traviolet spectra are also quite similar;[19] a plausible explanation for the observed differences is not evident at this time.

The several $^{183}W-^{13}C$ coupling constants measured (Table I) are observed to vary little with the identity of the ligand, increasing by only 6 Hz from $W(CO)_6$ to (cyclohexylamine)$W(CO)_5$. The parameters which can be considered to determine relative values of the metal–carbon coupling constants in a series of similar complexes are the M–C σ-bond order and the values of $|\Psi_c(0)|^2$, $|\Psi_m(0)|^2$.[20] Substitution of an amine for a CO would increase the value of $|\Psi_m(0)|^2$ but weaken the W–C σ bonds.[8] Thus the two effects might largely balance one another, producing the observed small variations. It will be of interest to compare $^{183}W-^{31}P$ and $^{183}W-^{13}C$ coupling constants in a series of complexes; such a study, which requires ^{13}C enrichment of the $LW(CO)_5$ molecules, is presently in progress.

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(19) See, *e.g.*, N. A. Beach and H. B. Gray, *J. Amer. Chem. Soc.*, **90**, 5713 (1968). However, the observed shifts do exhibit a linear inverse relationship to the energy separations between the $2t_{1u}$ and $4t_{1u}$ molecular orbitals for this series of complexes.

(20) Any assumption that $J(^{183}W-^{13}C)$ is dominated by the s character of the Fermi contact term must be considered tentative, since there is no evidence that the effective nuclear charge (Z^*), important for $J(^{13}C-^{1}H)$, may not be equally important here: D. M. Grant and W. Lichtman, *ibid.*, **87**, 3994 (1965).

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Structure of the Dimer of Niobocene

Sir:

Most of the parent bis (cyclopentadienyl) transition metal complexes studied have the familiar π-bonded "sandwich" structure. However, the bis(cyclopentadienyl) complexes of niobium, tantalum, and titanium have a more complex structure. Recently the bis(cyclopentadienyl)niobium complex was synthesized, and a novel dimeric structure was proposed to account for its nmr spectrum.[1] We report here the molecular and crystal structure of the dimeric bis(cyclopentadienyl)niobium complex, $[(C_5H_5)(C_5H_4)NbH]_2$.

The preparation and spectral characterization of $[(C_5H_5)(C_5H_4)NbH]_2$ were reported earlier.[1] We obtained triclinic or orthorhombic crystals depending on the solution concentration. At certain dilute concentrations we got both modifications, which were morphologically separable. The cell size and crystal density of the triclinic form are consistent with two dimeric molecules, $2[(C_5H_5)(C_5H_4)NbH]_2$, and two benzene molecules per unit cell. The ir spectrum also showed the presence of benzene. The unsolvated orthorhombic crystals were used in this study.

Crystals of niobocene dimer, $[(C_5H_5)(C_5H_4)NbH]_2$, are brown, space group $P2_12_12_1$, with cell dimensions of $a = 15.384$ (4), $b = 24.487$ (5), and $c = 12.879$ (3) Å. The observed and calculated densities for 12 dimeric molecules per cell are 1.85 and 1.83 g/cm^3, respectively. There are three cyrstallographically unique dimers per cell. Data were measured out to $2\theta = 45°$ on a Picker four-circle automatic diffractometer using the θ–2θ scan technique and Mo Kα radiation. The crystal was enclosed in a capillary for protection, although crystals are not nearly as reactive as solutions. The data were corrected for absorption effects; the linear absorption coefficient is 13.69 cm^{-1}. The niobium atoms were found using Patterson superposition techniques in conjunction with the minimum function. The remaining atoms were found on electron density difference maps. The structure was refined by least-squares to a current conventional R of 0.066 for the 2620 observed reflections. There was clear evidence in electron density difference maps for nearly all of the hydrogen atoms including two of the six unique hydride hydrogens.

The molecular structure is that of a dimeric metal hydride with a Nb–Nb bond, terminal hydride hydrogens and cyclopentadienyl groups, and bridging C_5H_4 groups, as shown in Figure 1. The C_5 rings are bent back to an angle of 39.7 (9)° to accommodate the novel bridging structure. In this way, the metal atoms are able to achieve an inert gas electronic structure. The hydride hydrogen positions in Figure 1, located as the highest peaks in an electron density difference map, were not refined. Clearly they are in the stereochemically active site expected for the hydrogen atom. The only other examples of C_5H_4 groups bridging metal atoms are in $(C_5H_5)(CO)M(C_5H_4)Mn(CO)_4$ (M = Mo, W)[2], $(C_5H_5)(H)Re(C_5H_4)Mn(CO)_4$,[2] and $[(C_5H_5)Ti(C_5H_4)Al(C_2H_5)_2]_2$.[3] The angles between the C_5H_5 rings in the latter structures are 35° in $(C_5H_5)(CO)Mo(C_5H_4)Mn(CO)_4$ and 44° in $[(C_5H_5)Ti(C_5H_4)Al(C_2H_5)_2]_2$. This angle is 34 (1)° in the monomeric $(C_5H_5)_2MoH_2$.[4]

The crystal structure consists of the packing of discrete molecules such as that depicted in Figure 1. Of the three crystallographically unique dimers, two are like that shown and one is the other enantiomorph. The molecular structures are the same within experimental errors. Hence the molecular dimensions quoted here have been averaged over all chemically equivalent distances (angles) and the errors estimated according to

$$\left[\sum_{1}^{n}(d_i - \bar{d})^2/n(n-1)\right]^{1/2}$$

where d_i and $\bar{d}$ are the distances (angles) and mean distance (angle), respectively.

