding intramolecular H···H contact distance in methane is 1.787 Å.[38]

The outer H–M–H angles found in these compounds [H(11)–Nb–H(13) = 126 (3); H(11)–Ta–H(13) = 125.8

Table VII. Nonbonding Hydrogen–Hydrogen Contact Distances in $H_3Ta(C_5H_5)_2$

A. Intramolecular H···H Contacts, Å			
H(1)···H(2)	2.647	H(6)···H(7)	2.713
H(2)···H(3)	2.678	H(7)···H(8)	2.668
H(3)···H(4)	2.730	H(8)···H(9)	2.704
H(4)···H(5)	2.696	H(9)···H(10)	2.693
H(5)···H(1)	2.721	H(10)···H(6)	2.709
H(3)···H(8)	2.551	H(4)···H(9)	2.676
H(11)···H(2)	2.423	H(11)···H(7)	2.475
H(12)···H(1)	2.727	H(12)···H(6)	2.762
H(13)···H(5)	2.430	H(13)···H(5)	2.430
H(11)···H(12)	1.847	H(12)···H(13)	1.855

B. Closest Intermolecular H···H Contacts (<2.6 Å) (arranged in ascending order)		
H(11)···H(10)	($\frac{1}{2} - x$, $\frac{1}{2} + y$, $\frac{1}{4} - z$)	2.002
H(13)···H(7)	($\frac{1}{2} - x$, $y - \frac{1}{2}$, $\frac{1}{4} - z$)	2.093
H(1)···H(1)	($-y$, $-x$, $\frac{1}{2} - z$)	2.117
H(7)···H(7)	(y, x, $-z$)	2.261
H(1)···H(3)	($y - \frac{1}{2}$, $\frac{1}{2} - x$, $z - \frac{1}{4}$)	2.271
H(12)···H(3)	($y - \frac{1}{2}$, $\frac{1}{2} - x$, $z - \frac{1}{4}$)	2.407
H(7)···H(10)	($\frac{1}{2} - x$, $\frac{1}{2} + y$, $\frac{1}{4} - z$)	2.435
H(11)···H(6)	(y, x, $-z$)	2.476
H(12)···H(5)	($-y$, $-x$, $\frac{1}{2} - z$)	2.489
H(13)···H(5)	($-y$, $-x$, $\frac{1}{2} - z$)	2.520
H(2)···H(9)	($-y$, $1 - x$, $\frac{1}{2} - z$)	2.530

(5)°] are considerably larger than those found in $(C_5H_5)_2ML_2$ complexes (range: 80–97°),[6a,b] and the smaller H–M–H angles are comparable to those in $H_4Mo[PMePh_2]_4$.[36] Interestingly, extended Hückel calculations on the $[H_3Ti(C_5H_5)_2]^-$ ion predict a value of 129° for the larger H–M–H angle.[7c]

Recently the structure of $D_2Mo(C_5H_5)_2$ has been analyzed by neutron diffraction methods, with a measured Mo–D distance of 1.96 Å and a D–Mo–D angle of 83.2°. This distance seems abnormally long, and may be subject to fairly large uncertainty. The data were obtained by profile analysis of a neutron powder diffraction pattern and the cyclopentadienyl rings did not appear well behaved in the structure refinement.[39]

Supplementary Material Available: a listing of structure factor amplitudes for $H_3Nb(C_5H_5)_2$ (x-ray data, Table A) and $H_3Ta(C_5H_5)_2$ (neutron data, Table B) (9 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Research performed partly under the auspices of the U.S. Energy Research and Development Administration.

(2) (a) University of Southern California; (b) Brookhaven National Laboratory; (c) Uppsala University.

(3) Alfred P. Sloan Fellow, 1974–1976; NIH RESEARCH Career Development Awardee, 1975–1980.

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(12) The two Bijvoet related sets of data, (*hkl*) and (*khl*), differ slightly because of anomalous dispersion effects. In our original x-ray structure analysis of $H_3Nb(C_5H_5)_2$, these two data sets were averaged. When the least-squares refinement was conducted with such an averaged data set, the H atoms refined to positions such that the central Nb–H bond appeared longer than the other two [Nb–H(11) = 1.55 (12), Nb–H(12) = 1.88 (12), Nb–H(13) = 1.58 (11) Å]. However, when anomalous dispersion effects are taken into account and the two data sets are not averaged, the three Nb–H bonds refined to essentially equidistant values (Table IV).

