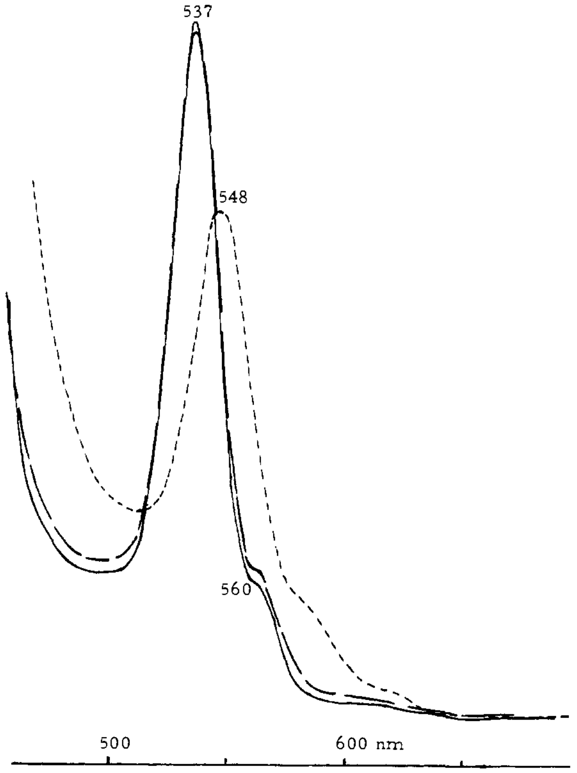

Figure 1. Visible spectrum of 3×10^{-5} *M* Fe(1-Me(imid))$_2$-($\alpha,\alpha,\alpha,\alpha$-TpivPP) with 10^{-4} *M* 1-Me(imid) in benzene: (——) under nitrogen, (.........) under oxygen (1 atm), (— — —) under nitrogen after two oxygenation–deoxygenation cycles.

side of the porphyrin) several cycles of oxygenation and deoxygenation can be achieved before any irreversible oxidation can be detected. In solutions of **5** without any excess ligand present gradual oxidation ensues. However, despite the gradual superposition of the spectrum of the oxidized product, [Fe($\alpha,\alpha,\alpha,\alpha$-Tpiv-PP)]$_2$O,[18a] several cycles of reversible oxygenation can be demonstrated. Total irreversible oxidation requires >12 hr at 25°! Similar spectral observations indicating reversible oxygen uptake have been made with a variety of axial bases L (L = imidazole, *N*-tritylimidazole, 4-*tert*-butylimidazole) but in none of these cases has a solid oxygen adduct been isolated. We believe this is simply related to solubility; the least soluble six-coordinate species is always preferentially precipitated.

As expected for a six-coordinate ferrous complex and as is found in oxyhemoglobin,[20] **6** is diamagnetic. Its Mössbauer spectrum like that of oxyhemoglobin[21] indicates a strong temperature dependence in its quadrupole splitting (for **6** at 194°K, δ = 0.24 mm/sec, ΔE_Q = 1.4 mm/sec; at 77°K, δ = 0.26 mm/sec, ΔE_Q = 1.8 mm/sec; δ values relative to iron metal). We have unsuccessfully searched the ir and Raman spectra of **6** for an absorption ascribable to coordinated oxygen, despite comparison with a sample prepared with $^{18}O_2$ (90% enrichment). This was unexpected in view of the strong ir absorptions observed for both angular-bound (σ) oxygen in Co(II) complexes[22] and sideways-bound (π) oxygen in d^8 complexes.[23] The ir absorption may, however, be weak and totally obscured by an abundance of strong porphyrin bands in the 900–1500 cm^{-1} region. A total X-ray crystallographic analysis is in progress which should shed light on the controversy[24] regarding the geometry of iron-bound dioxygen.

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The Aluminotitanium Hydrides [(C$_5$H$_5$)Ti]$_2$(H)(H$_2$AlEt$_2$)(C$_{10}$H$_8$) and [(C$_5$H$_4$)TiHAlEt$_2$]$_2$(C$_{10}$H$_8$)

Sir:

