J. Am. Chem. Soc. 1994, 116, 8259–8265

Planar Tetracoordinate Carbons in Dimetallic Complexes: Quantum Chemical Investigations

Charles N. Poumbga,[†] Marc Bénard,*,[‡] and Isabella Hyla-Kryspin[§]

Contribution from the Laboratoire de Chimie Quantique, UPR 139 du CNRS, Université Louis Pasteur, F-67000 Strasbourg, France, and Organisch-chemisches Institut der Universität Heidelberg, Im Neuenheimer Feld 270, D-69120 Heidelberg, Germany

Received March 24, 1994[⊛]

Abstract: Extended Hückel (EH) calculations have been carried out on V$_2$(DMP)$_4$ (DMP = dimethoxyphenyl) (**1**) and on [(C$_5$H$_5$)$_2$Zr]$_2$(μ-CH$_3$)(μ-DMP) (**2**). Ab initio Hartree–Fock calculations have been carried out on **1** and on a model complex of **2** with C_{2v} symmetry. In both complexes, the symmetrically bridging DMP ligands are usually considered as examples of planar tetracoordinate carbons (PTCs). Orbital interaction diagrams (from EH calculations) and electron deformation density maps (from ab initio calculations) show that those specific examples of planar tetracoordinate carbons are best represented by the formal electronic structure $\sigma^4\pi^1$. The σ lone pair of the PTC is stabilized through donation interactions toward fragment orbitals delocalized on the two metal atoms. The resulting two-electron, multicenter molecular orbitals have their major weight on the bridging ligands but display metal–metal bonding character. Some π donation, not involving the PTC, is present in **2**, but the π interactions are negligible in **1**. In the complex of (V$_2$)$^{4+}$, the out-of-phase combination of the σ lone pairs of carbons displaces the two metal π electrons in the plane of the PTCs. Those electrons are accommodated in the δ orbital, so the V–V triple bond corresponds to the electronic configuration $\sigma^2\pi^2\delta^2$, not $\sigma^2\pi^4$ as previously assumed.

I. Introduction

Hoffmann and co-workers suggested in 1970 that the seemingly impossible goal of stabilizing a planar tetracoordinate carbon (PTC) was not necessarily out of reach.[1] Achieving a planar conformation for a methane-like molecule implies that no more than two electrons from the carbon atoms are involved in σ-bonding with the four substituents.[1] The carbon therefore behaves in the molecular plane as an electron-deficient species, whereas its two remaining valence electrons occupy the undisturbed, high-lying π orbital. For methane itself, this planar conformation is destabilized with respect to the tetrahedral one by a considerable amount of energy. The strategy designed by Hoffmann and co-workers to reduce and possibly reverse this gap was based on the replacement of the four hydrogens by substituents that are (i) σ donors in order to facilitate the σ electron transfer toward the electron-deficient carbon and (ii) π acceptors in order to delocalize the π lone pair.[1] A systematic exploration of the most appropriate ligands was then carried out along those guidelines by Schleyer et al. by means of MNDO and ab initio calculations.[2] It was pointed out from those investigations that electropositive substituents having a propensity not only to delocalize the π lone pair but also to participate in multicenter σ-bonding are ideally suited to stabilize planar tetracoordinate carbons.[2e] Theoretical and experimental investigations were then successfully carried out on the tetramer of (2,6-dimethoxyphenyl)lithium.[2f]

The recent experimental work of Erker on dinuclear Zr/M complexes (M = Al, B, Ga, Zr) with a planar tetracoordinate carbon[3,4] has revived the interest in those unusual conformations.[5] In a subsequent theoretical work, Gleiter et al. interpreted the stabilization of the PTC in Erker's complexes by the presence of a σ *acceptor* substituent, the d^0 zirconocene fragment (Cp$_2$Zr)$^{2+}$.[6]

The experimental achievements of Erker's group and their interpretation by Gleiter et al. prompted us to investigate in more detail the case of planar tetracoordinate carbons stabilized in transition-metal complexes. In order to analyze more specifically the relationship between PTCs and the metal–metal coupling, we selected for the present study two dinuclear complexes. V$_2$(DMP)$_4$ (**1**, DMP = dimethoxyphenyl), synthesized first in 1976 by Seidel and co-workers,[7] was structurally characterized later by Cotton and Millar.[8] The V–V distance of 2.20 Å is in the range expected for a metal–metal triple bond, but two out of the four DMP ligands are shifted toward a symmetric position with respect to the V–V bond (Figure 1). This unexpected tridentate coordination makes V$_2$(DMP)$_4$ the first structurally characterized compound with PTC atoms. Even though this intriguing molecule is very often referred to in that context[2] and also as an example of a V–V triple bond,[9] no quantum chemical analysis of its electronic structure has been carried out to date. The second molecule investigated in the present work, **2**, has been synthesized and characterized by Buchwald and co-workers.[10] This is a symmetric

---

[†] Laboratoire de Chimie Quantique; on leave from the Université de Yaoundé, Cameroon.

[‡] Laboratoire de Chimie Quantique.

[§] Organisch-chemisches Institut der Universität Heidelberg.

[⊛] Abstract published in *Advance ACS Abstracts*, August 1, 1994.

(1) (a) Hoffmann, R.; Alder, R. W.; Wilcox, C. F., Jr. *J. Am. Chem. Soc.* **1970**, *92*, 4992. (b) Hoffmann, R. *Pure Appl. Chem.* **1971**, *28*, 181.

