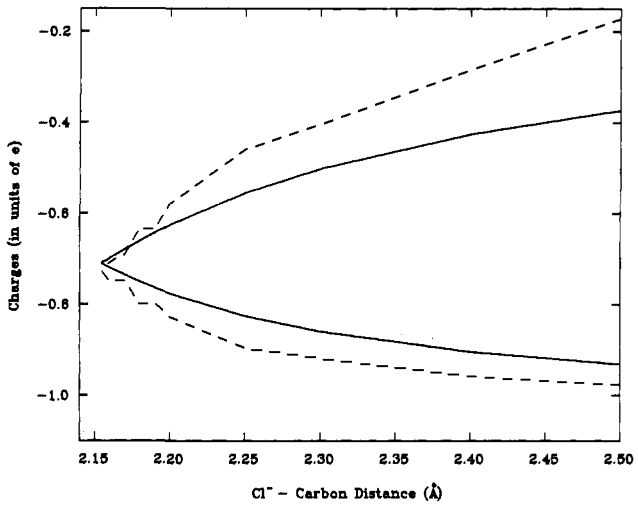

Figure 1. Comparison of average gas phase and solution charge transfer along the reaction coordinate for $Cl^- + CH_3Cl$. Values of Mulliken charges for the attacking Cl^- (lower curves) and the Cl (upper curves) of CH_3Cl are shown: (—) gas phase, (- - -) solution. The gas-phase analysis was done by minimizing each configuration with the Cl^- and C fixed at positions along the reaction pathway. The corresponding charge distributions were determined in solution by placing each of the minimized $Cl'\cdots CH_3Cl''$ complexes in a solvent water sphere with stochastic boundary molecular dynamics (see text) and doing dynamics runs at 300 K with 1 ps of equilibration followed by 2 ps of data collection; the Cl′ and C are fixed at their initial positions in all the simulations, and the Cl″ was also fixed for configurations near the transition state (i.e., for Cl′–C distances between 2.3 and 2.1545 Å).

the waters. Results of the calculations are given in Table I. For this reaction the free energy change and solvent effect in the reaction are insensitive to the inclusion of van der Waals parameters in the (qm),(mm) terms or the choice of quantum mechanical model. The results for the gas phase and solution are in satisfactory agreement with experimental estimates[23,25] and ab initio plus molecular mechanics calculations.[1]

To investigate the effect of solvation on the charge transfer during the reaction, we have compared the Mulliken populations obtained from gas-phase and solution simulations of the Cl^-,CH_3Cl system. The charges are shown in Figure 1. The charge transfer in solution lags behind that found in the gas phase due to the stabilization of the more asymmetric charge distribution by interaction with the solvent. This is in accord with the fact that the free energy of interaction between an ion and a dipolar solvent varies approximately quadratically with the charge on the ion.[26]

The present approach to potential surfaces of reactions in solution makes it possible to perform combined quantum, molecular mechanics calculations with molecular dynamics in large systems. The method avoids the need for extensive parameter fitting of the reaction pathway and permits one to obtain results concerning the effect of the solvent on the electronic structure of the solute. Applications to inhibitor binding and to enzymatic and solution reactions are in progress.

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Registry No. MeCl, 74-87-3.

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Divalent Titanium Chemistry. Synthesis, Reactivity, and X-ray and Neutron Diffraction Studies of $Ti(BH_4)_2(dmpe)_2$ and $Ti(CH_3)_2(dmpe)_2$

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Low valent organotitanium complexes have been implicated as Ziegler–Natta olefin polymerization catalysts[2] and as stoichiometric reagents in organic synthesis.[3] However, very few low-valent alkyls of titanium have been reported, and, in particular, the divalent oxidation state of titanium is virtually unexplored.[4,5] We now report the synthesis and characterization of the unusual divalent tetrahydroborate complex $Ti(BH_4)_2(dmpe)_2$, **1**, and its conversion to the methyl compound $Ti(CH_3)_2(dmpe)_2$, **2**. Complex **2** is unique among octahedral complexes of the 3d metals in being low-spin *within* the t_{2g} manifold and exhibits very unusual NMR features for the titanium methyl group.

