Electronic Structure of Planar-Tricoordinated Phosphorus in Titanium-Boron Complexes

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Received March 21, 1995

Key Words: Phosphorus, planar-tricoordinated / Calculations, RHF, MP2

The electronic structure of the recently synthesized complex 5 obtained by the reaction of $Cp_2Ti(PMe_3)(t\text{Bu-CP})$ with $(Et_2BH)_2$ was analyzed by means of molecular orbital (MO) calculations. The methods applied were the extended Hückel and the ab initio Hartree-Fock procedures. The highest occupied MOs were derived from molecular fragments. The geometrical parameters calculated for a simplified model (**6**) are close to those obtained from an X-ray investigation of **5**. The analysis of the results shows a strong donor-acceptor interaction between the P–B σ bond and the Ti center. The phosphorus lone pair is not involved in bonding.

That tetracoordinate carbon is tetrahedral is known since 1874 when van't Hoff[1a] and Le Bel[1b] recognized this fact. Nevertheless, it is due to the imagination of chemists to ask for the prize of a planar tetracoordinate carbon. Hoffmann, Alder, and Wilcox analyzed the bonding properties of such a system and pointed out several possibilities of stabilizing a planar-tetracoordinate carbon atom[2]. The bonding properties of a square-planar carbon atom in the valence bond framework gives a normal set of sp^2 hybrids at the carbon atom. Two of them are engaged in two-electron two-center bonds with one hydrogen atom each. The third hybrid participates in a two-electron three-center bond using two electrons of the two hydrogen atoms. The remaining two electrons are placed in the 2p orbital perpendicularly to the plane spanned by the five atoms (see **1**. Agostic interactions and/or two-electron three-center bonds are symbolized throughout by dotted lines.) The use of four substituents which exhibit σ-donor and π-acceptor properties should stabilize such a species[2]. These proposals were substantiated by Schleyer et al.[3] by carrying out ab initio molecular orbital calculations on several model species with ligand atoms or groups containing Li, B, and Si as well as by incorporating the carbon atom in small rings.

1

Contributions to this problem from the side of the experimentalists were the synthesis of the divanadium and dizirconium complexes **2**[4] and **3**[5]. These compounds can be looked at as having a sp^2 carbon atom incorporated in a benzene ring with two further metal centers in the molecular plane of this ring. A further complex which is built upon a similar scheme is **4** synthesized by Erker et al.[6]. The bonding features of **4** have been analyzed recently[7]. It was shown by means of molecular orbital (MO) calculations that the excellent acceptor properties of the d^0 zirconium fragment $(Cp_2Zr)^{2+}$ are mainly responsible for the structure found[7]. Similarly, a theoretical treatment of **2** and **3** shows that the lone pair of the sp^2 center is stabilized by acceptor orbitals localized at the metal centers[8]. Recently compound **5**, a congener of **4**, has been prepared[9]. This molecule can be derived from **4** by replacing the planar-tetracoordinated carbon atom by a phosphorus atom. In this paper we discuss the similarities and differences in the electronic structures of **4** and **5**, especially we examine the role of the lone pair at phosphorus in the bonding.

Computational Details

The electronic structure of **5** was explored by extended Hückel calculations using standard parameters for H, C, N, P and Ti[10]. Ab initio SCF calculations without and with correlation corrections (MP2) were carried out on model compounds **6** as well as **7** by using the Gaussian 92 program[11]. For all structures we assumed C_s symmetry. For Ti and P we applied an effective core potential[12] for the inner shell electrons. The valence orbitals are represented as a Gaussian orbital basis set (3s, 3p, 3d, 4s, 4p) for Ti and (3s, 3p) in the case of P. A split-valence basis for C (10s,

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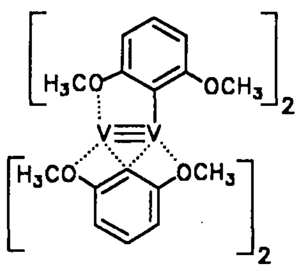

