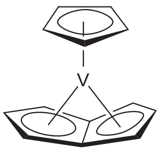
Is Ti(η^8-pentalene)$_2$ a 20-electron complex? A theoretical investigation of a pseudo electron-rich molecule

Karine Costuas and Jean-Yves Saillard*

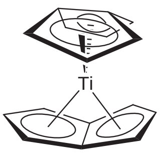
LCSIM-UMR 6511, Université de Rennes 1, 35042 Rennes Cedex, France. E-mail: saillard@univ-rennes1.fr

DFT calculations confirm the D_{2d} conformation of the title compound proposed by Jonas *et al*; only 9 of the 10 combinations of the π-type ligand orbitals interact with the metal atom: the remaining one, of a_2 symmetry, does not match with any metal orbital and therefore the title compound is not a 20-electron system, but a regular 18-electron complex; calculations predict that the 18-electron [Ti(η^8-pentalene)$_2$]$^{2+}$ cation should also be attainable.

Jonas and coworkers recently synthesised and characterised a very interesting series of transition metal complexes of V, Ti, Zr and Hf which exhibit a new type of coordination mode of pentalene (C_8H_6).[1–3] In these compounds, exemplified below



1



2

by CpV(C_8H_6) **1** and Ti(C_8H_6)$_2$ **2**, the pentalene ligand is folded in such a way that all its carbon atoms are bonded to the metal. Considering the η^8-bonded pentalene ligand in **1** as being formally a dianion, it is expected to provide the metal centre with its 10 π electrons, leading to a V^{III} 18-electron complex. A similar reasoning leads to the surprising count of 20 electrons in the case of **2**. Such an electron-rich situation generally corresponds to a Jahn–Teller instability due to the presence of two electrons in one (or two) antibonding orbital(s). Unlike **1** and other CpV systems, there is no X-ray characterisation published so far for **2** or related complexes. Its D_{2d} conformation was established on the basis of NMR data.[2] Simple symmetry considerations are fully consistent with the 18-electron count of **1**. Indeed, there is a perfect match between the five empty frontier orbitals of the CpV fragment (four of d-type and one sp-type hybrid)[4] and the five occupied π-type orbitals of (C_8H_6)$^{2-}$,[5] leaving two electrons in a dσ non-bonding level. On the other hand, of the ten occupied π-type combinations of the two (C_8H_6)$^{2-}$ ligands in the D_{2d} complex **2**, only nine have the correct symmetry to match with the nine vacant orbitals of the Ti^{IV} atom. The remaining one, being of a_2 symmetry, cannot overlap with the metal and should remain non-bonding. Thus, symmetry and frontier orbital theory predict an 18-electron count for the D_{2d} conformation of **2**.

Our current interest in transition metal sandwich complexes which do not obey the 18-electron rule[6] as well as in the coordination variability of pentalene with respect to electron count[5] prompted us to perform density functional theory (DFT) calculations[7] on **2**, in order to predict its structure (D_{2d} or less symmetrical), rationalise its electron count and understand its bonding. A full geometry optimisation carried out without any symmetry constraint confirmed the D_{2d} structure (see Fig. 1). The pentalene optimised folding angle is 149°, a value larger than that reported in **1** and related V and Ti complexes (119–127°).[1,2] As a consequence, the Ti–C(pentalene) distances are somewhat larger than those reported for the CpTi(pentalene) derivatives.[1,2] The MO diagram of **2** is shown in Fig. 2, based on the interaction of the (C_8H_6)$^{2-}$ ligands with the Ti^{IV} center. With an a_2 HOMO deriving from the π-type orbitals of pentalene, it shows clearly that the symmetry-based predictions are correct.[11] The significant HOMO–LUMO gap computed agrees with the stability of these diamagnetic species. The existence of an even larger energy gap below the HOMO suggest that **2**$^{2+}$ or isoelectronic species should also be stable diamagnetic compounds.[12] The optimised geometry of **2**$^{2+}$, for which a HOMO–LUMO gap of 1.93 eV was computed, is very similar to that of **2**. The major metrical data are given in Fig. 1. The folding angle of pentalene is also 149°. Since the a_2 HOMO of **2** has no metal participation, its depopulation in **2**$^{2+}$ has no effect on the Ti–C separations. Since this a_2 orbital derives from