The reaction of $TiCl_2(dmpe)_2$[5] with excess $LiBH_4$ in diethyl ether gives dark red crystals of the divalent tetrahydroborate complex $Ti(\eta^2\text{-}BH_4)_2(dmpe)_2$, **1**, after crystallization from toluene.[6]

$$\mathrm{TiCl_2(dmpe)_2} + 2\mathrm{LiBH_4} \rightarrow \underset{\mathbf{1}}{\mathrm{Ti(\eta^2\text{-}BH_4)_2(dmpe)_2}} + 2\mathrm{LiCl}$$

Complex **1** is paramagnetic with two unpaired electrons; this unfortunately prevents observation of the BH_4^- protons in the ^1H NMR spectrum. While the IR spectrum in the B–H stretching region is diagnostic of a bidentate bonding mode, the $\sim$110-cm^{-1} separation between the ν_{B-H}(terminal) and ν_{B-H}(bridging) modes is smaller than in all other transition-metal tetrahydroborate complexes[7] and is indicative of an unusually weak Ti–BH_4 interaction.[8] This suggestion is confirmed by the X-ray crystal structure of $Ti(BH_4)_2(dmpe)_2$ (Figure 1a)[9] which reveals that the Ti–H_b distances of 2.06 (2) Å are rather long and that the four

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[6] $Ti(BH_4)_2(dmpe)_2$: ^1H NMR (C_6D_6, 15 °C) δ 11.39 (PCH_2, fwhm = 770 Hz), −2.35 (PCH_3, fwhm = 290 Hz); IR (Nujol) 2332 s, 2297 s, 2220 s, 2138 m, 2062 w cm^{-1}.

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[9] Crystal data (T = 299 K): space group $P2_1/n$, with a = 9.404 (2) Å, b = 13.088 (2) Å, c = 9.466 (2) Å, β = 96.12 (1)°, V = 1158.4 (4) Å^3; Z = 2; R_F = 0.036, R_{wF} = 0.035 for 168 variables and 2139 unique data for which $I > 2.58\sigma(I)$. Hydrogen atom positions were refined with independent isotropic thermal coefficients.

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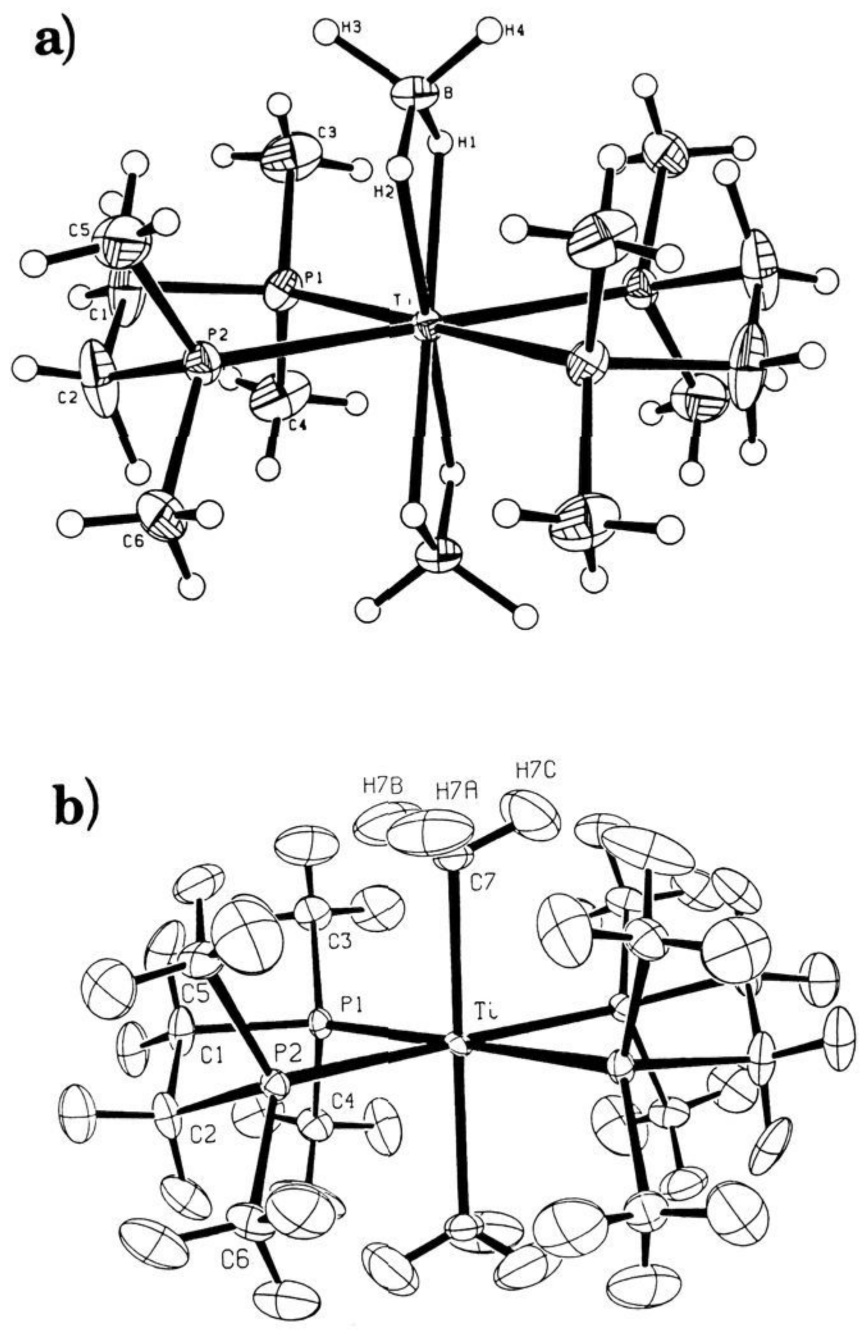

