Transition Metal Tetrahydridoborates as Models of Methane Activation: Synthesis and Structure of $Ti(BH_4)_3(PMe_3)_2$

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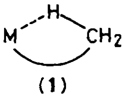
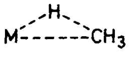
The *X*-ray crystal structure of $Ti(BH_4)_3(PMe_3)_2$ shows that two of the BH_4^- groups possess unusual geometries involving interaction of the titanium centre with *one* B–H bond in a 'side-on' manner; this geometry resembles one proposed transition state for the approach of a molecule of methane to a transition metal leading to C–H bond cleavage.

The activation of saturated hydrocarbons by transition metal complexes is of great current interest, and several chemical systems are now known to react with the C–H bonds of the simplest hydrocarbon, methane.[1—4] Little experimental information exists, however, about the *pathway* by which a molecule of methane might approach a transition metal, although there are several examples of weak intramolecular interactions between ligand methyl groups and metal centres, (**1**).[5] For methane itself, there are two principal models for the structure of the transition state that leads to C–H bond scission: the 'side-on' geometry (**2**) and the 'end-on' geometry (**3**).[6] We have recently been investigating whether the observed bonding modes of isoelectronic BH_4^- groups toward transition metals may be informative models of the nature of this transition state, despite the fact that CH_4 and BH_4^- are chemically rather different. We now describe a titanium tetrahydridoborate complex that exhibits an unprecedented bonding mode for the BH_4^- unit that closely resembles the 'side-on' model for C–H bond activation.

The reaction of trialkylphosphines with thermally unstable $Ti(BH_4)_3{\cdot}Et_2O$, prepared *in situ* from $TiCl_4$ and $LiBH_4$ in diethyl ether,[7] gives a dark blue solution from which the diadducts $Ti(BH_4)_3(PMe_3)_2$ and $Ti(BH_4)_3(PEt_3)_2$ may be



(1)



$M\overset{H}{\cdots\cdots}CH_3$

(2)

$M{\cdots}H{\cdots}CH_3$

(3)

obtained by crystallisation from pentane at −20 °C.[†] These adducts are stable at room temperature for several days under argon, and possess magnetic moments of 1.7 μ_B and e.s.r. spectra typical of monomeric Ti^{III} species. The ^1H n.m.r. spectra show only resonances due to the phosphine ligands; the tetrahydridoborate protons evidently experience large contact shifts due to their proximity to the paramagnetic centre. The i.r. spectra in the 1800—2600 cm^{-1} region clearly indicate the presence of at least one bidentate BH_4^- group, with additional peaks that cannot be ascribed to the usual BH_4^- binding modes.[8] In order to establish the nature of the bonding in these titanium tetrahydridoborate complexes, the *X*-ray crystal structure of $Ti(BH_4)_3(PMe_3)_2$ has been determined.[‡]

The $Ti(BH_4)_3(PMe_3)_2$ molecule (Figure 1) lies on a mirror plane that passes through Ti, P(1), P(2), and B(1), and possesses a distorted trigonal bipyramidal structure with the phosphines occupying the axial sites; the overall co-ordination geometry is similar to that previously observed for $Sc(BH_4)_3(thf)_2$ (thf = tetrahydrofuran).[9] Of the three equatorial BH_4^- groups, one adopts a normal bidentate structure that closely resembles the bridge geometry observed in $(C_5H_5)_2Ti(H_2BH_2)$[10] and several other transition metal complexes containing normal $H_2BH_2^-$ ligands.[8]

Undoubtedly the most remarkable feature of the structure is the unusual 'side-on' bonding of two of the tetrahydridoborate ligands. The Ti–B(2) distance of 2.27(1) Å is 0.13 Å shorter than that to the normal $H_2BH_2^-$ ligand, however, only one hydrogen atom is strongly interacting with the titanium centre, Ti–H(17) 1.73(7) Å, the next closest hydrogen atoms H(16) and H(15) being over 0.5 and 0.9 Å more distant. Even taking into account the shortened metal–hydrogen distances characteristic of *X*-ray crystal structures, it is evident that the short Ti–B(2) distance and the presence of only one significant Ti–H contact speak for the presence of marked, direct Ti–B bonding in the molecule as part of a Ti–H(17)–B(2) three-centre interaction.