Recently, we characterized a triethylaluminum derivative of $(C_5H_5)_2TiX_2$ (X = Ph, Cl, Cl/2) as [(C$_5$H$_5$)-(C$_5$H$_4$)TiHAlEt$_2$]$_2$ (**1**), with titanium atoms bridged by (h^1:h^5-C$_5$H$_4$) ligands.[1,2] Wailes and Weigold described a triethylaluminum derivative of [(C$_5$H$_5$)(C$_5$H$_4$)-TiH]$_2$ ("titanocene" [3–5]), (C$_{10}$H$_9$TiAlEt$_2$)$_2$, of uncertain structure.[6] We now report a new triethylaluminum derivative of "titanocene," [(C$_5$H$_5$)Ti]$_2$(H)(H$_2$AlEt$_2$)-(C$_{10}$H$_8$) (**2**), its structure, and the structure of the Wailes and Weigold compound, [(C$_5$H$_4$)TiHAlEt$_2$]$_2$(C$_{10}$H$_8$) (**3**). We find the titanium atoms in **2** (Figure 1) bridged by C$_{10}$H$_8$ (h^5-C$_5$H$_4$-h^5-C$_5$H$_4$), H, and H$_2$AlEt$_2$ ligands, a structure strikingly different from that of **1**. In contrast, the titanium atoms in **3** (Figure 2) are bridged by both (h^1:h^5-C$_5$H$_4$) and C$_{10}$H$_8$ (h^5-C$_5$H$_4$–h^5-C$_5$H$_4$) ligands, a structure combining the characteristics of **1** and **2**. Our identification of C$_{10}$H$_8$ in **2** provides the first confirmation of a transition-metal-assisted synthesis of the fulvalenide ligand, although such a ligand was incorporated in one of the Brintzinger and Bercaw structure proposals for "titanocene." [4]

Compounds **2** and **3** are obtained by the following reactions. Reaction **3** was reported by Wailes and

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(1) F. N. Tebbe and L. J. Guggenberger, *J. Chem. Soc., Chem. Commun.*, 227 (1973).

(2) Compound 1 was previously assigned the formula [(C$_5$H$_5$)$_2$Ti-AlEt$_2$]$_2$, based on heavy-atom X-ray data: P. Corradini and A. Sirigu, *Inorg. Chem.*, **6**, 601 (1967).

(3) "Titanocene" is a biscyclopentadienyltitanium complex of uncertain structure. It was formulated as [(C$_5$H$_5$)(C$_5$H$_4$)TiH]$_2$ by Brintzinger and Bercaw.[4] We prepared "titanocene" after the method of Watt, *et al.*,[5] and purified it by crystallization from hot toluene. The ir of the green solid matched that reported by Brintzinger and Bercaw.[4] Crystals were not suitable for X-ray studies.

(4) H. H. Brintzinger and J. E. Bercaw, *J. Amer. Chem. Soc.*, **92**, 6182 (1970).

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(6) P. C. Wailes and H. Weigold, *J. Organometal. Chem.*, **24**, 713 (1970).

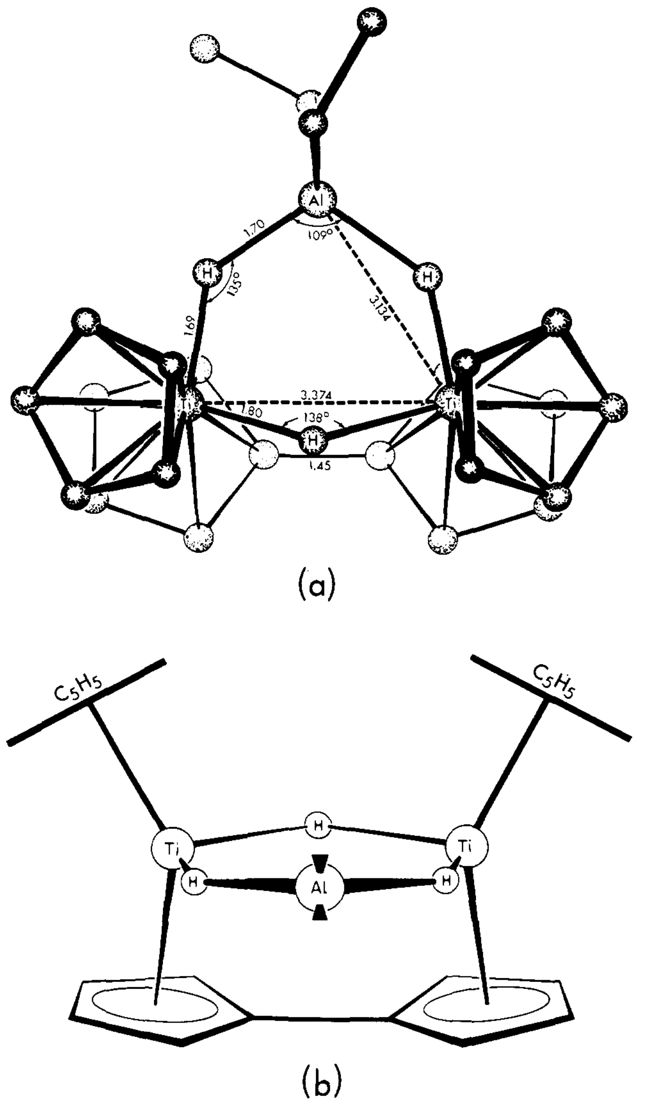


Figure 1. (a) The molecular structure of $[(C_5H_5)Ti]_2(H)(H_2AlEt_2)(C_{10}H_8)$ (hydrogen atoms omitted except for the hydride hydrogens). (b) A side view sketch of the molecule.