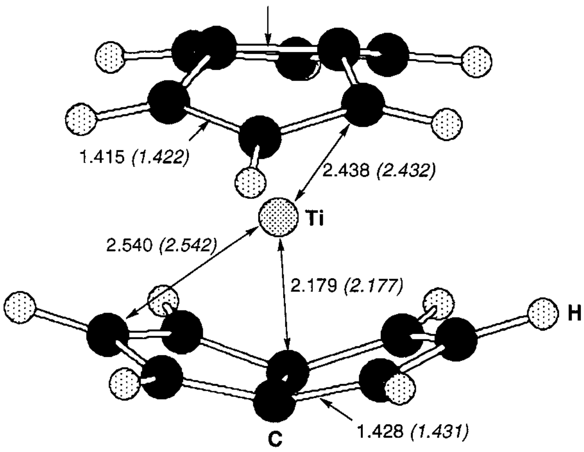


Fig. 1 DFT optimised molecular structure of **2** and **2**$^{2+}$. The values in parentheses correspond to **2**$^{2+}$.

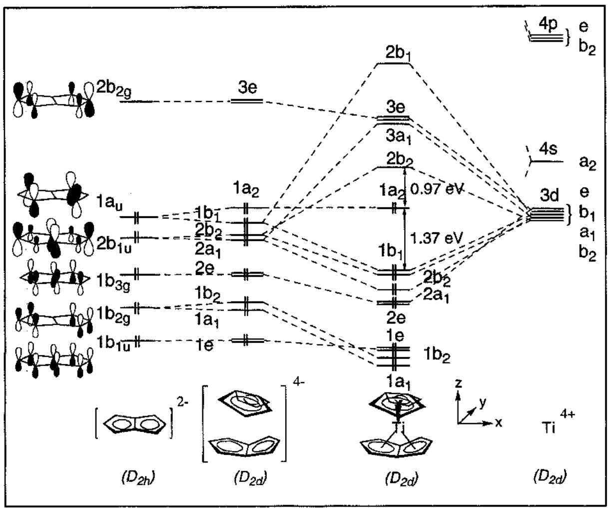


Fig. 2 MO interaction diagram of **2**

the C–C non-bonding $1a_u$ HOMO of $(C_8H_6)^{2-}$ (Fig. 2), there is also little difference between the ligand geometries of **2** and **2**$^{2+}$. The shortening by *ca.* 0.02 Å of the central C–C bond upon oxidation is probably due to the σ/π mixing within the non-planar ligands. The smaller folding of pentalene in **2** and **2**$^{2+}$, as compared to **1**, is consistent with the fact that in the bis-pentalene systems each ligand [$(C_8H_6)^{2-}$ in **2** and $(C_8H_6)^{-}$ in **2**$^{2+}$] is a 9-electron donor whereas in **1** $(C_8H_6)^{2-}$ is a 10-electron donor.

In order to check the possibility of extending the peculiar bonding mode of pentalene in **2** to other ligands, we are currently investigating the electronic structure of hypothetical sandwich complexes of fused conjugated rings such as indacene and naphthalene.

The authors thank the Centre de Ressources Informatiques (CRI) of Rennes and the Institut de Développement et de Ressources en Informatique Scientifique (IDRIS-CNRS) of Orsay for computing facilities.

Notes and References

1 K. Jonas, B. Gabor, R. Mynott, K. Angermund, O. Heinemann and C. Krüger, *Angew. Chem., Int. Ed. Engl.,* 1997, **36**, 1712.

2 K. Jonas, P. Kobl, G. Kollbach, B. Gabor, R. Mynott, K. Angermund, O. Heinemann and C. Krüger, *Angew. Chem., Int. Ed. Engl.,* 1997, **36**, 1714.