(2) (a) Collins, J. B.; Dill, J. D.; Jemmis, E. D.; Apeloig, Y.; Schleyer, P. v. R.; Seeger, R.; Pople, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 5419. (b) Krogh-Jespersen, K.; Cremer, D.; Poppinger, D.; Pople, J. A.; Schleyer, P. v. R.; Chandrasekhar, J. *Ibid.* **1979**, *101*, 4843. (c) Krogh-Jespersen, K.; Chandrasekhar, J.; Würthwein, E.-U.; Collins, J. B.; Schleyer, P. v. R. *Ibid.* **1980**, *102*, 2263. (d) Chandrasekhar, J., Würthwein, E.-U.; Schleyer, P. v. R. *Tetrahedron* **1981**, *37*, 921. (e) Chandrasekhar, J.; Schleyer, P. v. R. *J. Chem. Soc., Chem. Commun.* **1981**, 260. (f) Harder, S.; Boersma, J.; Brandsma, L.; van Heteren, A.; Kanters, J. A.; Bauer, W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1988**, *110*, 7802 and references therein.

(3) (a) Erker, G. *Nachr. Chem. Tech. Lab.* **1992**, *40*, 1099. (b) Erker, G. *Comments Inorg. Chem.* **1992**, *13*, 111.

(4) (a) Erker, G.; Zwettler, R.; Krüger, C.; Noe, R.; Werner, S. *J. Am. Chem. Soc.* **1990**, *112*, 9620. (b) Erker, G.; Albrecht, M.; Werner, S.; Nolte, M.; Krüger, C. *Chem. Ber.* **1992**, *125*, 1953. (c) Erker, G.; Albrecht, M.; Krüger, C.; Werner, S. *Organometallics* **1991**, *10*, 3791. (d) Erker, G.; Albrecht, M.; Krüger, C.; Werner, S.; Binger, P.; Langhauser, F. *Ibid.* **1992**, *11*, 3517. (e) Albrecht, M.; Erker, G.; Nolte, M.; Krüger, C. *J. Organomet. Chem.* **1992**, *427*, C1. (f) Erker, G.; Albrecht, M.; Krüger, C.; Werner, S. *J. Am. Chem. Soc.* **1992**, *114*, 8531.

(5) Horton, A. D.; Orpen, A. G. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 876.

(6) Gleiter, R.; Hyla-Kryspin, I.; Niu, S.; Erker, G. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 754.

(7) Seidel, W.; Kreisel, G.; Mennenga, H. *Z. Chem.* **1976**, *16*, 492.

(8) Cotton, F. A.; Millar, M. *J. Am. Chem. Soc.* **1977**, *99*, 7886.

(9) Cotton, F. A.; Walton, R. A. *Multiple Bonds between Metal Atoms*; Wiley: New York, 1982; pp 234–235.

(10) Buchwald, S. L.; Lucas, E. A.; Davis, W. M. *J. Am. Chem. Soc.* **1989**, *111*, 397.

0002-7863/94/1516-8259$04.50/0

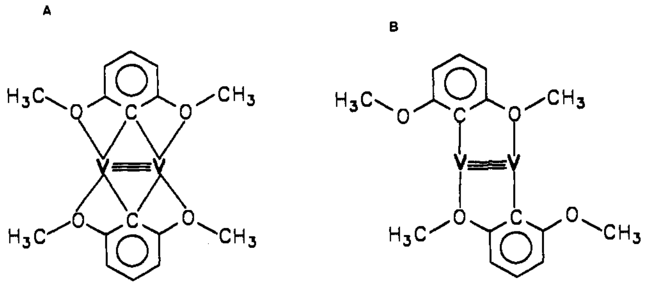


Figure 1. Schematic, partial structures of $V_2(DMP)_4$ (**1**) (A) in the *xz* plane and (B) in the *yz* plane.

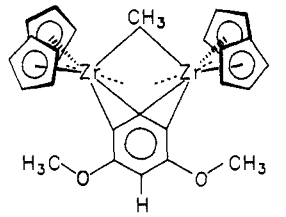


Figure 2. Schematic structure of $[(C_5H_5)_2Zr]_2(\mu\text{-}CH_3)(\mu\text{-}DMP)$ (**2**).

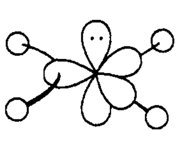
derivative of the zirconocene dimer, bridged by one methyl and one DMP ligand (Figure 2).

II. Computational Details

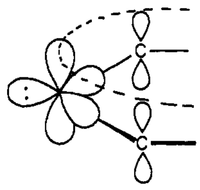
Extended Hückel calculations[11] were carried out, using for H, C, O, V, and Zr parameters taken from previous studies.[11,12] Ab initio SCF calculations were carried out on **1** and on a model of **2** in which the bridging methyl ligand was replaced by a chlorine atom in order to take advantage from a perfect C_{2v} symmetry. The ab initio calculations were performed by means of the ASTERIX program system[13] on Cray-2 and Cray C98 computers. Basis sets optimized by Huzinaga[14] for H (4s), C and O (9s, 5p), and Cl (11s, 7p) were contracted to split valence. The (13s, 7p, 5d) basis set optimized by Hyla-Kryspin and co-workers[15] for vanadium was augmented with one p function (exp 0.15) describing the 4p shell and one diffuse d function (exp 0.07) and contracted to (5s, 3p, 3d). We used for zirconium the (15s, 9p, 8d) basis set optimized by Dedieu and Veillard,[16] augmented with one p function (exp 0.12) and contracted to (6s, 4p, 4d). A proper description of the metal d valence orbitals in $V_2(DMP)_4$ was obtained by optimizing the V–V bonding molecular orbitals (MOs) and their antibonding counterparts by means of an open-shell SCF calculation carried out on the septet state $\sigma^1\pi^1\delta^1\delta^{*1}\pi^{*1}\delta^{*1}$. Using those orbitals, the ground-state configuration was obtained by coupling the six metal electrons into a singlet A_1 state. The natural orbital analysis of the $^1A_1$ ground state corresponds to $\sigma^{1.32}\pi^{1.30}\delta^{1.09}\delta^{*0.91}\pi^{*0.70}\sigma^{*0.68}$.

