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Preliminary communication

INTRAMOLECULAR CH. . .M INTERACTION: AB INITIO MO STUDY OF THE STRUCTURE OF $Ti(CH_3)(PH_3)_2(X)_2Y$

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Summary

Ab initio MO calculations indicate that the nature of ligands X and Y and the PTiP angle in $Ti(CH_3)(PH_3)_2(X)_2Y$ affect the distortion of its methyl group. For X = Cl, Y = Cl and angle PTiP 75°, the TiCH angle is found to be 100° and the H. . .Ti distance 2.51 Å. The methyl group is distorted, suggesting interaction between the methyl-CH bond and the metal atom. The origin of this distortion is attributed to direct interaction between the CH σ bond and an unoccupied Ti *d* orbital.

New evidence for direct interaction between CH bonds and metal centers has been rapidly accumulating, and unusually short CH. . .M distances have been found by X-ray and neutron diffraction studies [1]. The tendency of electron deficient metal atoms to satisfy the 18 electron rule has been suggested to be a driving force for this interaction. Recently we have reported the first theoretical evidence for CH. . .M activation found in ab initio molecular orbital calculations [2]. The fully optimized geometry of $Ti(C_2H_5)(PH_3)_2(Cl)_2(H)$ (I) has a small TiCC angle of 89°, a short TiH^β distance of 2.23 Å and a long CH^β bond of 1.11 Å. All these structural features, which are in good agreement with recent X-ray analysis data for $Ti(C_2H_5)(dmpe)(Cl)_3$ (II) (dmpe = dimethylphosphinoethane) [1b], except for the CH^β bond distances of which the X-ray values are unreliable, indicate that direct interaction exists between the CH^β bond and the titanium atom. The analysis of the effects of ligands X and Y in $Ti(C_2H_5)(PH_3)_2(X)_2(Y)$ has suggested that donative interaction from the CH^β bond to a vacant Ti *d* orbital is responsible for this distortion. We have also found a similarly distorted ethyl group in

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three-coordinate $Pd(C_2H_5)(PH_3)(H)$. The potential energy surface of this compound leads the distorted structure smoothly to a transition state with a low barrier, and then to the β-elimination product $Pd(C_2H_4)(PH_3)(H)_2$ [3]. Contrary to the case of the Pd complex, the β-elimination reaction in I does not occur, probably because the product is seven-coordinated and unstable.

In this communication we present results of ab initio structural optimization of a related methyl compound, $Ti(CH_3)(PH_3)_2(Cl)_3$ (III), and show that its methyl group is distorted. The optimized structure of III, along with the X-ray results for $Ti(CH_3)(dmpe)(Cl)_3$ (IV) [1a], is shown in Fig. 1. The PTiP angle was fixed at 75°, to simulate the situation of IV. The $TiCH^1$ angle α is 99.6°, substantially smaller than either the other TiCH angles of 113.1° or the standard tetrahedral bond angle of 109.5°. The methyl group is thus substantially distorted. The angle β between the pseudo-three-fold axis of CH_3 and each CH bond is calculated to be 109°, indicating that the distortion is due to twisting of tetrahedral CH_3 as a whole and not due to deviation from the tetrahedral structure. It is also noteworthy that the $TiCH^1$ angle of 99.6°

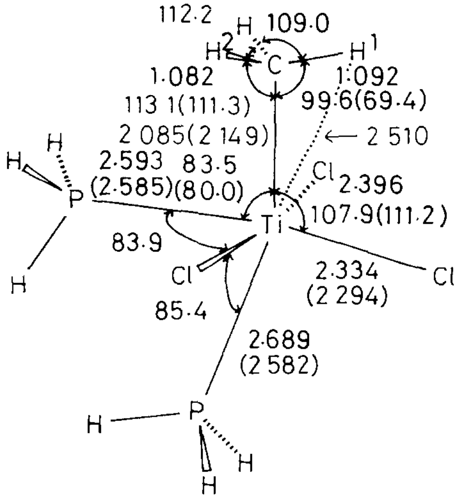

Fig. 1. Optimized geometry of III with bond distances in Å and angles in degrees. The PTiP angle is assumed to be 75.0° similar to the observed angle in IV. Numbers in parentheses are X-ray results for IV.

