# Quantum-Chemical Investigations of Stabilizing Interactions in $\mu$-Diborylcarbene Dicobalt Complexes with a Planar Tetracoordinate Carbon Atom

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*Dedicated to Professor Gerhard Herberich on the occasion of his 60th birthday*

**Abstract**: Quantum-chemical methods have been employed to study the nature of stabilization in dinuclear cobalt complexes of the general formula $[\{(C_5H_5)Co\}_2(\mu\text{-}CR^1_2BCBR^2R^3)]$ (**6**) as well as the "anti-van't Hoff–Le Bel" configuration of the planar tetracoordinate carbon (ptC) atom of the bridging diborylcarbene ligand **9**. Extended Hückel and ab initio Hartree–Fock calculations have been carried out for the model compounds **6b** ($R^1 = R^2 = R^3 = H$) and **6c** ($R^1 = R^2 = H$; $R^3 = C_6H_5$). Ab initio electron deformation density maps and natural population analysis calculations show that complexes **6** are stabilized through push–pull effects by which the ptC experiences $\pi$ electron density delocalization and $\sigma$ electron density accumulation. The calculated electronic configuration of the ptC in the free ligand **9b** is $\sigma^{2.978}\pi^{1.501}$, and in **6b** $\sigma^{3.944}\pi^{1.356}$. Electron density donation from one cobalt atom to an aryl group on the bridging ligand further contributes to the stabilization of the complexes **6**.

**Keywords**
ab initio calculations · cobalt · planar carbon

## Introduction

In 1970 Hoffmann et al.[1] suggested that the seemingly impossible goal of stabilizing a planar tetracoordinate carbon (ptC) is not necessarily out of reach. One strategy for stabilizing molecules with "anti-van't Hoff–Le Bel" configuration[2] is based on consideration of steric effects on the structure of the chemical species. The idea of incorporating the carbon atom into a strained polycyclic environment[1, 3] has inspired many theoretical[4, 5] and experimental studies.[5, 6] However, for fenestranes and bowlanes, the most likely candidates, both theory and experiment point to pyramidal rather than planar geometry of the bridgehead carbon atom.[4–6] Exciting predictions about the possible existence of strained compounds with a ptC have been made for a new class of neutral, saturated hydrocarbons, the alkaplanes.[4j, 4l] Recently, molecules of this type were identified theoretically by Radom as the first stable hydrocarbons containing a ptC.[4n]

Another strategy for stabilizing a ptC is based on the qualitative analysis of the electronic structure of planar methane.[1] Here, only two electrons from the carbon atom are involved in $\sigma$ bonds with the four hydrogen atoms; the two remaining valence electrons occupy an undisturbed, high-lying 2p$\pi$ orbital (Figure 1). Therefore, the ptC forms a three-center $\sigma$ bond in the molecular plane and is an electron-poor center. The planar

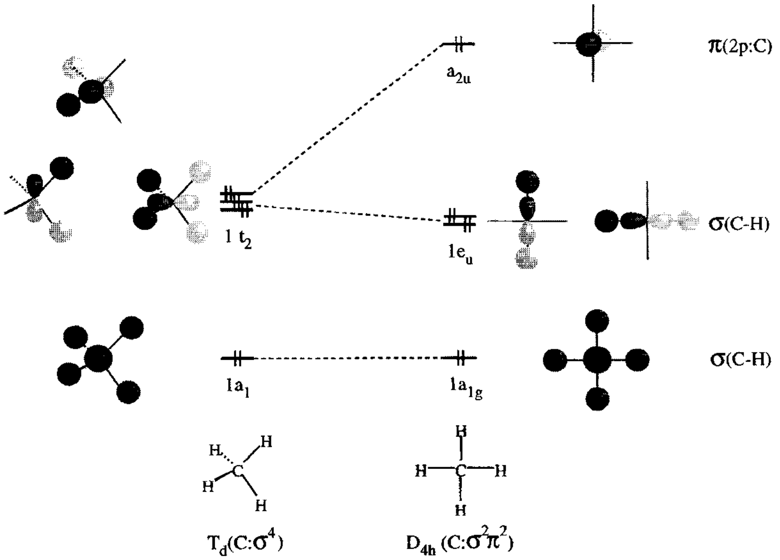

Figure 1. Electronic structures of tetrahedral ($T_d$) and planar ($D_{4h}$) methane.