III. Results and Discussion

III.1. PTCs in DMPs. The planar tetracoordinate carbons characterized in complexes **1** and **2** share a common character: the formal distribution of electrons in the four hybrid orbitals of carbon appears strikingly different from the one described by Hoffmann in the case of planar methane.[1] The PTCs belong to the aromatic ring of a DMP ligand. The structural information suggests that the aromatic character of the DMP cycles is not significantly modified in either complex. In both molecules, the



planar methane

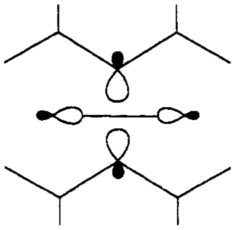


DMP ligand

C–C bonds involving a PTC have an average bond length of 1.392 Å.[8,10] In spite of a slight move of the bridging carbon atom toward the center of the ring,[10] those data suggest that neither the C–C σ bonds nor the π bonds are appreciably modified with respect to an isolated DMP molecule. This assumption is verified by the calculations reported in the present work. At variance from the electronic structure of the PTC in planar methane, the PTC in the DMP ligand displays a π orbital populated with a *single* electron. This π orbital as well as the two sp^2 hybrids giving rise to the C–C σ bonds is obviously quite stable. Since the donor carbon atom of the DMP ligand (the PTC) is considered as formally bearing a minus charge, the third sp^2 hybrid is populated with *two* electrons. This orbital is the only one to be high in energy. What is now left is to explain the stabilization of this orbital from its interactions with both neighboring metal atoms.

III.2. $V_2(DMP)_4$. Orbital interaction diagrams obtained from extended Hückel calculations are displayed in Figure 3 for $V_2(DMP)_4$ for (i) the conformation characterized experimentally, displaying two PTC atoms (right-hand side), and (ii) a hypothetic conformation in which all four DMP ligands are linked asymmetrically to the divanadium fragment, as in the equivalent complex of $[Cr_2]^{4+}$ (left-hand side). The orbital diagram corresponding to this latter conformation generates the well-known sequence of orbitals $\sigma < \pi < \delta < \delta^* < \pi^* < \sigma^*$, which leads to the metal–metal quadruple bond when applied to d^8 metal dimers.[9] The four combinations of the DMP σ lone pairs are stabilized by donation interactions to the δ and δ^* combinations of the metal $d_{x^2-y^2}$ orbitals and to low-lying combinations, both bonding and antibonding with respect to divanadium, of the metal 4s orbitals. The six metal electrons are accommodated in the σ and the degenerate π orbitals, giving rise to a V–V triple bond with $\sigma^2\pi^4$ electronic configuration.

Let us now shift to the right-hand side of the orbital diagram, describing the orbital interactions in the complex in its experimental conformation as displayed in Figure 1. It will be assumed in the following discussion, as in Figure 3, that the planar tetracoordinate carbons are lying along the *x* axis, whereas the metal atoms define the *z* direction. Two lone pair combinations, with symmetry b_u and a_g, are associated with the DMP ligands coordinated in the standard, nonsymmetric fashion. As in the former case, those two combinations are stabilized by means of a donation toward the metal $d_{x^2-y^2}$ orbitals. The two other lone pair combinations ($1a_g$ and a_u) are provided by the planar tetracoordinate carbons. The in-phase combination is stabilized by 0.9 eV from a donation interaction toward the low-lying σ level, mainly composed of the $4s/4p_z$ metal orbitals:



The most unexpected result, which explains the stabilization of

---

(11) (a) Hoffmann, R.; Lipscomb, W. N. *J. Chem. Phys.* **1962**, *36*, 2179, 3489; **1962**, *37*, 2872. (b) Hoffmann, R. *Ibid.* **1963**, *39*, 1397.

(12) (a) Tremel, W.; Hoffmann, R.; Jemmis, E. D. *Inorg. Chem.* **1989**, *28*, 1213. (b) Tatsumi, K.; Nakamura, A.; Hoffman, P.; Stauffert, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1985**, *107*, 4440.

(13) (a) Ernenwein, R.; Rohmer, M.-M.; Bénard, M. *Comput. Phys. Commun.* **1990**, *58*, 305. (b) Rohmer, M.-M.; Demuynck, J.; Bénard, M.; Wiest, R.; Bachmann, C.; Henriet, C.; Ernenwein, R. *Ibid.* **1990**, *60*, 127. (c) Wiest, R.; Demuynck, J.; Bénard, M.; Rohmer, M.-M.; Ernenwein, R. *Ibid.* **1991**, *62*, 107.

(14) (a) Huzinaga, S. Approximate Atomic Functions. Technical Report; University of Alberta: Alberta, Canada, 1971. (b) Huzinaga, S.; McWilliams, D.; Domsky, B. *J. Chem. Phys.* **1971**, *54*, 2283.

(15) Hyla-Kryspin, I.; Demuynck, J.; Strich, A.; Bénard, M. *J. Chem. Phys.* **1981**, *75*, 3954.

(16) Veillard, A.; Dedieu, A. *Theor. Chim. Acta* **1984**, *65*, 215.