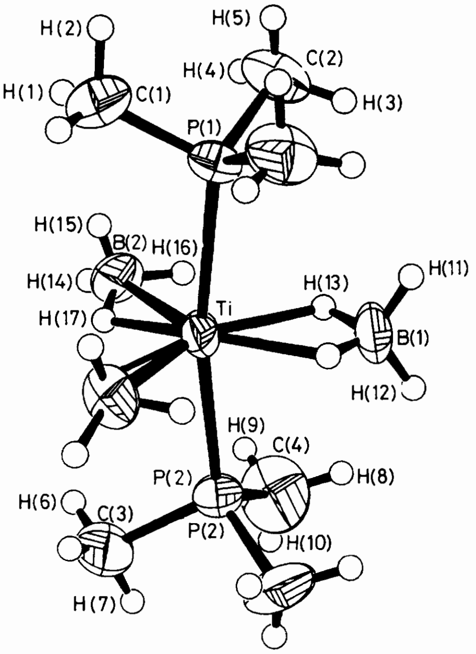


Figure 1. Molecular structure of $Ti(BH_4)_3(PMe_3)_2$. Important bond distances (Å) and angles (°): Ti–P(1) 2.571(3), Ti–P(2) 2.539(3), P(1)–Ti–P(2) 170.27(9), Ti–H(13) 1.90(6), Ti· · ·B(1) 2.40(1), B(1)–H(13) 1.03(7), B(1)–H(11),H(12) 1.00(8), H(13)–B(1)–H(13′) 100(5), Ti–H(17) 1.73(7), Ti· · ·H(16) 2.25(7), Ti· · ·H(15) 2.62(7) Ti–B(2) 2.27(1), B(2)–H(17) 0.95(6), B(2)–H(14),H(15),H(16) 0.96(6), H(17)–B(2)–H(16) 117(6), H(17)· · ·H(17′) 2.06(9), H(16)· · ·H(13) 2.40(9). Torsion angles (°): Ti–H(13)–B(1)–H(11), H(12) ±116(5), Ti–H(17)–B(2)–H(16) 28(7), Ti–H(17)–B(2)–H(15) −94(7), Ti–H(17)–B(2)–H(14) 151(5).

The geometries of the 'side-on' tetrahydridoborate ligands are quite unlike those observed for tridentate,[11] bidentate,[10] or unidentate[12—14] BH_4^- groups. The unusual 'agostic' nature of the BH_4^- groups is undoubtedly related to the electronically unsaturated nature of the titanium centre, and may be a type of Jahn–Teller distortion away from an orbitally degenerate D_{3h} structure. The nearest analogues of the structure of $Ti(BH_4)_3(PMe_3)_2$ are some metal cluster species,[15,16] where the presence of M · · · H · · · B bridging units parallels the well-known occurrence of bridging hydrogen atoms in polyhedral boron hydrides. The present structure is of considerable interest because of the unusual geometry of the tetrahydridoborate groups, and because the three-centre interaction provides the first experimentally-determined structural parameters for a chemical system closely related to the 'side-on' transition state for the activation of methane.[6]

These results prompt us to consider whether methane adducts of transition metals, analogous to the dihydrogen adducts recently described,[17] can be synthesised. Since the vast majority of BH_4^- ligands exhibit normal bidentate or tridentate bonding, it is reasonable to predict that isoelectronic CH_4 can interact with a transition metal similarly, albeit with a much smaller binding constant. Such geometries may be unproductive toward C–H bond cleavage since little direct M–C overlap would be present, so that weak methane adducts of transition metals may in fact be observable.[18] We propose that the key step leading to the productive activation of C–H bonds in methane and other alkanes is an energetically favourable rearrangement from a bidentate or tridentate CH_4 geometry to the 'side-on' geometry such as that in $Ti(BH_4)_3(PMe_3)_2$.

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[†] $Ti(BH_4)_3(PMe_3)_2$: m.p. 104 °C, decomp.; ^1H n.m.r. (C_6D_6, 25 °C): δ −1.65 (PMe_3, full width at half maximum height 325 Hz); *X*-band e.s.r. (PhMe, 25 °C): g_{iso} 1.98, $A_{iso}(^{31}P)$ 0.0025 cm^{-1}; i.r. (Nujol): 2532m, 2401s, 2358s, 2276w, 2230w, 2209w, 2110s, br. cm^{-1}. $Ti(BH_4)_3(PEt_3)_2$: m.p. 75 °C, decomp.; i.r. (Nujol): 2530m, 2414s, 2374s, 2283w, 2236w, 2218w, 2118s, br. cm^{-1}. Elemental analyses were consistent with the formulations.

[‡] *Crystal data:* $C_6H_{30}B_3P_2Ti$, M = 244.6, monoclinic, space group *Pnma*, a = 10.757(1), b = 11.145(2), c = 14.270(3) Å, U = 1710.8(8) $Å^3$; $Z = 4$; D_c = 0.950 g/cm³, $\mu_{calcd.}$ = 6.45 cm^{-1}; data were collected on an Enraf–Nonius CAD-4 automated diffractometer using graphite-crystal monochromated Mo-$K_{\bar{\alpha}}$ radiation, λ = 0.71069 Å, and ω/θ scans. The structure was solved by Patterson methods in the centric space group *Pnma*. The final residuals for 113 variables refined against the 777 data for which $I > 2\sigma(I)$ were $R_F = 6.4\%$, $R_{wF} = 4.8\%$. All heavy atoms were refined anisotropically, while hydrogen atoms were easily located in the difference maps, and independently refined using one common isotropic thermal parameter. The choice of space group was confirmed by refining the data in the acentric group $Pn2_1a$; this did not significantly change the model or improve the fit of the data, and this space group was rejected on the basis of a Hamilton *R*-factor ratio test.

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1986.

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