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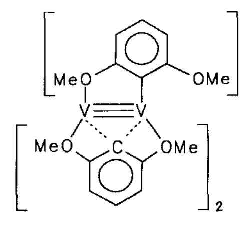
conformation of methane is destabilized with respect to the tetrahedral one by a considerable amount of energy and is thus not a viable species.[1,7] To reduce and possibly reverse this energy gap, Hoffmann et al.[1] suggested the replacement of the four hydrogen atoms by substituents that are in-plane $\sigma$ donors and out-of-plane $\pi$ acceptors in order to facilitate the $\sigma$ electron density transfer toward the electron-poor carbon and to delocalize the carbon 2p$\pi$ lone pair.

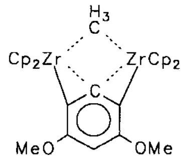
The simplest molecule containing a ptC is the methane dication $CH_4^{2+}$. This often overlooked example[8a] has been experimentally observed in the gas phase.[8b,c] A comparison of the measured and calculated vertical ionization energies of $CH_4^{2+}$ shows that the "anti-van't Hoff–Le Bel" isomer is indeed formed upon charge stripping from the methane monocation.[9a] High-level ab initio calculations indicate that the structure corresponding to a global minimum on the potential energy surface does not have $D_{4h}$ but rather $C_{2v}$ symmetry, with two long and two short C–H bonds.[9b] Thus, the methane dication can best be described as a complex between $CH_2^{2+}$ and molecular hydrogen, which is held together by a 3c–2e donor–acceptor interaction. These findings suggest that delocalization of electron density from the carbon 2p$\pi$ orbital could be sufficient for stabilizing the planar arrangement in neutral molecules, since the $\sigma$ electron density distribution in $CH_4^{2+}$ is similar to that in planar methane.

A systematic investigation of the barrier to planarization has been carried out by Schleyer et al.[10] for an extensive set of simple model compounds by means of MNDO and ab initio calculations. These studies pointed out that electropositive substituents such as Li or B, which are not only well-suited to participation in three-center bonding but also to delocalization of the carbon 2p$\pi$ lone pair, are particularly effective in stabilizing the planar arrangement.[10a] This was computationally confirmed for 1,1-dilithiocyclopropane and dimeric phenyllithium derivatives,[10a] a result that attracted attention for the synthesis of such species.[11] In spite of all efforts, neither organic nor organolithium/boron molecules with "anti- van't Hoff–Le Bel" configuration have been found. Carbon atoms can easily form more than four connectivities to surrounding groups or atoms,[12] but in the case of four substituents it is rather difficult for them to adopt anything other than tetrahedral geometry. However, in the last years, reports of experimentally verified organometallic compounds incorporating a ptC atom have been accumulating.[13–17]

Complexes **1**–**5** are similar in that the ptC is part of a $\pi$ system, and one can expect that the formal distribution of electrons in the four hybrid orbitals of the ptC will be different from that of planar methane. On the basis of ab initio and extended Hückel calculations Gleiter et al.[16j,18] interpreted the stabilization of the ptC in complexes **4** in terms of the presence of a $\sigma$-acceptor substituent, the $d^0$ zirconocene moiety. They pointed out that delocalization of the $\pi$ electron density of the ptC plays essentially no role. Similar conclusions were reached on the basis of extended Hückel, ab initio Hartree–Fock, and CI calculations carried out by Bénard et al. for complexes **1** and **2**.[19] It was shown from these investigations that the strategy designed by Hoffmann et al. and successfully investigated by Schleyer et al. for stabilizing a ptC in a $\sigma^2\pi^2$ electronic configuration is not adequate for ptC incorporated into an aryl ligand $\pi$ system. The ptC in the bridging dimethoxyphenyl ligand, formally bearing a minus charge, has a $\sigma^4\pi^1$ configuration; the planar geometry is stabilized through $\sigma$ donation into empty metal d orbitals with predominantly metal–metal bonding character.



**1**



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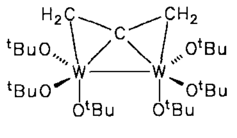

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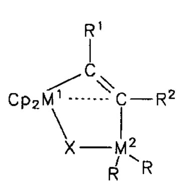
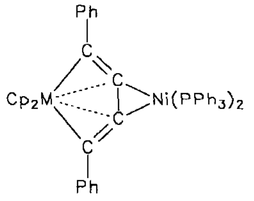
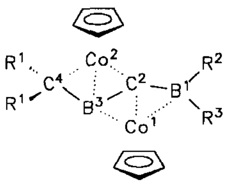