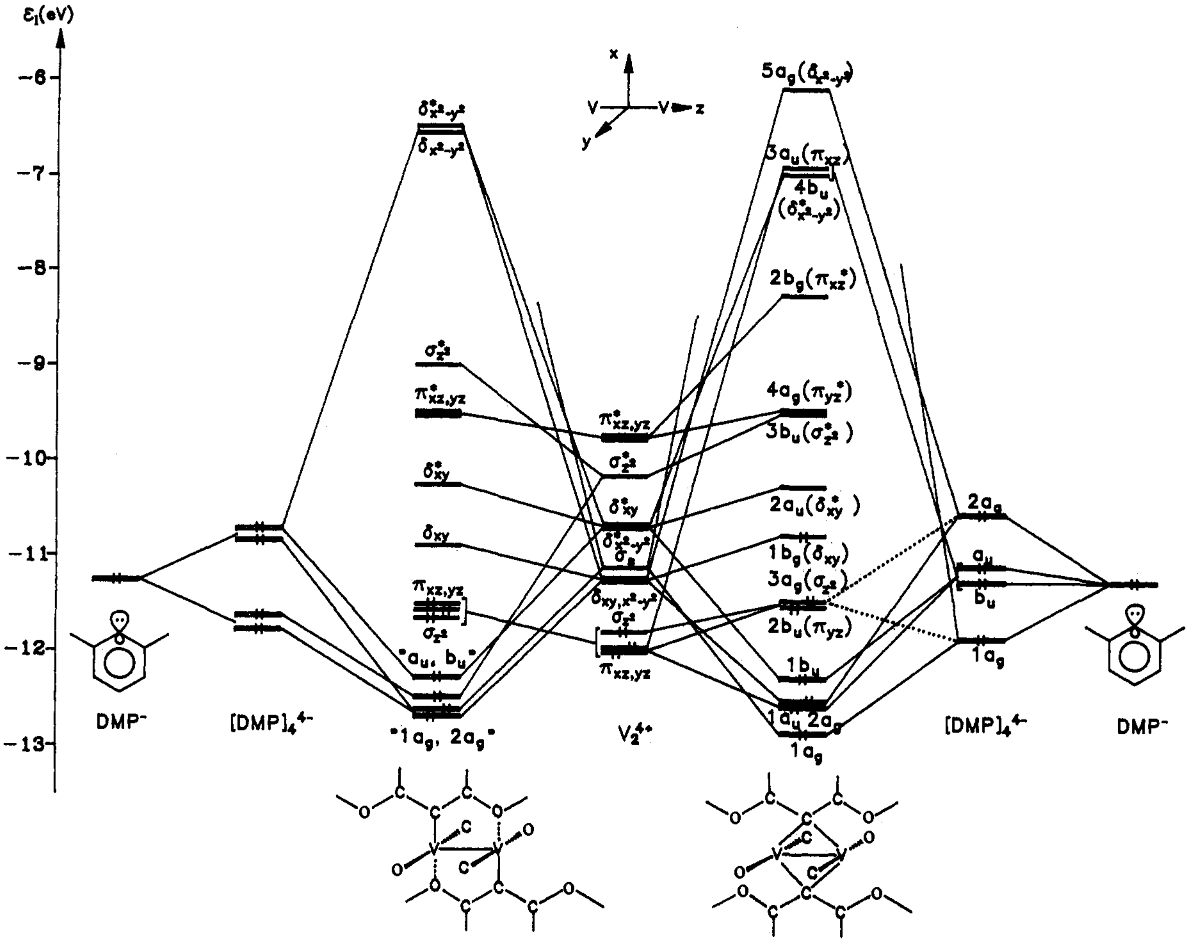


Figure 3. Orbital interaction diagram for $V_2(DMP)_4$ from extended Hückel calculations. Right-hand side: conformation with two planar tetracoordinate carbons, as characterized experimentally. Left-hand side: conformation without planar tetracoordinate carbon.

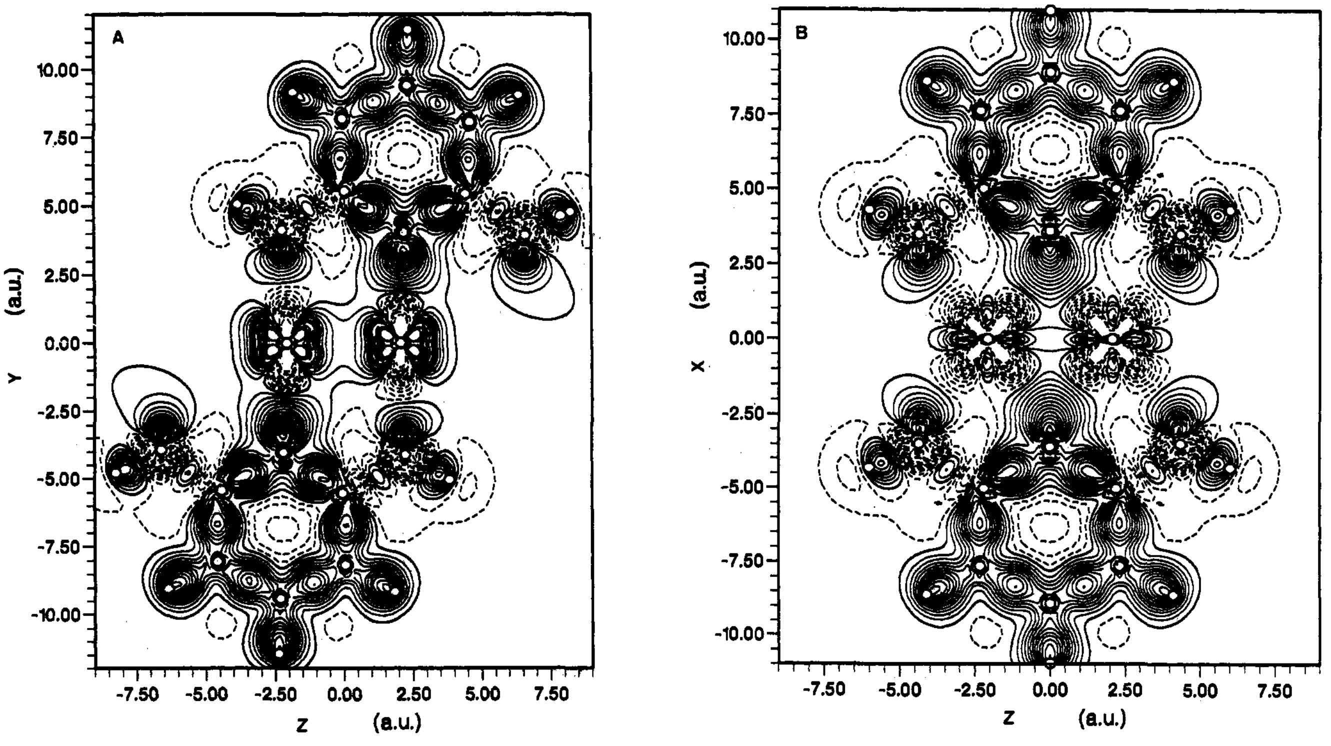
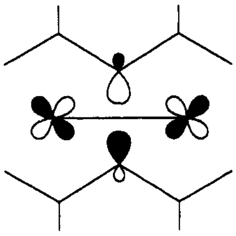