3 H. Butenschön, *Angew. Chem., Int. Ed. Engl.,* 1997, **36**, 1695.

4 (*a*) R. Hoffmann, *Angew. Chem., Int. Ed. Engl.,* 1982, **21**, 711; (*b*) T. A. Albright, J. K. Burdett and M.-H. Whangbo, *Orbital Interactions in Chemistry*, John Wiley and Sons, New York, 1984.

5 M. T. Garland, J.-Y. Saillard, I. Chávez, B. Oëclkers and J.-M. Manríquez, *J. Mol. Struct. (THEOCHEM)*, 1997, **390**, 199.

6 (*a*) M. Lacoste, H. Rabaâ, D. Astruc, F. Varret, N. Ardoin, J.-Y. Saillard and A. Le Beuze, *J. Am. Chem. Soc.*, 1990, **112**, 9548; (*b*) H. Rabaâ, M. Lacoste, M.-H. Delville-Desbois, J. Ruiz, B. Gloaguen, N. Ardoin, D. Astruc, A. Le Beuze, J.-Y. Saillard, J. Linares, F. Varret, J.-M. Dance and E. Marquestaut, *Organometallics,* 1995, **14**, 5078; (*c*) M.-H. Delville-Desbois, S. Mross, D. Astruc, J. Linares, F. Varret, H. Rabaâ, A. Le Beuze, J.-Y. Saillard, R. D. Culp, D. A. Atwood and A. H. Cowley, *J. Am. Chem. Soc.*, 1996, **118**, 4133; (*d*) M. T. Garland, J.-Y. Saillard, F. Ogliaro, M. Otero and E. Román, *Inorg. Chim. Acta,* 1997, **257**, 253; (*e*) F. Ogliaro, Thèse de Doctorat de l'Université de Rennes 1, 1997; (*f*) J. Ruiz, F. Ogliaro, J.-Y. Saillard, J.-F. Halet, F. Varret and D. Astruc, *J. Am. Chem. Soc.*, submitted.

7 The calculations were carried out with the ADF program[8] developed by Baerends and coworkers,[9] using non-local exchange and correlation corrections.[10] The standard ADF STO basis set IV, of triple-ζ quality for the valence orbitals (except for the single-ζ 4p orbitals), was used for Ti. The other atoms were treated with the standard basis set III, of double-ζ quality for the valence orbitals. The frozen-core approximation was considered.

8 Amsterdam Density Functional (ADF) program, release 2.3.0, Vrije Universiteit, Amsterdam, Netherlands, 1996.

9 (*a*) E. J. Baerends, D. E. Ellis and P. Ros, *Chem. Phys.,* 1973, **2**, 41; (*b*) E. J. Baerends and P. Ros, *Int. J. Quantum Chem.,* 1978, **S12**, 169; (*c*) P. M. Boerringter, G. te Velde and E. J. Baerends, *Int. J. Quantum Chem.,* 1988, **33**, 87; (*d*) G. te Velde and E. J. Baerends, *Int. J. Quantum Chem.,* 1992, **99**, 84.

10 D. A. Becke, *Phys. Rev. A,* 1988, **38**, 3098; (*b*) J. P. Perdew, *Phys. Rev. B,* 1986, **34**, 8822.

11 Situations somewhat related of pseudo electron-rich complexes with a pure non-bonding ligand HOMO have been reported. See for example (and references therein): (*a*) D. L. Morrison and D. E. Wigley, *Inorg. Chem.*, 1995, **34**, 2610; (*b*) D. L. Morrison, P. M. Rodgers, Y.-W. Chao, M. A. Bruck, C. Grittiny, T. L. Tajima, S. J. Alexander, A. L. Rheingold and D. E. Wigley, *Organometallics,* 1995, **14**, 2435; (*c*) H. Tang, D. M. Hoffman, T. A. Albright, H. Deng and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1616.

12 Extended Hückel calculations give a similar situation, with large gaps above (1.82 eV) and below (1.82 eV) the a_2 HOMO.

Received in Cambridge, UK, 21st July 1998; 8/05682J