$$[(C_5H_5)(C_5H_4)TiH]_2 \underset{H_2O}{\overset{Et_3Al,\ 25°}{\rightleftharpoons}} \underset{\mathbf{2}}{[(C_5H_5)Ti]_2(H)(H_2AlEt_2)(C_{10}H_8)} \quad (1)$$

$$\mathbf{2} \xrightarrow[100°]{Et_3Al} \underset{\mathbf{3}}{[(C_5H_4)TiHAlEt_2]_2(C_{10}H_8)} \quad (2)$$

$$[(C_5H_5)(C_5H_4)TiH]_2 \xrightarrow[100°]{Et_3Al} \mathbf{3} \quad (3)$$

Weigold.[6] In reaction 1, a mixture of 3.0 g (8.4 mmol) of $[(C_5H_5)(C_5H_4)TiH]_2$ and 5.0 g (44 mmol) of Et_3Al in 40 ml of toluene was stirred at room temperature for 5 days under nitrogen. Crystallization of the product from toluene produced 3.0 g (81% yield) of reddish purple $[(C_5H_5)Ti]_2(H)(H_2AlEt_2)(C_{10}H_8)$ (**2**). In reaction 2, a toluene solution of 100 mg (0.23 mmol) of **2** and 52 mg (0.45 mmol) of Et_3Al was heated at 100° in a sealed tube for 30 hr. The conversion of **2** to **3** was 70%, determined by the nmr spectrum of the mixture. The ^1H nmr spectrum of **2** (toluene-d_8, −48°) consists of resonances from C_5H_5 at τ 4.74 (relative intensity 10); C_5H_4 at 3.55 (2), 5.39 (4), and 6.20 (2); $C\mathit{H}_3CH_2$ at 8.63 (3) and 8.79 (3); $CH_3C\mathit{H}_2$ at 9.65 (2) and 9.87 (2); TiH_2AlTi at 21.62 (2); and TiHTi at 31.80 (1). The spectrum of **3** (C_6D_6, 23°) contains C_5H_4 resonances at τ 1.73 (1), 3.61 (1), 4.16 (1), 5.17 (1), 5.45 (1), 5.75 (1), 5.84 (2); $C\mathit{H}_3CH_2$ at 8.47 (3) and 8.77 (3); $CH_3C\mathit{H}_2$ at 9.21 (2) and 10.00 (2); and TiHAl at 16.59 (1).