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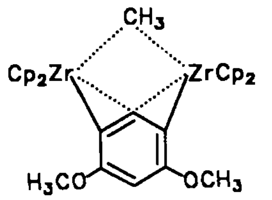

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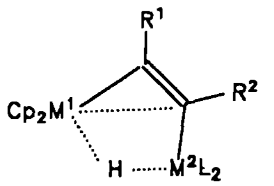

M¹ = Zr, Hf; M²=B, Al, Ga
R = alkyl, phenyl
X = halogen, alkyne, alkyl

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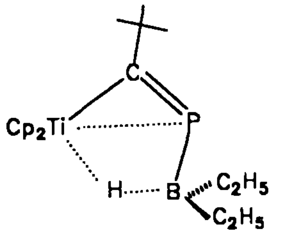
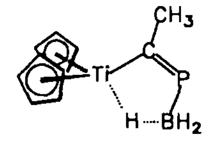
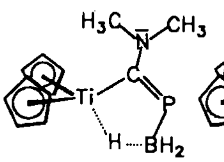


5

5p), B (10s, 5p), N (10s, 5p), and H (4s) as suggested by Dunning and Hay[13].

6





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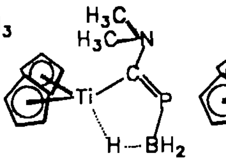

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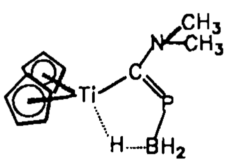
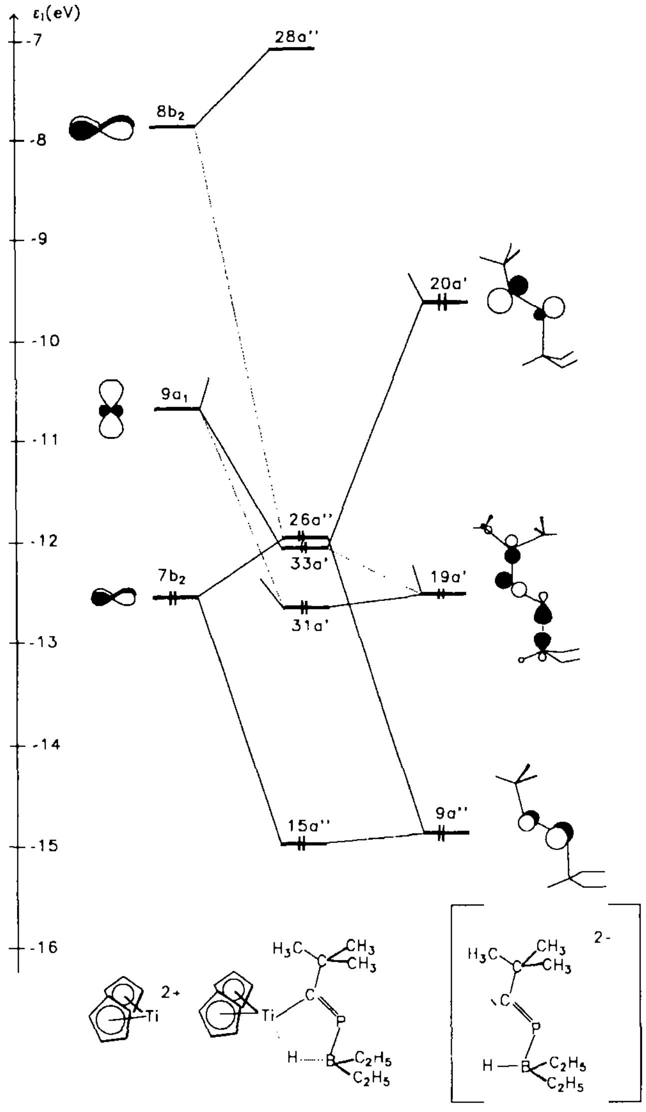