Figure 1. (a) Crystal structure of $Ti(BH_4)_2(dmpe)_2$. Selected bond lengths (Å) and angles (deg): Ti···B = 2.534 (3), Ti–P1 = 2.627 (1), Ti–P2 = 2.625 (1), P1–Ti–P2 ≈ 76.67 (2), H1–Ti–H2 = 53.0 (8). (b) Crystal structure of $Ti(CH_3)_2(dmpe)_2$. The ORTEP diagram, taken from the neutron diffraction data, shows the 20% probability density surfaces. Important bond distances (Å) and angles (deg) from the X-ray [neutron] diffraction experiments: Ti–C7 = 2.219 (2) [2.221 (4)], Ti–P1 = 2.518 (1) [2.529 (4)], Ti–P2 = 2.510 (1) [2.517 (5)], C7–H7A = 0.93 (3) [1.08 (2)], C7–H7B = 0.92 (2) [0.97 (2)], C7–H7C = 0.94 (3) [1.05 (2)], P1–Ti–P2 = 78.83 (1) [78.8 (1)], Ti–C7–H7A = 110 (1) [108.9 (8)], Ti–C7–H7B = 112 (1) [113.0 (10)], Ti–C7–H7C = 118 (1) [114.4 (11)], H7A–C7–H7B = 106 (2) [97 (2)], H7A–C7–H7C = 110 (2) [106 (2)], H7B–C7–H7C = 102 (2) [115 (2)].

B–H distances of 1.09 (3) – 1.16 (2) Å and the H–B–H angles of 107(1) – 113 (2)° describe a remarkably regular tetrahedron about boron.

Compound **1** reacts cleanly with 2 equiv of $LiCH_3$ in diethyl ether at 0 °C to afford the dark red titanium(II) alkyl $Ti(CH_3)_2(dmpe)_2$, **2**, after crystallization from pentane at −20 °C.[10]

$$Ti(BH_4)_2(dmpe)_2 + 2LiCH_3 \rightarrow \underset{\mathbf{2}}{Ti(CH_3)_2(dmpe)_2} + 2LiBH_4$$

This synthetic method succeeds presumably as a result of the weak $Ti–BH_4$ interaction, whereas previous attempts to synthesize $Ti(CH_3)_2(dmpe)_2$ directly from $TiCl_2(dmpe)_2$ resulted in incomplete exchange of the strongly bound chloride groups to give mixed alkyl/halide products.[5] Unlike the related paramagnetic compounds $TiCl_2(dmpe)_2$[5] and $Ti(BH_4)_2(dmpe)_2$, the methyl complex **2** is *diamagnetic*. The ^1H NMR spectrum at −70 °C shows a resonance at δ −5.72 for the $TiCH_3$ group; this chemical shift is farther upfield than all other diamagnetic methyl compounds except the δ −8.49 shift recently reported for the agostic methyl group in $Fe_3(\mu_3\text{-}CH_3)H(CO)_9$.[11a] The ^{13}C NMR spectrum of **2** at −70 °C reveals a J_{CH} coupling constant of 109.5 Hz that is unusually small for a sp^3 center.[11,12] Compound **2** is highly reactive and will polymerize ethylene in hydrocarbon solutions at 25 °C and 4 atm.