**4** $M^1$=Zr,Hf
$M^2$=B,Al,Ga



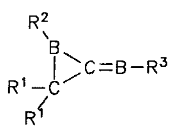
**5** M=Ti,Zr

Recently, Siebert et al.[20] synthesized the dinuclear complex **6a**, which has a ptC incorporated in the bridging ligand, by the reaction of the boriranylideneborane **8a** with $[Co(C_5H_5)(C_2H_4)_2]$. The nonclassical structure of boriranylideneboranes **8**[21] (the classical formulation is **7**) was predicted by quantum-chemical calculations[22] years before proof was provided by an X-ray structure determination of **8d**.[23] During the formation of **6a** a duryl group migrates from one boron to the other and cleavage of the C–C bond in the three-membered ring of **8a** occurs. In **6a** the boriranylideneborane **8a** has been transformed into the chain form **9a**, which can be viewed as the first example of a complex-stabilized diborylcarbene ligand. In **6a** the C-B-C-B chain and the two cobalt atoms lie in exactly the same plane. In the present study we describe the factors that are responsible for the stabilization of complexes **6** as well as the planar arrangement of the C2 carbon atom of the bridging diborylcarbene ligand.



a: $R^1$=SiMe$_3$; $R^2$=$R^3$=2,3,5,6-$C_6HMe_4$ (Dur)
b: $R^1$=$R^2$=$R^3$=H
c: $R^1$=$R^2$=H; $R^3$=$C_6H_5$
d: $R^1$=GeMe$_3$; $R^2$=$R^3$=Dur

**6**



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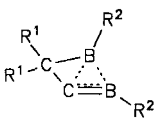

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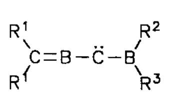

**9**

## Computational Details

Ab initio calculations were carried out by using the Gaussian 94 [24] and Asterix [25] system of programs. Two basis sets (BS) were adapted throughout the studies. The natural population analysis [26] was calculated with BS 1 and the electron deformation density maps were computed with BS 2. In BS 1, for Co a (14s, 9p, 5d)/[9s, 5p, 3d] basis [27] was selected, and for hydrogen, boron, and carbon atoms the 6-311G basis [28]. In BS 2 for Co a (14s, 9p, 6d)/[6s, 4p, 4d] basis was made by adding one s- and two p-type orbital exponents (exp(s) = 0.3572; exp(p) = 0.2728, 0.0886) and replacing the last d function with two functions (exp(d) = 0.3648, 0.1173) in the original (13s, 7p, 5d) basis set from reference [29]. The basis sets (4s)/[2s] [30] and (9s, 5p)/[3s, 2p] [31] were used for the hydrogen and carbon atoms of the $C_5H_5$ ligand, respectively. Boron and carbon atoms of the ligand **9b** were described with a (10s, 5p)/[4s, 3p] basis made from the original (9s, 5p) basis set by adding a diffuse s function with exponent 0.035 (B) and 0.05 (C) [32]. Extended Hückel calculations [33] were carried out with standard parameters for all atoms [33d, 34]. The calculations were carried out on the RS/6000 workstation at the Universitätsrechenzentrum (Heidelberg, Germany) and the Cray 98 computer at the Institut du Développement et des Ressources en Informatique Scientifique (Orsay, France).

## Results and Discussion

Extended Hückel and ab initio molecular orbital calculations were carried out for the model complexes **6b** and **6c**. In **6b** all substituents have been replaced by hydrogen atoms and $C_s$ symmetry (mirror plane *yz*) has been assumed. A convenient method for analyzing the bonding in the complex **6b** is to build up this molecule from the cobalt dimer fragment [$\{CpCo\}_2$] **10** (Cp = $C_5H_5$) and the bridging diborylcarbene ligand **9b**. A simplified interaction diagram is shown in Figure 2. The frontier orbitals of the cobalt dimer **10** can be easily derived from the well-known fragment MOs of two MCp units.[35] They are shown on the left side of Figure 2. For the sake of clarity, the six metal-centered levels and six MOs describing the Co–Cp bonding have been omitted. The HOMO, a near-quadruply degenerate combination of metal-like $d_{xz}$ and $d_{yz}$ levels, is occupied by four electrons in the cobalt dimer **10**.

