MO Explanation of the "Unexpected" Structure of (η^5-C_5Me_5)$_2$Ta(=NC_6H_5)H

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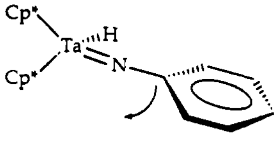
Received September 2, 1992

In a recent paper Bercaw et al. reported on the formation of the imido–hydrido and oxo–hydrido derivatives of permethyltantalocene.[1] The imido–hydrido permethyltantalocene Cp$^*_2$Ta(=NPh)H, **1**, was prepared by treatment of Cp$^*_2$Ta(=CH_2)H with aniline under elimination of methane.[1]



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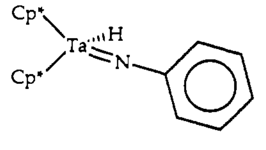

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The structure of **1** was determined by X-ray and a linear [Ta–N–C(ipso)] (177.8°) fragment was unexpectedly found, with both the phenyl group and the hydride atom lying in the equatorial plane.[1] In an attempt to understand the structure of **1**, three bonding structural arrangements were discussed:[1] (A) A tantalum 18-electron configuration in which the imido nitrogen is sp^2 hybridized, which would require a structure with a bent [Ta=N—C(ipso)] fragment (indicated by an arrow in **1**); (B) a 20-electron configuration having tantalum–nitrogen triple-bond character and the nitrogen sp hybridized; (C) an 18-electron configuration with double-bond character of the tantalum–nitrogen bond and the nitrogen as sp hybridized. The latter implies that the imido nitrogen has the lone-pair electrons. On the basis of structure of Cp$^*_2$Ta(=NPh)H and other complexes having tantalum–nitrogen bonds, the bonding for **1** was described as an intermediate between B and C.[1] Both Bergman[2] and Schrock[3] have also recently found structures with linear [M(Zr^2,Os^3)–N–R] fragments. A frontier-orbital approach is here presented here to explain why Cp$^*_2$Ta(=NPh)H, and similar type of complexes have a linear M–N–R structure, and why the phenyl group in **1** is lying in the equatorial plane and not perpendicular to it as outlined in **2**. The structure of a similar complex as **1** in which the phenyl group is exchanged with an alkyl group will also be discussed. For these purposes extended Hückel calculations have been performed.[4,5]

Figure 1 shows an interaction diagram for the frontier orbitals for the formation of **1** from Cp_2TaH^{2+} to the left and N–Ph^{2-} to the right.

The four frontier orbitals shown for Cp_2TaH^{2+} (only those located at tantalum are shown) to the left in Figure 1 are the d_{xz} at −9.24 eV, a combination of mainly $d_{x^2+y^2}$ mixed in with a small part of d_{xy} at −11.78 eV, the LUMO is calculated to be mainly the d_{xy} orbital at −12.73 eV, while the HOMO at −12.94 eV is the antibonding counterpart to the d_{xz} orbital. To the right in Figure 1 are the four highest occupied molecular orbitals of the N–Ph^{2-} fragment outlined. The HOMO at −7.89 eV is of p_z character and is mainly located at the phenyl ring, with only a small amplitude at the nitrogen, while for the second HOMO at −12.04 eV the situation is reversed, as the major contribution is found here at the nitrogen. The two first orbitals are $\pi^*_{\text{N-C(ipso)}}$ of *z* character, while the third HOMO is the $\pi^*_{\text{N-C(ipso)}}$ of *y* character, the latter found at −12.54 eV. The $\sigma_{\text{N-C(ipso)}}$ is located to be at −13.42 eV, and this orbital has its main amplitude at the nitrogen. The unoccupied tantalum d_{xz} orbital at −9.24 eV interacts with mainly the second HOMO of the N–Ph^{2-} fragment and this interaction is responsible for the HOMO of the Cp_2Ta(=NPh)H complex. However, in this interaction the HOMO of the Cp_2TaH^{2+} fragment, as well as the HOMO of the nitrogen fragment, is also involved, but the HOMO of the N–Ph^{2-} fragment interacts to a much smaller extent with the Cp_2TaH^{2+} fragment, compared to the interaction involving the second HOMO of the nitrogen fragment, because the amplitude at the nitrogen atom is much smaller in the HOMO, compared to the second HOMO. The second LUMO of the tantalum fragment interacts with the $\pi^*_{\text{N-C(ipso)}}$ of *y* character and this interaction is responsible for the LUMO of the Cp_2Ta(=NPh)H complex. The LUMO of the tantalum fragment interacts with the $\sigma_{\text{N-C(ipso)}}$ of the nitrogen fragment.