TABLE 1

DEPENDENCE OF GEOMETRICAL PARAMETERS OF $Ti(CH_3)(PH_3)_2(X)_2Y$ ON LIGANDS X AND Y AND PTiP ANGLES

X	Y	Angle PTiP (°)	Angle $TiCH^1$ (°)	β (°)	R—TiC (Å)	R—TiH^1 (Å)
H	H	91.6op [a]	108.3	110.6	2.135	2.685
H	H	75.0as	107.1	110.5	2.122	2.657
H	Cl	89.4op	106.2	110.6	2.135	2.653
Cl	H	87.9op	102.6	109.8	2.094	2.566
Cl	Cl	88.6op	100.2	109.2	2.102	2.533
Cl	Cl	75.0as	99.6	108.9	2.085	2.510

[a] op = optimized, as = assumed.

in III is larger and closer to normal than the TiCC angle of 89° in the ethyl analogue I and the Ti. . .H distance of 2.51 Å in III is longer than in I (2.23 Å). The CH[1] bond distance in III is only 0.01 Å longer than the CH[2] distance, while in I the difference in the β-CH bond distances was 0.03 Å. For these reasons it is suggested that the CH. . .M interaction in III is weaker than in I. The calculated structure of III (Fig. 1) agrees reasonably well with X-ray results of IV, except for the position of the hydrogen atoms, i.e., the TiCH bond angles. The X-ray TiCH[1] angle of 70° is much smaller than the theoretical value (100°). Considering an excellent agreement found between the calculated structure of I and the X-ray structure of II, we feel that the calculated positions of the hydrogen atoms in Fig. 1 are more reliable than the X-ray results and constitute a theoretical prediction for the structure of IV. A neutron diffraction experiment is awaited*.

The structural parameters of the CH_3 group were found to be sensitive to ligands X and Y as well as the PTiP angle, as shown in Table 1. Starting from nearly undistorted CH_3 for X = Y = H, the TiCH[1] angle α is reduced in the case of Y = Cl. The largest reduction of α occurs if X = Cl. The effects of X = Cl and Y = Cl are more or less additive as well as pinching the PTiP angle to 75°, the angle corresponding to the dmpe complex. Thus the predicted CH_3 distortion in III is the result of combined effects of chlorine ligands for X and Y and the small PTiP angle.

Though the electronic origin of this distortion is difficult to quantitize, the same factor that is responsible for the distortion of C_2H_5 in I, i.e., the donative interaction from the CH bond to an unoccupied Ti *d* orbital, appears to be

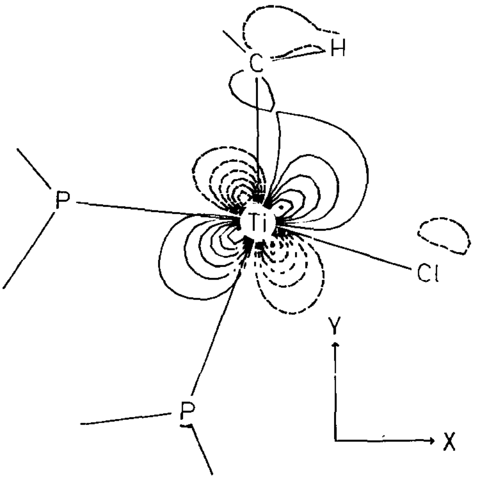

Fig. 2. Contour map of the LUMO of III at the optimized geometry of Fig. 1. The contours are ±0.05, ±0.10, ±0.15, ±0.20, ±0.25 and ±0.30 in a.u., and solid and dotted lines denote positive and negative values, respectively.

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*After submission of this manuscript, the molecular structure of IV was determined by a neutron diffraction analysis showing the TiCH[1] angle to be 93.7° and the Ti. . .H distance to be 2.45 Å [5], which agree well with our theoretical values.

operative. Figure 2 shows the LUMO for III at the geometry of Fig. 1. It is essentially the vacant Ti d_{xy} orbital with some contribution of s and p orbitals, and extends toward the $(x+y)$ direction, the direction favorable for an overlap with the CH^1 bond. In fact, a small out-of-phase mix of the CH^1 bonding orbital in this LUMO must be noticed. This suggests that the CH^1 bond is stabilized by a small bonding (in-phase) mix of the Ti d_{xy} orbital. Replacement of H ligands with Cl lowers the d_{xy} level, and thus would increase the donative interaction. The reduction of the PTiP angle promotes further extension of the LUMO toward the CH^1 bond and would also increase the interaction. It is noteworthy that the TiC bond distance becomes shorter and therefore stronger if H is replaced by Cl, but CH_3 twist occurs despite stronger TiC bonding.

Theoretical methods

For Ti, the valence double ζ basis set by Topiol et al. [4a] is used together with core orbitals of MINI-4 [4b] by Tatewaki et al. The 3-21G basis set is used for C and H of CH_3, MINI-4 [4c] for Cl, and STO-2G for P and H of PH_3 . The energy gradient technique is used to optimize all the geometrical parameters. All the calculations reported here are based on the closed-shell Hartree—Fock method, and were carried out with the GAUSSIAN80 program at the IMS Computer Center.

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