Figure 4. Deformation density maps obtained by subtracting from the molecular density computed for the singlet ground state the density generated by a superposition of neutral, spherical atoms. (A) Plane containing the asymmetrically bridged DMP ligands. (B) Plane containing the planar tetracoordinate carbons. Bold line for zero contour, solid lines for positive contours (electron accumulation), dotted lines for negative contours (electron depletion). Contour interval, 0.05 e·Å^{-3}.

the PTCs in this molecule, concerns the out-of-phase combination (a_u) of the carbon lone pairs. Those two lobes with opposite signs facing each other undergo a large stabilization interaction (1.5 eV) from the dimetal π_{xz} orbital lying in the same plane:



The resulting MO ($1a_u$) retains predominant ligand character, and, consequently, the dimetal π_{xz} orbital, as the destabilized term of the interaction, is rejected very high in energy, still higher than its metal–metal antibonding counterpart π^*_{xz} (orbital $2b_g$, Figure 3). This has an immediate consequence on the nature of the metal–metal bond: there is no more than one π orbital, located in the plane devoid of PTCs, remaining to accommodate the metal electrons. The six metal electrons will therefore populate that π_{yz} level ($2b_u$), then the σ orbital $3a_g$, and finally the MO next in energy, which happens to be the δ-bonding combination of the d_{xy} orbitals ($1b_g$). The vanadium–vanadium bond in this complex is indeed a triple bond, as predicted by Cotton and Millar,[8] but a triple bond corresponding to the electronic configuration $\sigma^2\pi^2\delta^2$, definitely nonsymmetric around the V–V axis.

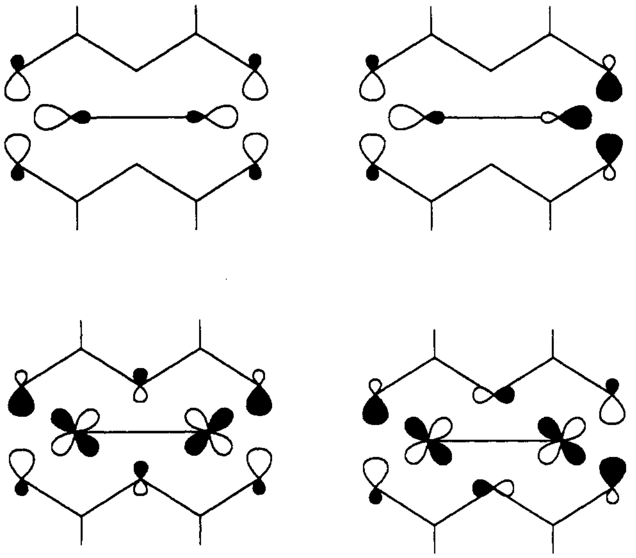
This dissymmetry of the metal–metal bond receives a straightforward illustration from the deformation density maps computed from the ab initio wave function derived for the $^1A_1$ ground state (Figure 4). The *yz* plane, devoid of PTCs, displays a relative excess of electron density (with respect to the population of the neutral, spherically averaged atom) in the region of the metal π orbitals. The equivalent region in the *xz* plane containing the PTCs is characterized by a relative *deficit* of electron density, illustrating the lack of metal π-bonding in this plane. *Considering the electronic structure of complex **1**, the metal π_{xz} combination behaves with respect to the PTC lone pairs as an empty, acceptor orbital.*

What about the planar tetracoordinate carbons? The same maps of deformation density show that the charge distribution is strikingly similar in all four DMP rings (Figure 4). This is confirmed by the Mulliken population analysis. The PTC is therefore characterized by three sp^2 hybrids quite similar to those of the donor carbon of a "standard" DMP ligand. In the standard ligand, the hybrid formally bearing the lone pair is directed toward the empty $d_{x^2-y^2}$ orbital of a specific metal atom. In the case of planar tetracoordination, the same hybrid is pointing toward the center of empty orbital combinations belonging to the dimetal fragment and susceptible to interact. One of those orbitals, the $4s/4p_z$ metal bonding combination, is already unoccupied in the $(V_2)^{4+}$ fragment.[17] The other metal orbital in position to interact, π_{xz}, is doubly occupied in $(V_2)^{4+}$ but becomes formally empty in **1** as a consequence of the stabilization of the PTC lone pair combination with proper symmetry. *In both cases, the dimetal entity therefore acts as a σ acceptor.*

The π interactions are at the limit of significancy. A slight destabilization of the remaining π metal orbital is observed with respect to the isolated V_2 fragment and should be attributed to a four-electron interaction with the in-phase combination of the PTC π orbitals. The out-of-phase combination of the same π orbitals yields a similar rise of the δ HOMO.

What would then happen if all four DMP ligands were symmetrically bridging, giving the molecule a conformation with D_{4h} symmetry and four planar tetracoordinate carbons? Interactions similar to those previously described would then occur also in the perpendicular plane, destabilizing the second metal–metal π level. Deprived of this level, the metal electrons would occupy the orbital next to the σ and δ levels, which is the δ^* combination of the d_{xy} orbitals. The metal–metal coupling would be formally described as a single σ bond. Even though several frontier orbitals with predominant ligand character would retain an important V–V bonding contribution, such a change in the formal electronic structure would yield an important stretching of the metal–metal bond. Ab initio calculations indicate that such a structure with D_{4h} symmetry would be largely destabilized with respect to the experimental one.