7c

Results and Discussion

To derive the frontier molecular orbital of **5** we consider in Figure 1 the interaction between the frontier MOs of a $[Cp_2Ti]^{2+}$ unit[14] (left) and a $[tBu-C=P-B(H)(C_2H_5)_2]^2$ unit at the right. The HOMO (26a″) of **5** results from a three-orbital four-electron interaction between the 9a″ MO of the dianion fragment $[tBu-C=P-B(H)(C_2H_5)_2]^2$ and the $7b_2$ and $8b_2$ levels of the $[Cp_2Ti]^{2-}$ units. The MO $7b_2$ describes the bonding interaction between the π orbitals of the Cp ligand and the $3d_\pi$-Ti molecular orbital and is mainly localized at the Cp ligands. The antibonding counterpart of $7b_2$ represents $8b_2$ with large d_π-Ti character. Stabilization of the HOMO (26a″) of **5** is due to the admixture of $8b_2$ producing partial Ti−C-π bonding character.

Figure 1. Interaction diagram between the frontier orbitals of a $[Cp_2Ti]^{2-}$ unit (left, C_{2v}) and a $[tBu-C=P-B(H)(C_2H_5)_2]^2$ unit (right, C_s) to derive the highest occupied MOs of **5** (C_s); the values are taken from an EH calculation



Important for the bonding in **5** is the interaction between the 20a′ (HOMO) and 19a′ MO of the dianion with the $9a_1$ (LUMO) of the $[Cp_2Ti]^{2-}$ unit. In the resulting bonding combination (33a′) (see Figure 2a) we recognize besides the anticipated in-phase relation between Ti and C a strong Ti−P−B three-center interaction. We notice that the phosphorus lone pair is not involved in the bonding with Ti and B due to its strong 3s character. The natural bond orbital (NBO) analysis predicts 80% s character (see also Figure 2a). This result is corroborated by the ^{31}P-NMR signal at $\delta = 34.8$[9], the strong deshielding being in line with a free lone pair. The total electron density in the plane of the five-membered heterocyclic ring shows (Figure 2b) a considerable electron density between Ti, B, and P. These qualitative considerations suggest a threefold coordination for the phosphorus atom and an additional interaction between the P–B σ bond and the titanium centers. The geometrical parameters of **6** and **7** were optimized at the MP2 and RHF levels, respectively. The calculated structures of both species are in very good agreement with the X-ray data obtained from **5** (see Table 1).

Figure 2. a) Isosurface (0.08) of 33a′ of **5**, b) total electron density of **5** in the plane of the five-membered heterocycle; the values refer to the MP2 wave function

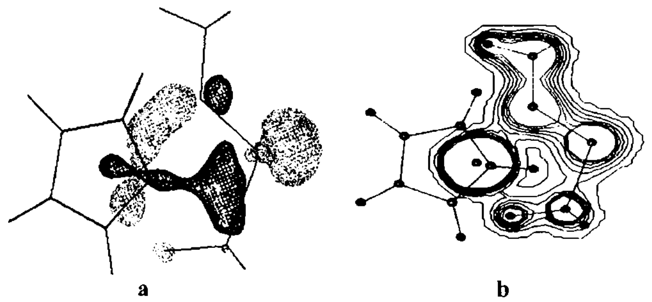


Table 1. Comparison between experimental (**5**) and calculated bond lengths and bond angles for **6** (RHF and MP2 level) and **7** (THF level)

Bond [Å]	**5** (exp.)	**6** (RHF)	**6** (MP2)	**7a** (RHF)
Ti–C	2.099	2.042	2.136	2.063
B–P	2.054	2.167	2.118	2.173
Ti–P	2.648	2.712	2.738	2.708
C–P	1.666	1.678	1.743	1.722
B–H	1.25	1.262	1.303	1.268