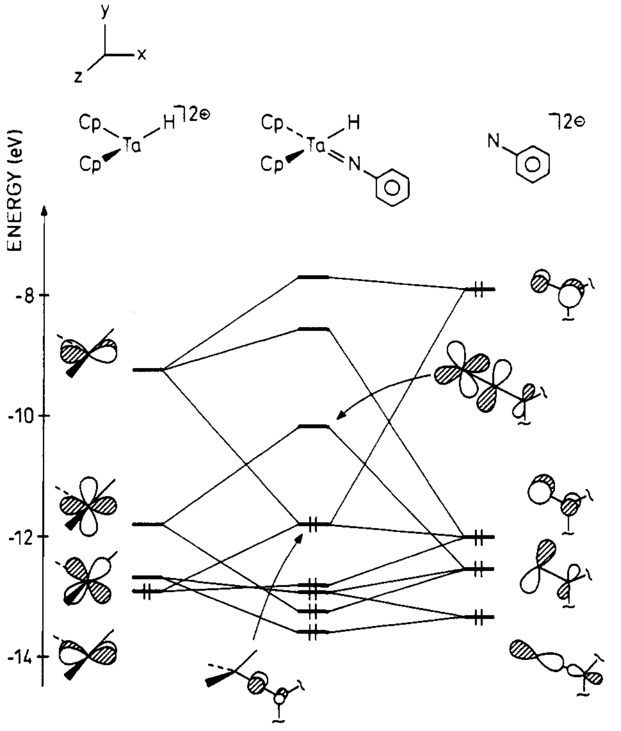

Figure 1. Interaction diagram for the formation of **1** from Cp_2TaH^{2+} to the left and N–Ph^{2-} to the right. Some of the frontier orbitals of **1** are shown in the middle.

The reason for the linearity of the [Ta–N–Ph] fragment emerges from the Walsh diagram outlined in Figure 2 for four of the frontier orbitals for a bending of the phenyl group out of the equatorial plane.

The Walsh diagram shows that all the orbitals, except the HOMO—the $\pi^*_{\text{N-C(ipso)}}$—are unaffected by the bending of the phenyl group. The $\pi^*_{\text{N-C(ipso)}}$ orbital energy increases by about 0.7 eV by the bending of the phenyl group 60° out of the equatorial plane. The total energy of the system increases also by the bending; for the phenyl group located in the equatorial plane a total energy of −1593.91 eV is calculated, whereas it has been calculated to be −1591.50 eV for $\theta = 120°$, which corresponds to bending the phenyl group 60° out of the equatorial plane. The Ta–N overlap

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(1) Parkin, G.; van Asselt, A.; Leahy, D. J.; Whinnery, L.; Hua, N. G.; Quan, R. W.; Henling, L. M.; Schaefer, W. P.; Santarsiero, B. D.; Bercaw, J. E. *Inorg. Chem.* **1992**, *31*, 82.

(2) Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 8729.

(3) (a) Anhaus, J. T.; Kee, T.P.; Schofield, M. H.; Schrock, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 1642. (b) Schofield, M. H.; Kee, T. P.; Anhaus, J. T.; Schrock, R. R.; Johnson, K. H.; Davis, W. M. *Inorg. Chem.* **1990**, *30*, 3595.

(4) (a) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397. (b) Hoffmann, R.; Lipscomb, W. N. *J. Chem. Phys.* **1962**, *36*, 2179; *J. Chem. Phys.* **1962**, *37*, 2872.

(5) The parameters were taken from: Schiøtt, B.; Jørgensen, K. A.; Calhorda, M. J.; Galvao, A. M. *Organometallics* **1992**, *11*, 4213. Cp is used instead of Cp*.

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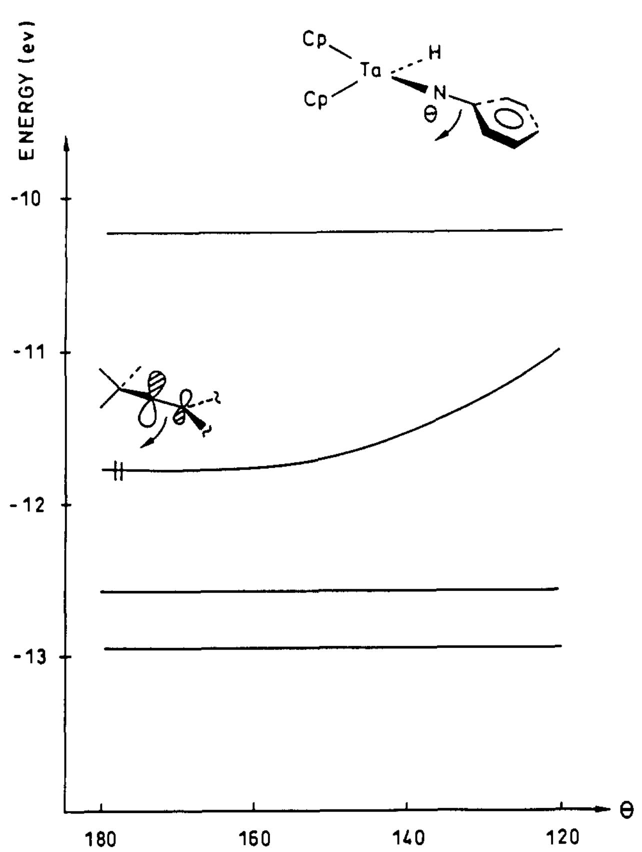

Figure 2. Walsh diagram for the bending of the phenyl group out of the equatorial plane.