(13) For the x-ray portion of this work, the major computations were performed on the USC IBM 370-155 computer using CRYM, an amalgamated set of crystallographic programs developed by Dr. Richard Marsh's group at the California Institute of Technology. For the neutron diffraction work, most of the calculations were performed on the CDC 7600 of the Brookhaven Central Scientific Computing Facility using programs from the Brookhaven Crystallographic Computing Library which have been described briefly in E. O. Schlemper, W. C. Hamilton, and S. J. LaPlaca, *J. Chem. Phys.*, **54**, 3990 (1971).

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(15) $R_F = \Sigma |F_o - |F_c|| / \Sigma F_o$; $R_{wF} = \{\Sigma w |F_o - |F_c||^2 / \Sigma wF_o^2\}^{1/2}$; $R_{F^2} = \Sigma |F_o^2 - |F_c|^2| / \Sigma |F_o^2|$; $R_{wF^2} = \{\Sigma w |F_o^2 - |F_c|^2|^2 / \Sigma wF_o^4\}^{1/2}$; $w^{-1} = \sigma^2(F_o^2) = [\sigma^2_{count}(F_o^2) + 0.02F_o^2)^2]^{1/2}$.

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(22) Selected results derived from the room temperature neutron diffraction analysis of the first $H_3Ta(C_5H_5)_2$ crystal are summarized here:

Ta–H(11)	1.730 (31) Å	H(11)–Ta–H(12)	61.4 (17)°
Ta–H(12)	1.751 (34) Å	H(11)–Ta–H(13)	124.7 (15)°
Ta–H(13)	1.754 (33) Å	H(12)–Ta–H(13)	63.4 (17)°
Ta–C(av)	2.386 (4) Å	ring–Ta–ring	141.2°
Ta–ring	2.065 Å		

The basic geometry of the molecule as reported above is not significantly different from that derived from the low-temperature data set (Table IV), but the final molecular parameters of the latter analysis are, of course, much more accurate.

(23) Air Products and Chemicals Inc., DISPLEX Model CS-202.

(24) An extinction parameter, *g*, as defined by Zachariasen[25] and used by us earlier,[26] was included in the final cycles of refinement. Here

$$E_{hkl} = \left[1 + \frac{2\bar{T}/F_c|^2 g}{V \sin 2\theta} \right]^{1/4}$$

where E_{hkl} is the extinction correction which divides F_o for reflection *hkl*, F_c is the calculated structure factor, $\bar{T}$ is the absorption weighted mean beam path length in the crystal for reflection *hkl*, calculated as $(-\ln t)/\mu$, $V = (V_c^2/\lambda^3)$, V_c is the volume of the unit cell, $\lambda = 1.019$ Å, the wavelength of neutrons employed, and 2θ is the Bragg diffraction angle.

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(27) See paragraph at the end of the paper for details of supplementary material (structure factor tables).

(28) The bending angle is defined as the angle between the normals to the C_5H_5 rings. This angle is referred to as ω in ref 4, ϕ in ref 6b, and θ in ref 7c.

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(33) We have also examined the x-ray structure of [H₃W(C₅H₅)₂]⁺Cl⁻, prepared as described in ref 9: Space group P4₁2₁2 (tetragonal), a = 9.645 (2) Å, c = 13.519 (3) Å, V = 1257.6 Å³, Z = 4, R factor = 0.067 for 466 nonzero reflections. The structure closely resembles that of H₃Nb(C₅H₅)₂, with a slightly less bent geometry and a shorter metal-ring distance: W-ring = 1.873 Å, W–C = 2.261 Å (average), bending angle ω = 148.2°. In this case, the hydrogen positions were not located.
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(39) A. K. Cheetham, private communication. Referenced in Table 17 of ref 6b.
(40) Several gas-phase electron diffraction studies of π-arene and π-cyclopentadienyl complexes have found hydrogens bent out of the plane of the ring carbons. See, for example, E. Gard, A. Haaland, D. P. Novak, and R. Selp, *J. Organomet. Chem.*, **88**, 181 (1975), and references cited therein.
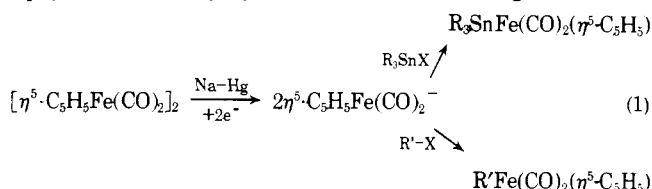
Chemical and Electrochemical Reduction of η^5-Cyclopentadienyldicarbonylcobalt(I) and η^5-Cyclopentadienyl(triphenylphosphine)carbonylcobalt(I). Synthesis, Crystal and Molecular Structure, and Chemistry of Sodium and Bis(triphenylphosphine)iminium Bis(η^5-cyclopentadienyl)di-μ-carbonyl-dicobaltate, a Binuclear Cobalt Radical Anion