The reason why the experimental structure is favored with respect to the conformation without PTC is not so clear-cut. The energy balance in the set of frontier orbitals is not in favor of the experimental form due to the high energy of the δ orbital (Figure 3). A close examination of the underlying orbitals in the *xz* plane, however, indicates that all four oxygen lone pair combinations of the methoxy substituents receive stabilization from the following interactions:



If we consider the asymmetric complexation of the DMP ligands, two methoxy lone pairs only are stabilized in each ligand plane. The existence of planar tetracoordinate carbons in $V_2(DMP)_4$ should then be ascribed to the participation of both methoxy substituents to the donation interactions in the symmetrically bridged DMPs, compatible with the preservation of a metal–metal triple bond.

We are presently planning a joint experimental/theoretical study in order to investigate in more detail the electron deformation density distribution of the divanadium complex.

III.3. $(C_5H_5)_2Zr(\mu\text{-}CH_3)[\mu\text{-}C_6H(OCH_3)_2]Zr(C_5H_5)_2$. As in the divanadium complex, the PTC in this molecule is part of a dimethoxyphenyl ring, but in the present case, the methoxy substituents are in β position. The carbons in α position with respect to the PTC (α-carbons) are standard σ donors, connected each to one specific zirconium atom (Figure 2). Formally, the DMP ligand is therefore $(DMP)^{3-}$, and the metal in both zirconocene fragments is d^0, as in Erker's complexes.[4,6] Due to the presence of the bridging CH_3 ligand, the complex has only one plane of symmetry. If this plane is considered perpendicular to the DMP ring, the CH_3 ligand provides no more than a small perturbation to the σ/π separation, and a C_{2v} symmetry will be assumed for the analysis of the interaction diagram (Figure 5).

The interaction diagram is slightly more complex in this molecule, since the $(DMP)^{3-}$ ligand, with three σ donor carbon atoms, displays three frontier orbitals in the σ plane, occupied

---

[17] This interaction with the $4s/4p_z$ *bonding* combination of divanadium contributes to strengthen the metal–metal bonding character of the wave function and may provide some compensation to the loss of one π interaction.

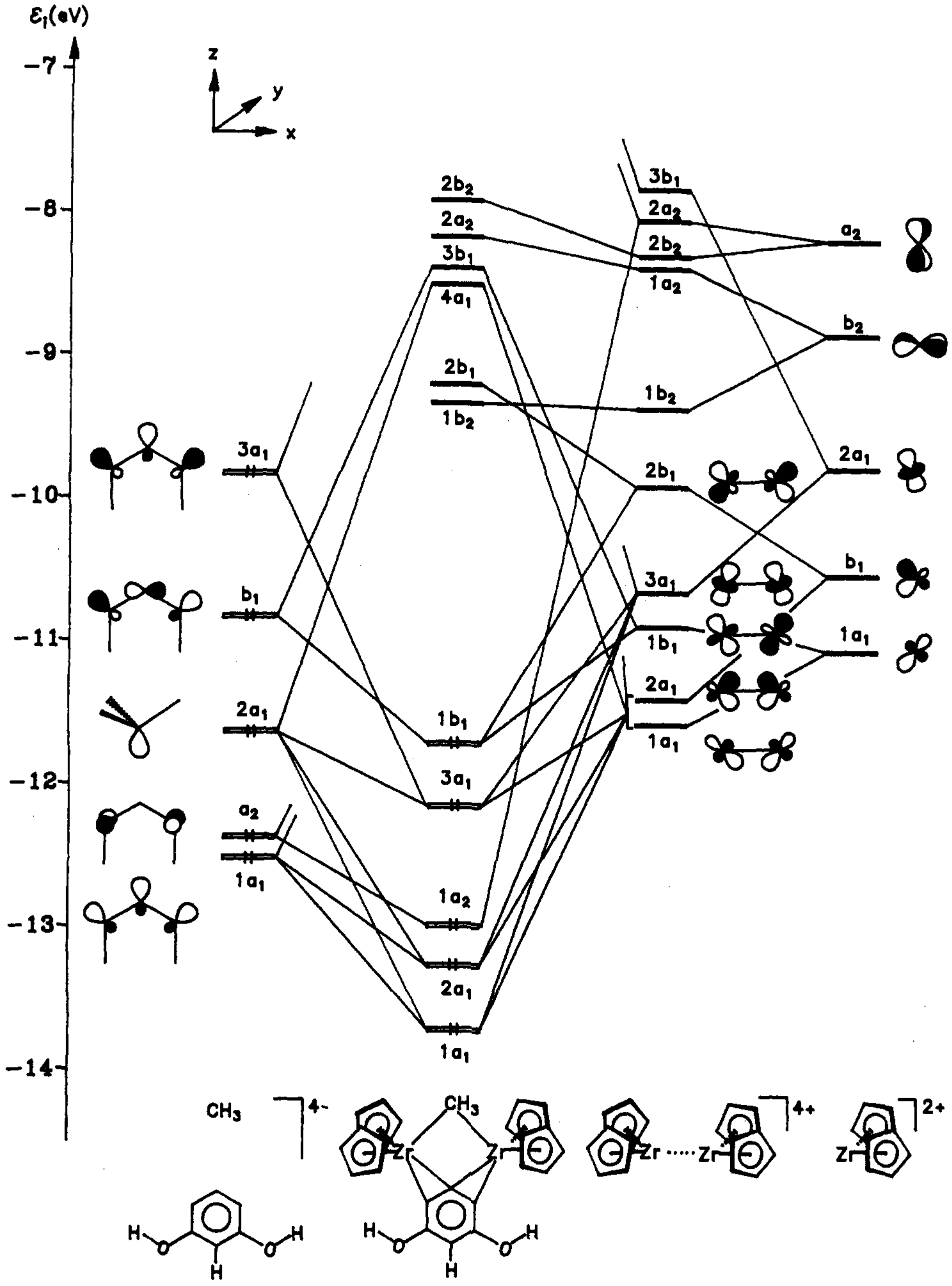


Figure 5. Orbital interaction diagram for $(Cp_2Zr)_2(\mu\text{-}CH_3)(\mu\text{-DMP})$ from extended Hückel calculations. The levels with major Cp character have been omitted for clarity.