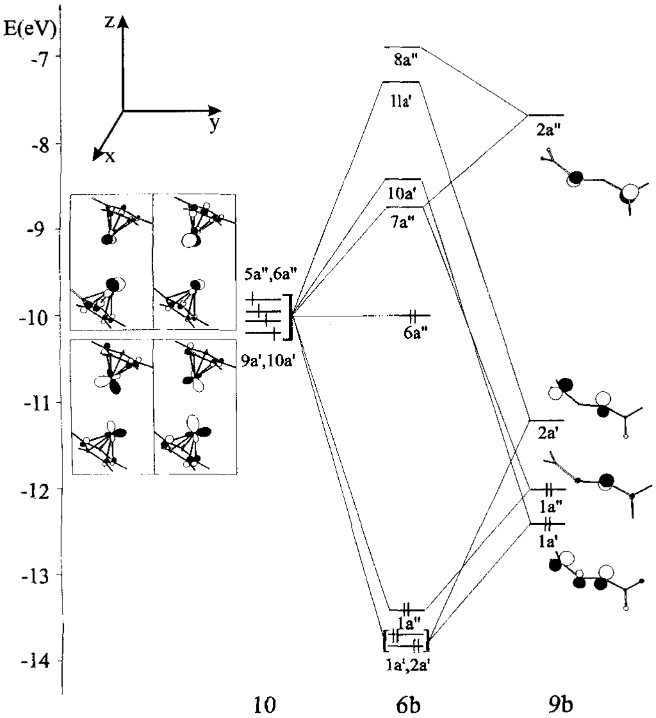

Figure 2. Interaction of the MOs of the molecular fragments [$\{CpCo\}_2$] (**10**) and the diborylcarbene ligand **9b** to yield **6b**.

The frontier MOs of the bridging ligand **9b**, shown on the right side of Figure 2, display interesting features. An analysis of their shapes shows that there is a situation similar to, but electronically a little more favorable than, that of planar methane. The HOMO (1a″) of **9b**, which is of moderate energy, is localized on the ptC atom and has almost pure 2pπ character. The low-lying LUMO (2a′), an out-of-phase combination of the in-plane 2p orbitals of the two carbon atoms of **9b**, is well positioned to accept σ electron density from the metal dimer fragment. The electronic situation is complicated due to the HOMO-1 (1a′), which is slightly lower in energy and describes the C–B π bond. In the presence of appropriate accepting levels on the cobalt dimer fragment, the 1a′ MO should have a propensity for σ donor interactions.

The resulting MOs of **6b** are shown in the middle of Figure 2. The MO shapes of the bonding levels of **6b** as well as of the corresponding antibonding counterparts are displayed in Figure 3. The out-of-phase combination of Co $d_{xz}$ levels of **10** does

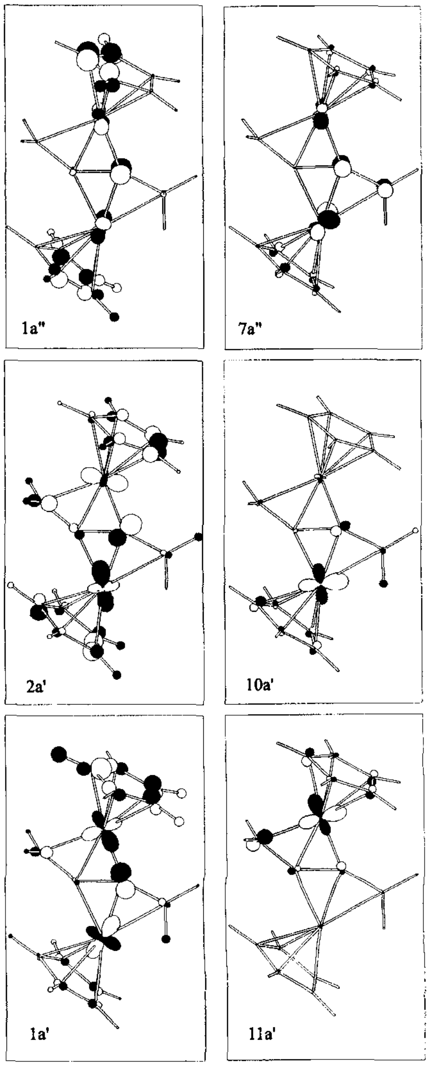

Figure 3. MO shapes of the bonding levels and the corresponding antibonding counterparts of **6b**.

not overlap with the MOs from **9b** and gives rise to the nonbonding HOMO (6a″) of **6b**. Thus, the in-phase combination of Co $d_{xz}$ orbitals of **10** is formally empty and can accept π electron density from the HOMO (1a″) of **9b**. This interaction gives rise to the strongly bonding 1a″ MO and the antibonding LUMO (7a″) of **6b**. The LUMO is not high in energy due to the bonding admixture of the LUMO + 1 (2a″) of **9b** (Figures 2 and 3). Consequently, the π electron density from the HOMO (1a″) of **9b** can be delocalized toward the in-phase combination of Co $d_{xz}$ orbitals and the 2pπ orbitals of the boron atoms.

