Transition Metal Tetrahydridoborates as Models of Methane Activation: Synthesis and Structure of Ti(BH₄)₃(PMe₃)₂

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The X-ray crystal structure of Ti(BH₄)₃(PMe₃)₂ shows that two of the BH₄⁻ 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 BH₄⁻ groups toward transition metals may be informative models of the nature of this transition state, despite the fact that CH₄ and BH₄⁻ are chemically rather different. We now describe a titanium tetrahydridoborate complex that exhibits an unprecedented bonding mode for the BH₄⁻ unit that closely resembles the 'side-on' model for C–H bond activation.

The reaction of trialkyphosphines with thermally unstable Ti(BH₄)₃·Et₂O, prepared in situ from TiCl₄ and LiBH₄ in diethyl ether,⁷ gives a dark blue solution from which the diadducts Ti(BH₄)₃(PMe₃)₂ and Ti(BH₄)₃(PEt₃)₂ may be

(1)  
(2)  
(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 \mu_B and e.s.r. spectra typical of monomeric Ti^{III} species. The \textsuperscript{1}H n.m.r. spectra show only resonances due to the phosphine ligands; the tetrahydridoborate proton signals 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.\textsuperscript{8} In order to establish the nature of the bonding in these titanium tetrahydridoborate complexes, the X-ray crystal structure of Ti(BH\(_4\))\(_3\)P(Me\(_3\))\(_2\) has been determined.\textsuperscript{2}

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).\textsuperscript{9} Of the three equatorial BH\(_4^-\) groups, one adopts a normal bidentate structure that closely resembles the bridge geometry observed in (C\(_5\)H\(_5\))\(_2\)Ti(H\(_2\)BH\(_3\))\(_10\) and several other transition metal complexes containing normal H\(_2\)BH\(_3^-\) ligands.\textsuperscript{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\(_2\)BH\(_3^-\) 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.

The geometries of the ‘side-on’ tetrahydridoborate ligands are quite unlike those observed for tridentate,\textsuperscript{11} bidentate,\textsuperscript{10} or unidentate\textsuperscript{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 serve as 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,\textsuperscript{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.\textsuperscript{6}

These results prompt us to consider whether methane adducts of transition metals, analogous to the dihydrogen adducts recently described,\textsuperscript{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.\textsuperscript{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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