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Intramolecular CH···M Interaction: Theoretical Study of the Structure of Six-Coordinate $Ti(C_2H_5)(PH_3)_2(X)_2(Y)$

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Activation of rather inert aliphatic CH bonds by transition-metal compounds is one of the hot topics of organometallic syntheses and catalysts.[2] X-ray and neutron diffraction studies have yielded several examples in which there exist short CH···M distances, considered to be an incipient CH activation.[3] All the cases involve electron-deficient metals, and the inclination to satisfy the 18-electron rule has been considered to be a necessary driving force for the interaction. Though the interaction is supposed to be of an electronic origin, no concrete theoretical evidence for the existence of such an interaction has been available.

In the present communication we report the first theoretical evidence of CH···M activation found in an ab initio molecular orbital calculation. The optimized geometry of the six-coordinate Ti d^0 complex $Ti(C_2H_5)(PH_3)_2(Cl)_2(H)$ (**1**) has a distorted ethyl group with a short ethyl H^β···Ti distance. We also suggest that the CH···M interaction may be occurring more commonly than has so far been detected.

The complex **1** has been chosen to simulate the expermental studied complex, $Ti(C_2H_5)(dmpe)(Cl)_3$ (**2**) (dmpe = dimethylphosphinoethane), in which a direct interaction between the ethyl H^β and Ti has been reported on the basis of the X-ray structural analysis.[3a]

The ab initio LCAO–SCF–MO method with the energy gradient was used for the optimization of the complex geometry.[4] The basis sets used are of double-ζ quality for valence electrons of Ti and C_2H_5 and minimal for core electrons and for all the other ligands.[5]

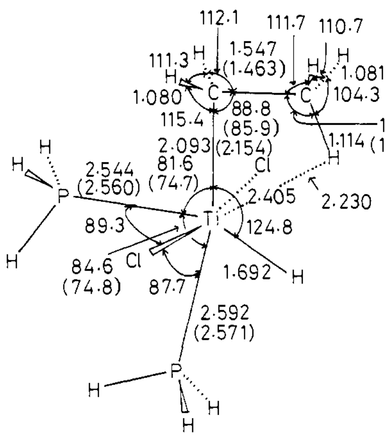
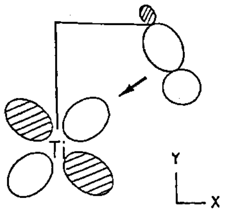


Figure 1. Optimized geometry of **1**. The bond distances are in Å and the angles in degrees. The numbers in parentheses are corresponding experimental values for **2**.[3a]

Table I. Energy Difference ΔE (kJ/mol) between Distorted and Undistorted Structures of $Ti(C_2H_5)(PH_3)_2(X)_2(H)$

X	H	F	Cl	CF_3
ΔE	42	−49	−75	−173

The fully optimized geometry of **1** is shown in Figure 1. It is noted that the C–C–Ti bond angle of 89° is much smaller than that expected in the sp^3 hybridization (109°), that the distance between H^β of the ethyl group and the Ti atom is 2.23 Å (a very small value indicating a direct H···Ti interaction), and that the length of the CH^β bond is 1.11 Å, longer by 0.03 Å than the other CH bonds in the same ethyl group. These three features are in good agreement with experiment.[3a] This agreement indicates that the structural features found in experiments are caused not by the effect of packing forces in the crystal but by the direct intramolecular interaction between the CH^β bond and the transition-metal center. Consistent with the fact that the metal center has a formal electron count of only 12 and is electronically unsaturated, analysis of the wave function reveals that the complex has low-lying unoccupied molecular orbitals consisting of Ti d_{xy}, to which the electron delocalization is to take place from the CH^β bonding orbital (**3**).



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Additional calculations show that ligands make a large difference in the distortion of the ethyl group. The optimized geometry of $Ti(C_2H_5)(PH_3)(H)_3$ (**4**), where the axial chlorines of **1** are replaced by hydrogens, has an undistorted alkyl group with a large H···M distance of 3.01 Å, normal CH bond distances, and a normal C–C–Ti angle of 114°. The optimized geometry of $Ti(C_2H_5)(PH_3)_2(H)_2(Cl)$ (**5**), where the equatorial H of **4** is replaced by Cl, also gives a normal, undistorted ethyl group. The above results suggest that the electron-withdrawing axial ligands would enhance the CH···M interaction.

In order to further explore the effect of axial ligands, we have calculated for $Ti(C_2H_5)(PH_3)_2(X)_2(H)$ (**6**) (X = H, F, Cl, CF_3) the energy difference ΔE between a structure with a distorted ethyl group and another with an undistorted ethyl group. The geometries of distorted and undistorted structures are taken to be those of optimized **1** and **4**, respectively, except for Ti–axial ligand X bond distances which are assumed to have standard values. Results in Table I show clearly that a large axial ligand effect exists. For X = halogens, the distorted structure is more stable than the

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undistorted structure. Actually the fully optimized structure for X = F has the C–C–Ti angle of 88.0°. A large $|\Delta E|$ suggests that the CF_3 complex might have an ethyl group even more distorted than has been found in the Cl complex, or possibly might rearrange to be a β-elimination product. An analysis shows that $|\Delta E|$ becomes larger, as Ti d_{xy} containing unoccupied orbitals come lower in energy, facilitating the electron delocalization from the CH^β bond. As neither σ nor π orbitals of the axial ligands can mix with the Ti d_{xy} orbital, this lowering of unoccupied orbitals has to be purely inductive.