Single-crystal X-ray and neutron diffraction studies of $Ti(CH_3)_2(dmpe)_2$ were carried out at 173 and 20 K, respectively (Figure 1b).[13,14] The titanium center adopts a regular octahedral structure, with Ti–C = 2.219 (2) Å and Ti–P = 2.514 (1) Å; these distances are somewhat longer and shorter, respectively, when compared with the values Ti–C = 2.149 (5) Å and Ti–P = 2.583 (1) Å in the tetravalent complex $Ti(CH_3)Cl_3(dmpe)$.[11g] Of greatest interest is that all of the Ti–C–H angles are 109° or greater, thus indicating that *there are no agostic interactions in the solid state*. This situation contrasts sharply with the clearly distorted structure found in $Ti(CH_3)Cl_3(dmpe)$ where one of the Ti–C–H angles was 93.5 (2)°.[11g]

The spectroscopic parameters of **2** in solution, particularly the ^1H NMR chemical shift and the $^1J_{CH}$ coupling constant, fall in regions usually associated with agostic interactions.[15] The CP-MAS ^{13}C NMR chemical shift of **2** in the solid state, δ 22.8, was found to be essentially identical with the value obtained in solution, δ 18.9. Although ^{13}C chemical shifts of agostic alkyl groups in some instances occur as much as 25 ppm downfield of nonagostic groups,[16] in other cases the difference is less than 5 ppm.[11e] Accordingly, the possibility remains that **2** adopts an agostic structure in solution but not in the solid state. The diamagnetism of the molecule both in solution and the solid state may be due to π-interactions with C–H bonding orbitals of the methyl groups that raise the d_{xz} and d_{yz} orbitals in energy and cause spin-pairing of the two d-electrons in the d_{xy} orbital. This interaction, which implies that methyl groups are strong π-donors, is similar to the bonding model that has been proposed for the flattened methyl groups in $Ti(CH_3)Cl_3$.[11h] Studies in progress are being undertaken to further characterize the structure of **2** in solution and to explore the reactivity of divalent titanium complexes in general.

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[10] $Ti(CH_3)_2(dmpe)_2$: ^1H NMR (C_7D_8, −70 °C) δ 1.64 (m, PCH_2), 1.51 (s, PCH_3), −5.72 (quintet, J_{PH} = 3.7 Hz, Ti-CH_3); ^{13}C NMR (C_7D_8, −70 °C) δ 31.2 (t, J_{CH} = 128.0 Hz, PCH_2), 15.8 (q, J_{CH} = 182.0 Hz, PCH_3), 18.9 (quartet of quintets, J_{CH} = 109.5 Hz, J_{CP} = 2.0 Hz, Ti-CH_3); ^{13}C NMR (CPMAS, 25 °C) δ 34.5 (s, PCH_2), 18.9 (s, PCH_3), 16.6 (s, PCH_3), 22.8 (s, Ti-CH_3); $^{31}P\{^1H\}$ NMR (C_7D_8, −70 °C) δ 67.3 (s). Anal. Calcd: C, 44.5; H, 10.1; Ti, 12.7. Found: C, 44.2; H, 10.0; Ti, 12.6.

[11] Known agostic methyl groups exhibit ^1H NMR chemical shifts of δ −1.5 to δ −8.5 and $^1J_{CH}$ coupling constants of 105–121 Hz,[11a–e] except the d^0 group 4 examples, where δ = +2.9 to −0.2 and $^1J_{CH}$ = 130 to 136 Hz.[11f–h] (a) Dutta, T. K.; Vites, J. C.; Jacobsen, G. B.; Fehlner, T. P. *Organometallics* **1987**, *6*, 842–847. (b) Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1978**, *100*, 7726–7727. (c) Dawkins, G. M.; Green, M.; Orpen, A. G.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1983**, 41–43. (d) Casey, C. P.; Fagan, P. J.; Miles, W. H. *J. Am. Chem. Soc.* **1982**, *104*, 1134–1136. (e) Watson, P. L. *J. Am. Chem. Soc.* **1983**, *105*, 6491–6493. (f) Waymouth, R. M.; Santarsiero, B. D.; Grubbs, R. H. *J. Am. Chem. Soc.* **1984**, *106*, 4050–4051. (g) Dawoodi, Z.; Green, M. L. H.; Mtetwa, V. S. B.; Prout, K.; Schultz, A. J.; Williams, J. M.; Koetzle, T. F. *J. Chem. Soc., Dalton Trans.* **1986**, 1629–1637. (h) Berry, A.; Dawoodi, Z.; Derome, A. E.; Dickenson, J. M.; Downs, A. J.; Green, J. C.; Green, M. L. H.; Hare, P. M.; Payne, M. P.; Rankin, D. W. H.; Robertson, H. E. *J. Chem. Soc., Chem. Commun.* **1986**, 520–522.