each with two electrons. The in-phase and out-of-phase combinations of the three carbon σ orbitals give rise to two fragment orbitals with a_1 symmetry at -12.5 and -9.8 eV, respectively. A nonbonding combination with b_1 symmetry is obtained at -10.8 eV. The orbital accommodating the lone pair of the CH_3 bridging ligand (-11.7 eV) and the occupied π orbital of DMP localized on the α-carbons are also taking part in the most important interactions.

The fragment orbitals of the $ZrCp_2$ dimer derive from the standard frontier levels of metallocene.[18] In spite of the large metal–metal distance (3.515 Å), the combinations in the dimer are characterized by an important splitting and mixing of the MCp_2 orbitals. It has been shown elsewhere that the d valence shell of zirconium retains nonnegligible overlap even at very large distances.[19] Since the metal is formally d^0 in the present complex, none of the 10 metal orbitals of the zirconocene dimer is occupied.

In spite of the relatively high energy of the DMP HOMO (Figure 5), *none of the resulting molecular orbitals has more than 30% metal character.* In agreement with the formal electron count, the zirconium dimer acts as a σ acceptor and also as a π acceptor. The π acceptor character is illustrated by the stabilization (0.65 eV) of the ligand π orbital mainly localized on the α-carbons through an interaction with the metal δ^* combination (d_{yz}–d_{yz}). However, most of the stabilization originates in donation interactions occurring in the σ plane. To understand those interactions, it is important to notice that the Cp centroids Ω do not project along the metal–metal axis. The angle between the Zr–Zr axis and the Zr–Ω lines projected in the molecular plane is close to 160°, and the projected Zr–Ω lines approximately bisect the $C\alpha$–Zr–CH_3 angles (Figure 2). This tilting affects the standard orbitals of the metallocene fragment, along with their bonding and antibonding combinations in the

---

[18] (a) Albright, T. A.; Burdett, J. K.; Whangbo, M. H. *Orbital Interactions in Chemistry*; Wiley: New York, 1985. (b) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729.

[19] (a) Rohmer, M.-M.; Bénard, M. *Organometallics* **1991**, *10*, 157. (b) Bénard, M.; Rohmer, M.-M. *J. Am. Chem. Soc.* **1992**, *114*, 4785. (c) DeKock, R. L.; Peterson, M. A.; Reynolds, L. E. L.; Chen, L.-H.; Baerends, E. J.; Vernooijs, P. *Organometallics* **1993**, *12*, 2794.

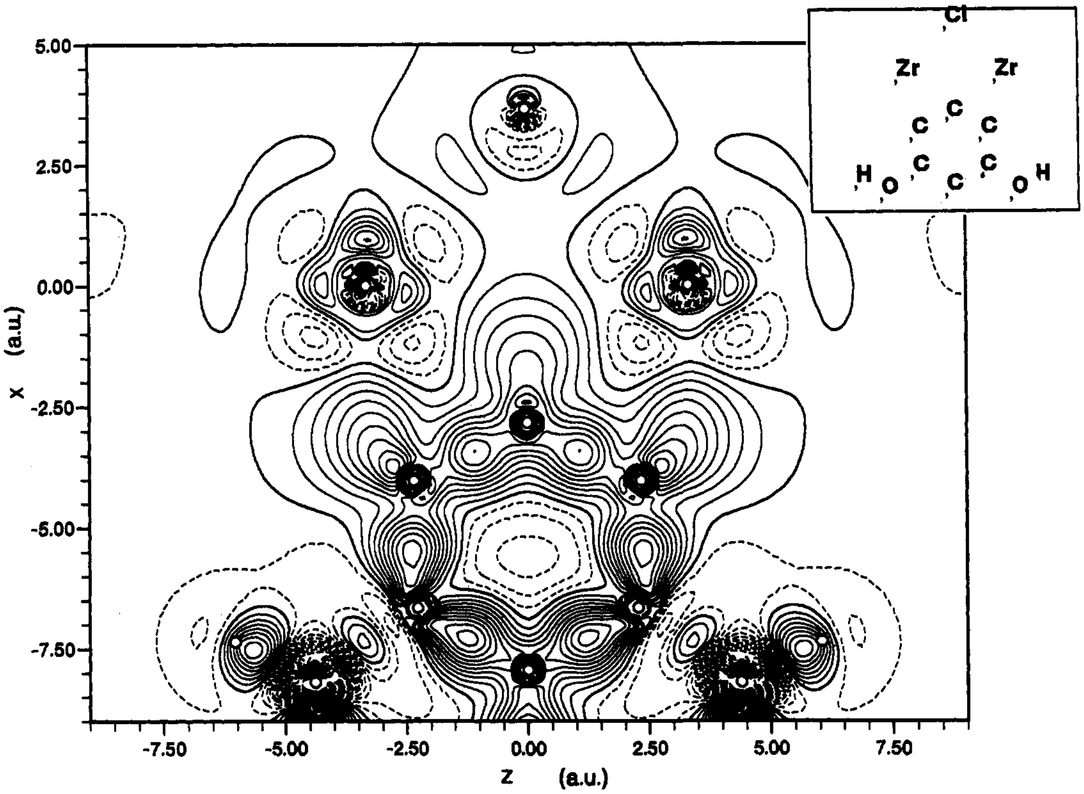


Figure 6. Electron deformation density computed in the molecular plane of the model system $(Cp_2Zr)_2(\mu\text{-Cl})(\mu\text{-DMP})$. Contours as in Figure 4.

zirconocene dimer. More specifically, the dimer orbital lowest in energy is shaped as the σ-bonding orbital characteristic of a bent metal–metal bond.[20] This fragment orbital is best suited to interact with the lone pair orbital of the planar tetracoordinate carbon, which contributes to both the in-phase and the out-of-phase ligand orbitals with a_1 symmetry (Figure 5). As in the divanadium complex, the PTC is stabilized by a donation from the carbon lone pair toward an empty metal–metal bonding orbital. It is interesting to notice that in both cases, the carbon–dimetal interaction is enhanced because the three overlapping lobes are pointing toward the inner part of the M–C–M triangle.