As will be reported elsewhere, in the course of theoretical study of reaction pathways of palladium complexes,[6] we have also found a distorted ethyl group in an electron-deficient, coordinatively unsaturated three-coordinate d^8 complex $Pd(H)(C_2H_5)(PH_3)$. Its optimized geometry has an ethyl structure quite similar to that in **1**. Though such unsaturated intermediates may not be easily detectable experimentally, our theoretical finding suggests that an intramolecular CH···M interaction may be taking place more commonly than has been established.

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Registry No. 1, 91084-14-9; **4**, 91084-15-0; **5**, 91084-16-1; **6** (X = H), 91084-17-2; **6** (X = F), 91084-18-3; **6** (X = CF_3), 91084-19-4.

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Excited-State Chemistry of a 1,5-Biradical: Laser-Induced Ejection of a 1,3-Biradical

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We recently reported some new photocyclizations of α-(*o*-tolyl)acetophenones which were concluded to involve 1,5-biradical intermediates.[2] We have studied these biradicals by laser flash spectroscopy and have observed that additional products resulting from excitation of the biradicals are formed under intense laser irradiation. Although there are several examples of the photochemistry of cryogenically isolated biradicals,[3] demonstrations of discrete photochemistry of transient intermediates in solution are rare.[4,5]

The compounds that we have examined most closely are α-(2,4,6-trimethylphenyl)acetophenone (MesAP) and α-(2,4,6-triisopropylphenyl)acetophenone (TipAP). When dilute (0.02–0.20 M) solutions of these ketones are irradiated with conventional lamps, they isomerize quantitatively to mixtures of the corresponding 2-phenyl-2-indanol derivatives[2] and, in the case of TipAP, enol.[6] The products formed under low-intensity conditions are just those expected from a 1,5-biradical in thermal equilibrium with its surroundings.[7]

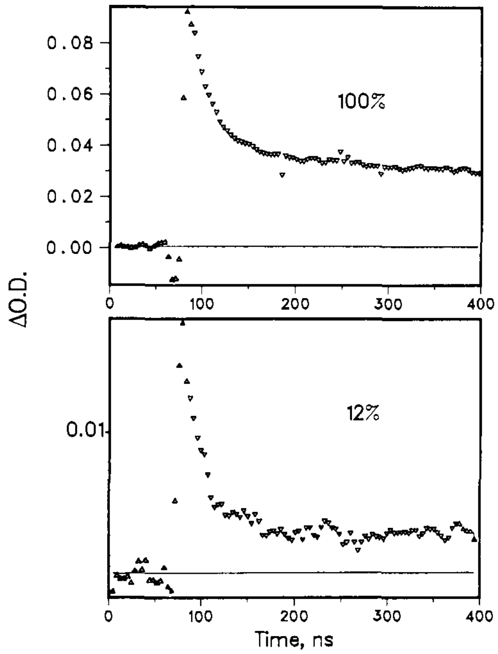

Figure 1. Computer-averaged biradical decay traces for TipAP in cyclopentane, monitored at 320 nm. Both samples were irradiated with the 308-nm excimer laser: the top one with no filter, the bottom one with a 12% neutral density filter. Note the differences in ratios of residual to maximum signal and the slow decay of the residual in the upper trace.

Quenching studies indicate triplet lifetimes shorter than 1 ns for both ketones.[2] Therefore the triplet ketones should be invisible to nanosecond flash spectroscopy.[8] Indeed they are, but the transient decay profiles observed depend strongly on laser power and wavelength. With nitrogen laser excitation at 337 nm (~10 mJ/8-ns pulse), both compounds produce transients which exhibit clean first-order decay and lifetimes in various solvents of 40–50 ns for TipAP and 15 ns for MesAP. The spectra and lifetimes of these transients are similar to those of many other phenyl ketone derived biradicals that have been reported previously, with maxima at 415 (weak) and 310–330 nm. Moreover, the transients reduce paraquat with rate constants $\geq 10^9$ M^{-1} s^{-1} in methanol, as expected for biradicals containing a ketyl radical center.[10] Therefore we are confident in assigning the 1,5-biradical structure to these transients.

When a more powerful excimer laser (~80 mJ/4-ns pulse) is used to produce 308-nm excitation, the transient absorption below 400 nm no longer decays to the preexcitation level (Figure 1). New transients with lifetimes $>10^{-5}$ s can be observed, and the relative amount of long-lived transient increases with excitation intensity. Final/total intensity ratios at 320 nm of 0.15, 0.21, 0.27, 0.36, and 0.42 were measured with neutral density filters of 12%, 25%, 40%, 70%, and 100% transmission, respectively. Time-resolved spectra of the long-lived transient absorption in cyclopentane indicate that it has two discrete components. Spectra recorded after a 10-μs delay show a sharp maximum at 329 (MesAP) or 334 nm (TipAP) characteristic of benzylic radical centers[11] and a broader underlying absorption with a maximum $\leq$300 nm. The broad band is much more prominent for TipAP than for MesAP, is the predominant absorption at delays >100 μs, and has a profile identical with that of the enol form of TipAP.[6]

The linear increase in the fractional contribution of long-lived transient as a function of excitation intensity indicates that some biphotonic process occurs under these irradiation conditions to produce new transients. In order to see whether this biphotonic

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