All of the C_5 rings are essentially planar with the maximum deviation being 0.02 Å. The average Nb–

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$C(C_5H_5)$ distance of 2.400 (4) Å is slightly less than the distances of 2.46 Å in $(C_5H_5)Nb(CO)[(C_6H_5)_2C_2]_2$[5] and 2.45 Å in $\{(C_5H_5)Nb(CO)[(C_6H_5)_2C_2]\}_2$.[6] The Nb–$C(C_5H_4)$ distances according to type are 2.443 (8) Å for Nb(1)–C(3), 2.333 (6) Å for Nb(1)–C(2), and 2.302 (5) Å for Nb(1)–C(1). There do not appear to be any systematic variations in the C–C ring distances, with the average distances being 1.422 (8) Å for the C_5H_4 rings and 1.406 (6) Å for the C_5H_5 rings, similar to frequently observed distances.[7] The Nb(1)–C(1)–Nb(2) bridge angle is 86.5 (2)°, while the dihedral angle between the Nb(1)C(1)Nb(2) and Nb(1)C(6)Nb(2) planes is 128 (1)°.

The presence of the Nb–Nb bond is consistent with the diamagnetism of the complex; the niobium atoms may be considered to be in a formal oxidation state of IV (corresponding to a d^1 electronic configuration). Perhaps the Nb–Nb bond length of 3.105 (5) Å can best be compared with the Ti–Ti distance of 3.110 (7) Å in $[(C_5H_5)Ti(C_5H_4)Al(C_2H_5)_2]_2$ which has similar bridging geometry.[3] The Mo–Mn length for a singly bridging C_5H_4 group in $(C_5H_5)(CO)Mo(C_5H_4)Mn(CO)_4$ is 2.961 Å.[2] Other Nb–Nb bond lengths observed are 2.74 in $\{(C_5H_5)Nb(CO)[(C_6H_5)_2C_2]\}_2$, where double bond character is postulated,[6] 2.85 Å in the $[Nb_6Cl_{12}]^{2+}$ cluster,[8] 2.86 Å in niobium metal,[9] and 3.31 Å in α-NbI_4.[10] A single bond value[11] of 3.20 Å is obtained with the niobium atom radius derived from the Nb–C–(C_5H_5) distance (2.40–0.80). The short Nb(1)–Nb(2) and Nb(1)–C(6) distances observed here probably indicate "bent" bonds as required by the constraints of the bridging system (the Nb(2)–Nb(1)–C(1) and Nb(2)–Nb(1)–C(6) angles are 45.8 (2) and 47.7 (1)°, respectively).

An interesting detail of the bridging structure here is the geometry imposed upon the hydrogen atoms attached to C(2) and C(7). In addition to the close contact (*ca.* 1.9 Å), each hydrogen atom is positioned near the plane of the adjacent ring. Possibly, the combined steric and ring current effects cause this hydrogen to be shifted 1.7 ppm downfield from the other three C_5H_4 hydrogens as observed in the 220-MHz proton nmr spectra of the niobium and tantalum complexes.[1]

We believe the tantalocene dimer has the same structure as the niobocene dimer structure reported here, based on the very similar Hägg–Guinier X-ray powder patterns and spectral properties. Also, there is a strong possibility[12] that the structure of the titanocene dimer, $[(C_5H_5)(C_5H_4)TiH]_2$,[13] contains bridging C_5H_4 groups as found here. Brintzinger and Bercaw[13] proposed a double-hydrogen-bridged structure for the titanocene dimer. Additional supportive evidence for bridging C_5H_4 groups is the fact that the $[(C_5H_5)Ti(C_5H_4)]_2$ part of the $[(C_5H_5)Ti(C_5H_4)Al(C_2H_5)_2]_2$ structure[3] is practically identical with the structure found here. The $[(C_5H_5)Ti(C_5H_4)Al(C_2H_5)_2]_2$ framework is obtained in Figure 1 by replacing the hydride hydrogen atoms with $Al(C_2H_5)_2$ groups bridging the Ti(2)–C(1) and Ti(1)–C(6) type bonds.

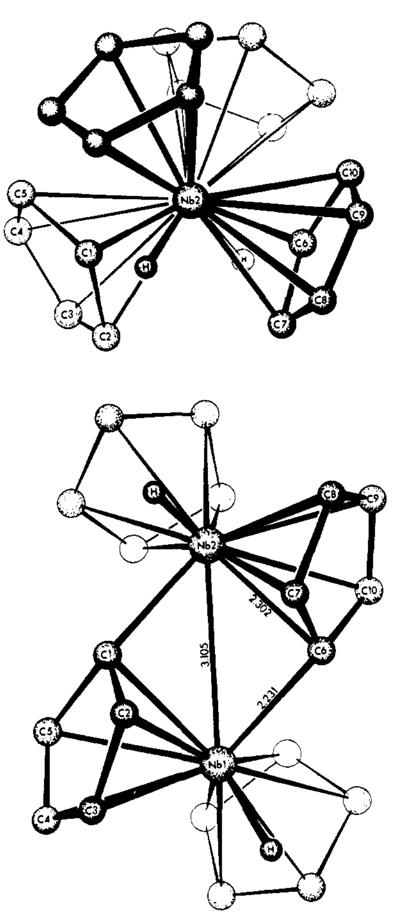

Figure 1. The front and top views of the molecular structure of $[(C_5H_5)(C_5H_4)NbH]_2$. The ring hydrogen atoms have been omitted.

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Chemical Consequences of Strong Hydrogen Bonding in the Reactions of Organic Ions in the Gas Phase. Induced Fragmentation of Aliphatic Alcohols

Sir:

The strong hydrogen bond is formed when two n-donor bases are bound together by a proton. This functional group has recently received considerable attention from both an experimental[1–5] and theoretical

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