The in-phase lobes of the dimetal orbital next in energy are pointing toward the lone pair of the bridging methyl ligand (Figure 5). The resulting molecular orbital, still belonging to the a_1 representation, also receives some stabilizing contribution from the two DMP frontier orbitals with same symmetry. At −12.3 eV, a third molecular orbital with a_1 symmetry appears as a mixture of the bridging methyl lone pair with the out-of-phase σ orbitals of DMP, stabilized from an interaction with the M–M bonding combinations of the zirconocene dimer. The nonbonding DMP orbital, with b_1 symmetry, mainly centered on the α-carbons, is stabilized through an interaction with the two lowest dimetal orbitals of proper symmetry, that is, with Zr–Zr antibonding character.

The interaction diagram appears somewhat complex because three stabilizing interactions occur within the same irreducible representation a_1, giving rise to intricate mixing. To summarize, the five frontier orbitals of the bridging ligands are shifted altogether to low energies through σ and π donation interactions toward the metal orbitals of the zirconium dimer. Three interactions out of four occurring in the plane of the molecule involve zirconium orbitals with Zr–Zr bonding character. As a consequence, the map of electron deformation density plotted from the ab initio SCF wave function (Figure 6) displays some character of a metal–metal bent bond with an accumulation of density inside the triangle defined by the metal atoms and the planar tetracoordinate carbon.

A comparison between the deformation density maps computed for the divanadium and those for the dizirconium complexes shows that the electron distribution in the region of σ donation appears much more diffuse in the dizirconium complex than in the divanadium one. This should be attributed first to the polarizability of the d valence shell of zirconium and to the propensity of those d orbitals to generate important bonding overlaps even at large distance.[19] The second reason for electron delocalization in the $(DMP)^{3-}$ bridging ligand is the presence of three contiguous centers for σ donation. The mixing that occurs between the three DMP orbitals belonging to the a_1 symmetry eventually results in a predominance of the in-phase contribution and therefore to a spreading of the electron density along the three donor carbons.

IV. Conclusion

Extended Hückel and ab initio Hartree–Fock and CI calculations have been carried out on two dimetallic complexes of transition metals with one or two dimethoxyphenyl (DMP) ligands in a symmetrically bridging conformation. In those complexes, the DMP carbon atoms symmetrically coordinated to the dimetallic unit are generally considered as examples of planar tetracoordinate carbons (PTCs). It is shown that the scheme designed and successfully investigated by Hoffmann and coworkers[1] and by Schleyer et al.[2] for stabilizing a planar carbon in a $\sigma^2\pi^2$ electronic configuration is not adequate to describe the present molecules. The PTC carbon in a bridging DMP ligand should be formally described as $\sigma^4\pi^1$, with a σ lone pair pointing toward the center of the metal–metal axis. The lone pair is stabilized through donation interactions to orbital combinations delocalized on the two metal atoms. The acceptor orbitals are metal–metal π- and σ-bonding MOs in $V_2(DMP)_4$ (**1**), which contains two planar tetracoordinate carbons, and the fragment orbital characteristic of a bent metal–metal bond in $(Cp_2Zr)_2(\mu\text{-CH}_3)(\mu\text{-DMP})$ (**2**). Formal electron counting ascribes the zirconium dimer to be d^0, and donation interactions in the plane

---

[20] Teo, B. K.; Hall, M. B.; Fenske, R. F.; Dahl, L. F. *Inorg. Chem.* **1975**, *14*, 3103.

of the molecule delocalize the lone pairs of the PTC and of the adjacent carbons into d orbitals with predominant metal–metal bonding character. π donation, mainly originating in the α-carbons, is also present in complex **2**, but not in **1**. In the vanadium dimer, the most important donation interaction, originating in the symmetrically bridged DMP ligands, involves the V–V π orbital lying in the plane of those ligands. This orbital is doubly occupied in the standard description of the $(V_2)^{4+}$ fragment. In complex **1**, the two metal π electrons accommodated on that level are therefore displaced toward the metal orbital next in energy, that is, the δ bonding orbital. The metal–metal triple bond assumed from the short observed V–V distance (2.20 Å) therefore corresponds to the electronic configuration $\sigma^2\pi^2\delta^2$. Proper correlation of the six d metal electrons yields the natural orbital distribution $\sigma^{1.32}\pi^{1.30}\delta^{1.09}\delta^{*0.91}\pi^{*0.70}\sigma^{*0.68}$, in agreement with the usual description of metal–metal multiple bonds.[9,21]

Acknowledgment. Calculations were carried out in part on the Cray-2 computer of the Centre de Calcul Vectoriel de la Recherche (CCVR) and in part of the Cray C98 computer of the Institut de Développement et de Ressources en Informatique Scientifique (IDRIS).

---

(21) (a) Wiest, R.; Strich, A.; Bénard, M. *New J. Chem.* **1991**, *15*, 801 and references therein. (b) Mougenot, P.; Demuynck, J.; Bénard, M.; Bauschlicher, C. W., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 4503. (c) Poumbga, C.; Daniel, C.; Bénard, M. *Ibid.* **1991**, *113*, 1090.