population is not affected by the bending, whereas the N–C(ipso) overlap population decreases from 0.829 for θ = 180° to 0.809 for θ = 120°. The reason for the decrease in N–C(ipso) overlap population and the increase in the HOMO energy of **1** by the bending of the phenyl group can be traced to the $\pi^*_{N-C(ipso)}$ orbital. The bending causes an increase of the population of this orbital, the HOMO, located mainly at the nitrogen and the carbon atoms. This higher population of this orbital leads to an increase in the antibonding nitrogen–carbon overlap population causing the instability of the system, compared to the linear form. The increase in population of the HOMO at the nitrogen and the carbon atoms is also readable from the atomic charges at these two centers. For θ = 180° the charges at nitrogen and carbon are –0.68 and 0.39, while for θ = 120°, –0.75 and 0.35, respectively, are calculated. The phenyl substituent thus arranges itself to maximize the overlap with the nitrogen p orbital. The arguments applied here to account for the linear [Ta–N–C(ipso)] fragment for $Cp_2Ta(=NPh)H$ can also be applied to Schrock's $Os(=N-2,6-C_6H_3i\text{-}Pr)_3$ complex.[3]

The phenyl group in **1** has been exchanged with a methyl group, $Cp_2Ta(=NMe)H$, in an attempt to investigate if aliphatic substituents would also have a linear or bent [Ta–N–C] arrangement. Two different bending modes of the methyl group is studied; one is a bending in the Ta–H–N plane, and the other is a bending out of the this plane. Both types of bending causes no change in the HOMO energy (the second and third HOMOs are also unaffected by the bending) similar to the one depicted for $Cp_2Ta(=NPh)H$ outlined in Figure 2. The Ta–N and N–C(methyl) overlap populations are also constant as the angle is changed from 180° to 135°. The reason for constant N–C(methyl) overlap population is the lack of an efficient p orbital on the methyl substituent to overlap with the nitrogen p orbital. The total energy for $Cp_2Ta(=NMe)H$ increases less than 0.6 eV by this bending, indicating that the bent form is only slightly more unstable—in terms of total energy—than the linear form. Furthermore, the orbital energy and overlap population arguments indicate that the bent arrangement of the [Ta–N–C] bond in the aliphatic analogue to **1** is not that different from the linear arrangement. It would be interested with a X-ray structure of an aliphatic analogue to $Cp_2Ta(=NPh)H$ to see if the [Ta–N–C] bond angle is linear or bent.

Let us finally discuss the orientation of the phenyl group, as one could also imagine a perpendicular orientation as outlined in **2**, as the N=Ph fragment thus has an orientation similar to the CH_2 fragment in $Cp_2Ta(CH_2)CH_3$.[6] It has been found that the total energy of **1** is 0.25 eV lower than the total energy of **2**, indicating that **1** is the most stable. Although the energy difference between **1** and **2** is diminutive, the preferred stability of the former relative to the latter can be accounted for by a decrease in N–C(ipso) overlap population when going from **1** to **2** and to a certain extent be traced to a better interaction of the HOMO $\pi^*_{N-C(ipso)}$ orbital of $N\text{-}Ph^{2-}$, in the planar orientation, with mainly the LUMO of Cp_2TaH^{2+} in **1**, compared to the perpendicular orientation.

Acknowledgment. Thanks are expressed to Professsor John Bercaw for some fruitful comments.

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(6) Structure: (a) Guggenberger, L. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1975**, *97*, 6578. Theoretical calculations: (b) Goddard, R. J.; Hoffmann, R.; Jemmis, E. D. *J. Am. Chem. Soc.* **1980**, *102*, 7667. (c) Upton, T. H.; Rappé, A. K. *J. Am. Chem. Soc.* **1985**, *107*, 1206. (d) Nakatsuji, H.; Ushio, J.; Han, S.; Yonezawa, T. *J. Am. Chem. Soc.* **1984**, *106*, 5892. (e) Ushio, J.; Nakatsuji, H.; Yonesawa, T. *J. Am. Chem. Soc.* **1984**, *106*, 5892. (f) Sodupe, M.; Lluch, J. M.; Oliva, A.; Bertrån, J. *New. J. Chem.* **1991**, *15*, 321. (g) Cundari, T. R.; Gordon, M. S. *J. Am. Chem. Soc.* **1991**, *113*, 5231; *Organometallics* **1992**, *11*, 55. (h) Carter, E. A.; Goddard, III, W. A. *J. Am. Chem. Soc.* **1986**, *108*, 2180, 4746. (i) Taylor, T. E.; Hall, M. B. *J. Am. Chem. Soc.* **1984**, *106*, 1576. Hall, M. B. In *Quantum Chemistry: The Challenge of Transition Metals and Coordination Chemistry*; Veillard, A., Ed.; NATO ASI Series; Reidel: Dordrecht, 1986. (j) Spangler, D.; Wendoloski, J. J.; Dupuis, M.; Chen, M. M. L.; Schaefer, III, H. F. *J. Am. Chem. Soc.* **1981**, *103*, 3985.