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Supplementary Material Available: Tables of atomic coordinates, thermal parameters, and a full listing of bond lengths and angles for both the X-ray and neutron diffraction studies of $\mathrm{Ti(BH_4)_2(dmpe)_2}$ and $\mathrm{Ti(CH_3)_2(dmpe)_2}$ (10 pages); tables of observed and calculated structure factors for $\mathrm{Ti(BH_4)_2(dmpe)_2}$ and $\mathrm{Ti(CH_3)_2(dmpe)_2}$ (22 pages). Ordering information is given on any current masthead page.

Observation of the $\mathrm{Fe^{IV}{=}O}$ Stretching Raman Band for a Ferryl Porphyrin π Cation Radical

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High valent oxo-metalloporphyrins have attracted chemists' attention[1-5] since the first demonstration by Groves et al.[6] that an oxo-iron(IV) porphyrin exhibits the monooxygenation activity to olefins like cytochrome P-450. Originally, the presence of the ferryl heme was pointed out for the catalytic intermediates of peroxidases called compound I and II,[7,8] which have the oxidation states higher than the ferric state by 2 and 1 equiv, respectively. On the basis of the close similarity in their visible spectra, Dolphin et al.[9] suggested that compound I had the ferryl porphyrin π cation radical, and subsequent studies with ESR,[10] NMR,[11] and ENDOR[12] confirmed this conclusion. Since then the physicochemical properties of the ferryl porphyrin complexes have been investigated with various techniques.[13-16] While the $\mathrm{Fe^{IV}{=}O}$ stretching ($\nu_{\mathrm{Fe{=}O}}$) Raman band has been identified for compound II of peroxidases[17,18] and the ferryl porphyrin complexes,[19-22] the

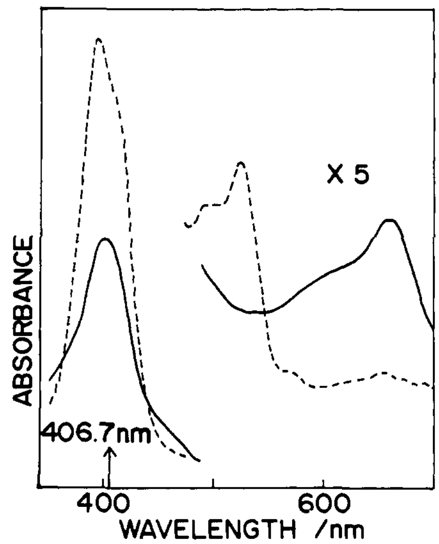

Figure 1. Visible absorption spectra of $\mathrm{(TMP)Fe^{III}Cl}$ (broken line) and its green complex (solid line) in the $\mathrm{CH_2Cl_2/CH_3OH}$ mixed solvent at −80 °C. An arrow indicates the excitation wavelength for Raman scattering.

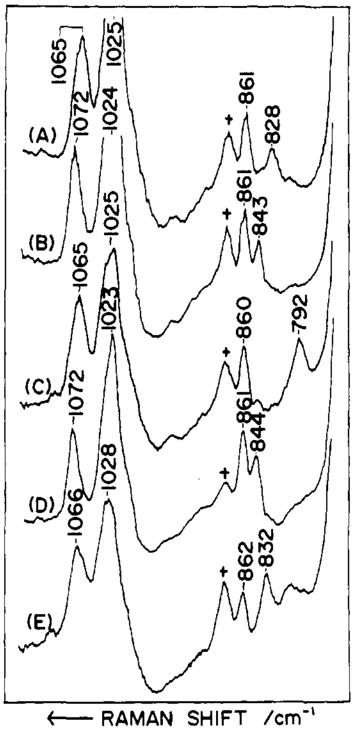

Figure 2. Resonance Raman spectra of the green complex observed at −80 °C: (A) the ^{16}O-derivative under the spinning condition; (B) the ^{16}O-derivative without spinning; (C) the ^{18}O-derivative under the spinning condition; (D) the ^{18}O-derivative without spinning; (E) the green complex derived from $\mathrm{(TMP)^{54}Fe^{III}Cl}$ and ^{16}O-*m*-CPBA. Excitation, 406.7 nm, 5 mW at sample point. Accumulation time, 320 s.

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