Evidence for a Direct Bonding Interaction between Titanium and a β-C–H Moiety in a Titanium–Ethyl Compound; X-Ray Crystal Structure of [Ti(Me₂PCH₂CH₂PMe₂)EtCl₃]

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The X-ray crystal structure of [Ti(Me₂PCH₂CH₂PMe₂)EtCl₃] (1) shows that the Ti–C–C angle and the Ti–C(methyl) distance of the Ti–Et moiety are 85.9(6)° and 2.516(10) Å, respectively, and that the Ti–H–C-(methyl) distances are 2.29(Ti–H) and 1.02(H–C) Å; a direct bonding interaction between the titanium atom and the β-C–H system is proposed.

We have long been interested in the role of transition metal centres in the modification of the properties of simple hydrocarbon systems attached to them. Earlier studies on simple transition metal-alkyls established the β-hydride elimination reaction[1] whilst crystal structure and acidity studies of some carboxymethyl derivatives [M]–CH₂CO₂H provided evidence for a direct interaction between the metal centre and the β-carbon of the carboxy-group.[2]

In a further development of this work we set out to synthesise and study transition metal-alkyls in which the metal centre is both electronically unsaturated and sterically uncrowded and in which the metal orbitals have relatively high energies. It was anticipated that in these circumstances the alkyl group might show evidence for unusual bonding towards the metal centre.

[Ti(Me₂PCH₂CH₂PMe₂)EtCl₃]

(1)

The compound [Ti(Me₂PCH₂CH₂PMe₂)EtCl₃] (1) has been synthesised and its crystal structure has been determined. Compound (1) was selected for several reasons. The metal centre is highly electronically unsaturated having a formal electron count of only twelve. Compounds such as [Ti(Me₂PCH₂CH₂PMe₂)Me₄] are known[3] and therefore it is likely that the titanium centre in (1) would be steric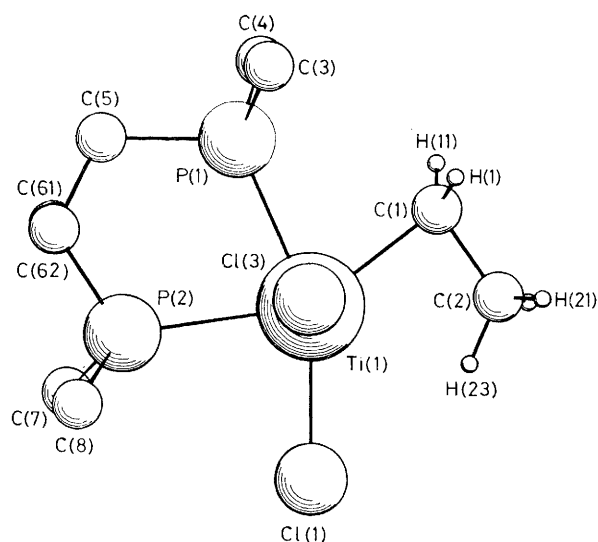ally uncrowded. Titanium has a low atomic number compared to most d-block transition metals so that there would be a greater probability of locating hydrogen atoms held close to the titanium. The ligand Me₂PCH₂CH₂PMe₂ is relatively compact and is electron releasing so that the metal orbitals would be encouraged to have a relatively high energy.

The compound [TiEtCl₃] was prepared as previously described[4] and addition of Me₂PCH₂CH₂PMe₂ gave an immediate reaction. Crystallisation of the red reaction product from dichloromethane–light petroleum (b.p. 40—60 °C) gave the desired compound [Ti(Me₂PCH₂CH₂PMe₂)EtCl₃] (1) as deep red crystals. Compound (1) is decomposed immediately by traces of water and oxygen and samples under argon at −30 °C show evidence for slow decomposition.

Crystal data: $C_8H_{21}Cl_3P_2Ti$, $M = 333.5$, monoclinic, space group $P2_1/n$, $a = 7.827(4)$, $b = 16.411(6)$, $c = 12.019(6)$ Å, $\beta = 93.24(4)°$, $U = 1541.4$ Å³, $Z = 4$, $D_c = 1.436$ g cm⁻³; data were collected on an Enraf–Nonius CAD-4F diffractometer using graphite monochromated Mo-K_α radiation ($\lambda = 0.71069$ Å) up to $2\theta = 60°$. The structure was solved by Patterson and Fourier methods and refined first isotropically and then anisotropically by full-matrix least-squares using 1762 independent reflections with $I > 3\sigma(I)$. The refinement has converged to $R = 5.60(R_w = 6.63)$.† The Me₂PCH₂-PMe₂ ligand stereochemistry is disordered with preferred conformations similar to those frequently observed in other chelate diphosphine–transition metal complexes.[5]

The most interesting aspects of the structure concern the titanium–ethyl moiety which is well defined and whose hydrogens have been located from a difference map but not yet refined. The relevant data and structural details of this feature are shown in Figure 1. The Ti–C–C angle of 85.9(6)° indicates clearly that the methyl group is being drawn towards the titanium centre. All previously reported M–C–C angles of transition metal–ethyl derivatives are typically 108—123° and in these compounds the metal centres have 18- or 16-electron environments.[6]

There is no evidence that the unusual disposition of the Ti–ethyl group arises from either intermolecular interactions or steric crowding by other ligands.