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Abstract: Reduction of η^5-C₅H₅Co(CO)₂ (**1**) in THF at room temperature under air- and water-free conditions gave Na-Co(CO)₄ and a new pyrophoric binuclear paramagnetic complex, Na⁺[(η^5-C₅H₅)₂Co₂(CO)₂]·⁻ (Na⁺3·⁻). IR studies show that the new material is contact ion-paired in THF, but exists as dissociated ions (or perhaps solvent-separated pairs) in HMPT or THF containing 18-crown-6. An air-stable crystalline salt of **3·⁻** was obtained by exchanging Na⁺ for (PPh₃)₂N⁺, and its structure was determined by x-ray diffraction methods. This revealed an unusually short Co–Co bond in **3·⁻**, consistent with both MO and valence bond predictions of partial double bond character. In agreement with this picture, it was found that **3·⁻** could be oxidized to [(η^5-C₅H₅)Co(CO)]₂, which presumably has a full Co–Co double bond. Reduction of (η^5-C₅H₅)Co(CO)PPh₃ (**8**) occurred more slowly than did reduction of **1**, giving a dark (presumably oligomeric) cobalt complex. This material also led to NaCo(CO)₄ and **3·⁻** upon carbonylation.

The reduction of transition metal carbonyl complexes provides access to a number of interesting anionic organometallic species.[2] Monoanions such as Co(CO)₄⁻ and η^5-C₅H₅Fe(CO)₂⁻ have shown considerable utility in the preparation of compounds with metal–metal and metal–carbon bonds (e.g., eq 1). More recently, synthetic routes to a few organometallic

$$R_3SnFe(CO)_2(\eta^5\text{-}C_5H_5)$$

$$R_3SnX \nearrow$$

$$[\eta^5\text{-}C_5H_5Fe(CO)_2]_2 \xrightarrow[+2e^-]{Na–Hg} 2\eta^5\text{-}C_5H_5Fe(CO)_2^- \quad (1)$$

$$R'-X \searrow$$

$$R'Fe(CO)_2(\eta^5\text{-}C_5H_5)$$

di- and trianions have become available,[3] certain of which have proven very useful in organic synthesis.[4]

Singly charged anionic metal carbonyl complexes are generally prepared by reduction of neutral binuclear complexes (e.g., [η^5-C₅H₅Fe(CO)₂]₂). The few low-valent polyanionic metal carbonyls known have been obtained by reduction of neutral mononuclear precursors (e.g., Fe(CO)₅ → Fe(CO)₄²⁻). Little information is available, however, on the reduction chemistry of mononuclear organometallic carbonyl complexes which are relatively CO deficient. One might expect that in such cases either (a) reduction itself will be very slow,

(b) reduction will occur at a reasonable rate but the reduced species will undergo chemical reaction before the dianionic stage is reached, or (c) an extremely reactive dianion might be formed. In order to determine which of these possibilities was most likely in a specific case, we investigated the chemical reduction of η^5-C₅H₅Co(CO)₂ and η^5-C₅H₅Co(CO)PPh₃. This paper reports the details of our experiments.[5]

Results and Discussion

Reduction of η^5-Cyclopentadienyldicarbonylcobalt (1). The reduction of η^5-cyclopentadienyldicarbonylcobalt (**1**) may be effected using sodium metal or sodium amalgam in a variety of solvents. Treatment of an 0.019 M solution of **1** in hexamethylphosphoric triamide (HMPT) with aliquots of a freshly prepared 0.031 M solution of Na in HMPT causes a decrease in the intensity of the carbonyl IR bands of **1** at 1955 and 2020 cm⁻¹, and the appearance of two new bands at 1690 and 1890 cm⁻¹ (Figure 1). The reaction is over within minutes, and the starting material is completely consumed by approximately 0.6 equiv of Na. A similar transformation takes place in acetonitrile, using 0.74% sodium amalgam (Na–Hg) as the reductant.

Reduction of a 2.2 M solution of **1** in tetrahydrofuran (THF) with 0.74% Na–Hg leads to a heterogeneous mixture