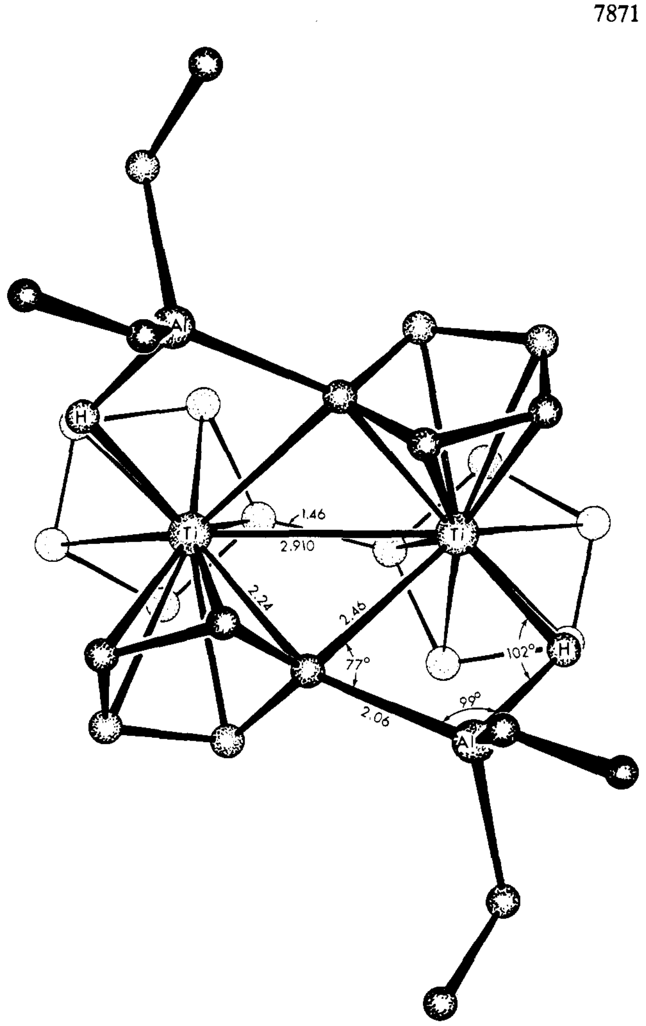


Figure 2. The molecular structure of $[(C_5H_4)TiHAlEt_2]_2(C_{10}H_8)$ (hydrogen atoms omitted except for the hydride hydrogens).

X-Ray data for both compounds were measured on a Picker four-circle automatic diffractometer using the θ–2θ scan technique and Zr-filtered Mo radiation. No absorption corrections were applied to the data; the linear absorption coefficients are 7.91 cm^{-1} for **2** and 5.83 cm^{-1} for **3**. The structures were solved by heavy-atom techniques and refined by least squares. All hydrogen atoms were located except those of the solvent molecule, and the hydride hydrogen positions were refined; hydrogens had isotropic thermal parameters while all other atoms had anisotropic thermal parameters. Crystals of $[(C_5H_5)Ti]_2(H)(H_2AlEt_2)(C_{10}H_8)$ are monoclinic, space group $C2/c$, with a = 33.310 (14) Å, b = 8.407 (4) Å, c = 17.921 (6) Å, β = 117.89 (2)°, and ρ_{calcd} = 1.32 g/cm³ for eight molecules per cell; a conventional R of 0.060 was obtained for 2588 observed reflections. Crystals of $[(C_5H_4)TiHAlEt_2]_2(C_{10}H_8) \cdot C_7H_8$ (C_7H_8 = toluene of solvation) are monoclinic, space group $C2/c$, with a = 24.367 (18) Å, b = 9.090 (4) Å, c = 17.832 (12) Å, β = 123.77 (6)°, and ρ_{calcd} = 1.25 g/cm³ for four molecules per cell; a conventional R of 0.089 was obtained for 1323 observed reflections.

The structure of **2** is presented in Figure 1 along with some average distances and angles. There is no crystallographically imposed molecular symmetry, but there is idealized $C_s(m)$ symmetry, the mirror plane being vertical through Al and H (Ti–H–Ti). Each titanium atom is bonded to two bridging hydrides and h^5 bonded to cyclopentadienide and fulvalenide ligands. Individual C_5 rings are planar (maximum deviation 0.01 Å). The Ti–C distances are 2.353 (4) for C_5H_5 and 2.33–2.39 Å for $C_{10}H_8$; C–C distances are normal. Relative to the TiAlTi plane, two hydride hydrogens (Ti–H–Al) are 0.14 Å below the plane and the third (Ti–H–Ti) is 0.43 Å above the plane (Figure 1b). The angle between C_5 rings on the same Ti atom is 43.2°.

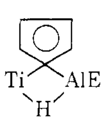
The structure of **3** is shown in Figure 2 along with some distances and angles. The molecule has space group imposed $C_2(2)$ symmetry; the twofold axis is the view direction of Figure 2, with half of the dimer being crystallographically unique. In addition to a Ti–Ti bond, each titanium is h^5 bonded to a bridging C_5H_4, h^1 to the other bridging C_5H_4, and h^5 to half of the $C_{10}H_8$ fulvalenide ligand. Both Ti atoms and C_5H_4 groups are bridged by hydridodiethylaluminum ligands. All individual C_5 rings are planar (maximum deviation 0.02 Å), but the combined fulvalene is not planar (maximum deviation 0.25 Å). The angle between the C_5 planes on the same Ti atom is 45.9°.

The important question arises regarding the presence of Ti–Ti bonds in these compounds. The Ti–Ti distance alone is not a good bond criterion,[7] especially in these systems where the bridging constraints are substantial. The combined data of disposition of valence orbitals, Ti–Ti distance of 2.910 Å, and diamagnetism support a Ti–Ti single bond in **3**. We feel the stereochemistry and 3.374 Å Ti–Ti distance indicates the absence of a regular Ti–Ti bond in **2**. According to the usual electron counting schemes (which are not totally unambiguous here), we might then expect **2** to be paramagnetic; however, the diamagnetism of the compound (Evans method, 30°) could result from superexchange through the bridging hydride hyrogen which is in a good position to participate in Ti atom spin coupling.[8]