The H(23) atom of the methyl group is located 2.29 Å from the metal and this distance is considerably shorter than the sum of the Van der Waals' radii. There are other examples where a hydrogen of formally saturated C–H systems closely approaches a metal centre, as for example, in the binuclear compound [Fe₂(μ-Me)(μ-CO)(μ-Ph₂PCH₂PPh₂)(η-C₅H₅)₂]PF₆ (Fe–H 1.64 or 1.78 Å)[7] and in {[Et₂B(pyrazolyl)₂](η-2-phenylallyl)(CO)₂Mo} (Mo–H 2.27 Å).[8]

Figure 1. Crystal structure of (1) showing the plane containing the P₂TiC₂H(23) atoms; the Cl(2) atom (not shown) is located symmetrically on the Cl(3)–Ti axis below the plane. Selected distances and angles are: Ti–Cl(1) 2.408(3), Ti–Cl(2) 2.313(3), Ti–Cl(3) 2.303(3), Ti–C(1) 2.154(9), Ti–C(2) 2.516(10), Ti–H(23) 2.29, C(1)–C(2) 1.463(13), C(2)–H(23) 1.02 Å; Ti–C(1)–C(2) 85.89(58), C(1)–C(2)–H(23) 124.41, C(2)–H(23)–Ti 90.4°.

We conclude, therefore, that in this otherwise apparently simple titanium–ethyl compound there is a direct interaction between the C–H system of the methyl group and the titanium atom which can be described in terms of a covalent bond utilising a two-electron three-centred molecular orbital system.

The ^{1}H n.m.r. spectrum of (1) at $-90\ ^\circ$C may be assigned in terms of the crystal structure but shows no features unambiguously assignable to an anomalous β-hydrogen. There is no inconsistency in this fact since even if the Ti–H–C(β) interaction was quite substantial it is quite possible, indeed likely, that the three methyl hydrogens would become equivalent in the n.m.r. experiment owing to a fluxional process, e.g. rotation about the C–C bond. By analogy, the strongly bonded M–(μ-H$_2$)BH$_2$ systems normally show only a single hydrogen resonance.[9]

The ^{1}H n.m.r. spectra of (1)‡ above 0 $^\circ$C show that the four methyl and two methylene groups of the Me$_2$PCH$_2$CH$_2$PMe$_2$ ligand have become chemically equivalent. It is as though the Cl(1) and the ethyl group in this formally octahedral compound were rapidly exchanging places. Further studies are in progress to identify the mechanism of the intramolecular rearrangement.

In conclusion, we attribute the severe distortion of the Ti–Et system to direct titanium–methyl bonding via a bridging C–H–Ti interaction, which therefore provides further striking evidence for the β-effect in transition metal–hydrocarbon systems. The configuration of the Ti–ethyl system may be regarded as a model for the transition state for the widely occurring β-elimination process of transition metal-alkyls forming metal–olefin–hydrides.

The β-elimination reaction does not occur for (1) and this can be associated with that fact that d^0 transition metal centres may not undergo formal oxidative–addition reactions, i.e. all d^0 transition metal–ethyl and related alkyl derivatives may be classed as β-elimination-stabilised.

This ability of a metal centre of a metal–alkyl system to organise the geometry of the alkyl group would be expected to have implications in the stereochemistry of transition metal–alkyl reactions.

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‡ (1): δ(CD$_2$Cl$_2$, $-90\ ^\circ$C) 2.70 (3H, quint., $J_{HH} \approx J_{PH}$ 7.8 Hz, CMe), 2.53 (2H, m, CH$_2$), 2.29 (2H, m, PCH$_2$), 2.15 (2H, m, PCH$_2$), 1.68 (6H, d, J_{PH} 9.99 Hz, 2 × PMe), and 1.53 (6H, d, J_{PH} 10.28, 2 × PMe); at + 40 $^\circ$C: δ 2.76 (2H, 7-line m, C–CH$_2$), 2.57 (3H, m, Me), 2.24 (4H, m, 2 × PCH$_2$), and 1.66 (12H, d, J_{PH} 9.85 Hz, 2 × PMe$_2$).