Angle [°]	**5** (exp.)	**6** (RHF)	**6** (MP2)	**7a** (RHF)
C–P–Ti	52.4	48.7	51.3	49.6
P–C–Ti	88.6	93.0	89.2	90.8
H–P–B	109.0	115.3	114.9	114.2
H–Ti–P	72.9	77.2	77.0	77.6
C–Ti–P	39.0	38.2	39.5	39.5
B–P–Ti	64.6	61.5	60.7	61.1
B–H–Ti	113.0	105.9	107.3	107.0

In the case of **7** our results predict that the dimethylamino group prefers conformation **7a** in which the nitrogen lone pair is in conjugation with the π system. For a better understanding of the interactions prevailing in **6** we used the NBO program where the canonical molecular orbitals obtained for **6** are transformed into a set of natural bond orbitals (NBOs) by using the Weinhold NBO localization procedure[15]. This allowed us to quantify the above-mentioned interactions between occupied and unoccupied MOs.

Table 2 contains the most important σ bonds and the π bond and the empty acceptor orbitals localized at the Ti center. These bonds are shown schematically in Figure 3. As a measure of the interaction between the orbitals we calculate ΔE_{ij} according to eq. (1) from the occupation number b_i, the off-diagonal element of the Fock matrix (F_{ij}) and the difference of the orbital energies ε_i.

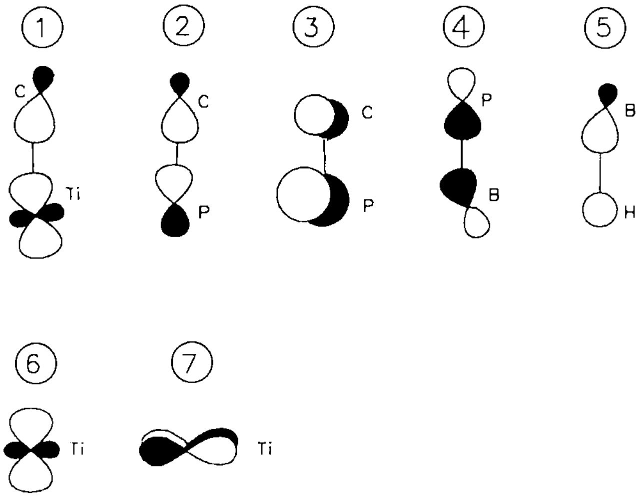
$$\Delta E_{ij} = b_i \frac{F_{ij}^2}{\varepsilon_i - \varepsilon_j} \qquad (1)$$

We notice large ΔE_{ij} values for the interaction between NBO 4 (P–B σ bond) and the empty orbital (NBO 6) at the Ti center. The P–B σ bond exhibits a high p character and shows a relatively small energy difference to the empty $dx^2 - y^2$ and 4s orbital at Ti. The considerable contribution of the π-MO (27.2 kcal/mol for **6** and 21.8 kcal/mol for **7a**) indicates a double bond character between Ti and C. In accord with this result is the relative short Ti–C distance observed in **5** and the interaction diagram in Figure 1.

Table 2. Interaction energies ΔE_{ij} [kcal/mol] between the occupied natural bond orbitals (NBOs) no 1–5 and the empty NBOs 6 and 7 of **6** and **7a**

Donor NBO	No.	Acceptor NBO	No.	ΔE_{ij} **6**	ΔE_{ij} **7a**
Ti–C (σ)	1	Ti	6	10.3	8.6
C–P (σ)	2	Ti	6	10.0	11.2
C–P (π)	3	Ti	7	27.2	21.8
P–B (σ)	4	Ti	6	74.8	93.8
H–B (σ)	5	Ti	6	50.3	45.8

Figure 3. Representation of the natural bond orbitals no 1–7 of Table 2



To conclude, we can say that the electronic structure of **5** is related to that of **4**. The phosphorus lone pair plays no role in stabilizing the structure. Important is a donor-acceptor interaction between the P–B σ bond and the empty orbital of the Ti center.

We are grateful to the *Volkswagenstiftung* and the *Fonds der Chemischen Industrie* for financial support.

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