The localized $TiC_5H_4AlEt_2$ geometries of **1** and **3** are closely related. This confirms our earlier prediction of the hydride location in **1**.[1] In addition to the h^5 bonding to Ti, the C_5H_4 group in these compounds is part of a three-center two-electron bond system involving Ti, C, and Al, similar to the situation of C_6H_5 in $(Me_2AlC_6H_5)_2$[9] and $[(C_6H_5)_3Al]_2$.[10,11]

The fulvalenide geometry is quite flexible. The dihedral angle between C_5H_4–C_5H_4 rings varies from 12.5° in **2** (Ti–Ti distance 3.374 Å) to 25.8° in **3** (Ti–Ti distance 2.910 Å), partially in response to the change in metal–metal separation.

A great deal of speculation has appeared in the literature on the structure of "titanocene."[12] Our



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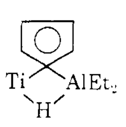

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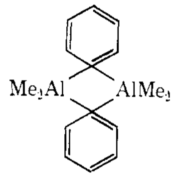

Al–$C(C_5H_4)$, 2.06 Å	Al–$C(C_5H_4)$, 2.11 Å[2]	Al–$C(C_6H_5)$, 2.14 Å
Al–Ti, 2.82 Å	Al–Ti, 2.79 Å	Al–Al, 2.69 Å
Al–$C(C_5H_4)$–Ti, 77°	Al–$C(C_5H_4)$–Ti, 77°	Al–$C(C_6H_5)$–Al, 78°

structure for $[(C_5H_5)Ti]_2(H)(H_2AlEt_2)(C_{10}H_8)$ (**2**) is closely related to a fulvalenide-bridged structure for "titanocene" proposed by Brintzinger and Bercaw.[4] Removal of $HAlEt_2$ from **2**, followed by movement of the remaining hydride to bridge the titanium atoms, would produce $[(C_5H_5)TiH]_2(C_{10}H_8)$ with their proposed structure. We find that hydrolysis of **2** with 1 equiv of water produces "titanocene"[13] in 70% yield after recrystallization. Although the structure of **2** and its facile conversion to "titanocene" do not unambiguously determine the "titanocene" structure, these data support the fulvalenide and hydride bridged structure proposed by Brintzinger and Bercaw.

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(8) P. W. Anderson, *Magnetism*, **1**, 25 (1963).

(9) J. F. Malone and W. S. McDonald, *J. Chem. Soc., Dalton Trans.*, 2649 (1972).

(10) J. F. Malone and W. S. McDonald, *ibid.*, 2646 (1972).

(11) Similar AlC_5H_4M bonding has been found in trimethylaluminum derivatives of $(C_5H_5)_2MH_2$ (M = Mo). R. A. Forder, M. L. H. Green, R. E. MacKenzie, J. S. Poland, and K. Prout, *J. Chem. Soc., Chem. Commun.*, 426 (1973).

(12) Recent proposals are reviewed by F. Calderazzo, *J. Organometal. Chem.*, **53**, 179 (1973).

(13) "Titanocene" produced by hydrolysis of **2** was identical with an authentic sample by its ir and mass spectra, X-ray powder pattern, elemental analyses, and its conversion to **2** on treatment with Et_3Al.

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Effect of Electronic Excitation on Intermolecular Force Constants of Bromine Molecules

Sir:

Observed effects of molecular electronic excitation on intermolecular forces should offer new tests of theories of electronic structure. Changes in polarizabilities $\Delta\alpha = \alpha^* - \alpha$ have been reported for molecules in condensed phases.[1,2] Here, we report the first related results for a molecular vapor; pressure broadening and shift of rotational lines in the electronic absorption spectrum of the Br_2 molecule have been measured and used to calculate changes in Lennard-Jones force constants $\Delta C_6 = C_6^* - C_6$ and $\Delta C_{12} = C_{12}^* - C_{12}$. The change of only 6% inferred for $\Delta\alpha$ contrasts with $\Delta\alpha$ values found for other molecules in condensed phases.

Line shapes of the $B^3\Pi_{0^+u} \leftarrow X^1\Sigma^+{}_g$ transition of bromine were studied by means of a Fabry–Perot interferometer spectrometer. Since publication of earlier work with the instrument,[3] a Michelson interferometer has been incorporated for calibration of spectra. Absorption line widths and shifts were measured for lines near a krypton emission secondary standard at 5570.2895 Å and at Br_2 pressures between 0.6 and 132 Torr. The results in Table I exhibit no dependence on quantum numbers. Assuming full-width at half-maximum and position to vary linearly with pressure, we therefore

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