For the in-plane interactions in **6b**, a synergic ligand–metal and metal–ligand shift of σ electron density is possible. An analysis of the MO shapes in Figure 3 shows that the 1a′ and 2a′ MOs of **6b** are stabilized through multicenter in-plane interactions; the two electrons from the 9a′ and 10a′ MOs of **10** occupy the strongly bonding 1a′ MO of **6b**. In other words, electron density from the cobalt center is transferred through σ donation interaction toward the LUMO of **9b** and the 9a′ and 10a′ MOs of **10** are formally empty in **6b**. An electron density shift can then take place in the *opposite* direction, from the 2a′ MO of **9b** to the empty cobalt levels. The ratio of the density shift of ligand–metal σ donation to metal–ligand σ back-donation in this synergic multiorbital interaction cannot be inferred from the orbital interaction diagram. In order to quantify these donor–acceptor interactions, a natural population analysis has been carried out for the ab initio wavefunction of **6b** and the molecular fragments CpCo1, CpCo2, and **9b**. The resulting data have been summarized in Table 1. The electronic configuration of the ptC (C2: $\sigma^{2.978}\pi^{1.501}$) in the free diborylcarbene ligand is electronically different from that of planar methane (C: $\sigma^2\pi^2$). With respect to planar methane, in **9b** 0.499e of C2 π electron density has already been delocalized onto the boron atoms and the σ electron density has increased by 0.978e. Upon complexation an additional electron density shift is observed from the CpCo units to the bridging ligand **9b**. In **6b** the integrated natural charge on CpCo1 and CpCo2 amounts to +0.211 and +1.022, respectively. During formation of the complex, 1.233e are transferred from the CpCo fragments to the bridging ligand. A more precise description of the bonding as well as of the stabilization manner of the ptC atom in **6b** can be obtained by a comparison of the atomic natural charges and occupancies on the valence natural atomic orbitals (NAOs) of the particular atoms in the free molecular fragments with those in **6b**. The natural charge accompanying the ptC atom increases from −0.482 in **9b** to −1.310 in **6b**. Due to the electron density reorganization in **6b**, the ptC atom receives 0.828e from its neighboring groups or atoms, but the in-plane σ electron density reorganization is not the same as that of the out-of-plane π electron density. Upon going from the free to the complexed ligand, the occupancy of the 2pπ orbital (NAO-a″) of the ptC diminishes from 1.501e to 1.356e and that of the in-plane σ NAOs (a′) increases from 2.978e to 3.944e. Thus in **6b** the overall stabilization manner of the ptC atom is exactly the same as that predicted by Hoffmann et al. in the case of planar methane-like molecules. In **6b** both boron atoms act as σ donors and π acceptors; however, the π-acceptor properties of B1 are weakened upon complexation.

Table 1. Natural population analysis of **6b** and the fragments CpCo1, CpCo2, and **9b**.

| | Complex **6b** | | | Molecular fragments | | |
|---|---|---|---|---|---|---|
| | Charge | NAO(a′) | NAO(a″) | Charge | NAO(a′) | NAO(a″) |
| Co1 | +0.955 | 4.157 | 3.886 | +1.022 | 5.007 | 2.968 |
| Co2 | +1.437 | 5.206 | 2.340 | +1.021 | 5.007 | 2.970 |
| C2 | −1.310 | 3.944 | 1.356 | −0.482 | 2.987 | 1.501 |
| B1 | +0.413 | 2.397 | 0.172 | +0.288 | 2.476 | 0.230 |
| B3 | +0.478 | 2.070 | 0.418 | +0.491 | 2.201 | 0.288 |
| C4 | −0.980 | 3.735 | 1.232 | −0.612 | 3.408 | 1.199 |

The natural charges accompanying the cobalt atoms change from +1.022 (Co1) and +1.021 (Co2) in the free fragments to +0.955 (Co1) and +1.437 (Co2) in the complex **6b**. Therefore the two cobalt atoms are not equivalent in **6b**. Although both cobalt atoms as a whole can be regarded as donors of electron density, their in-plane (σ) and out-of-plane (π) interactions with the ptC atom are of different character. An analysis of the occupancies of the in-plane NAOs (a′) and out-of-plane

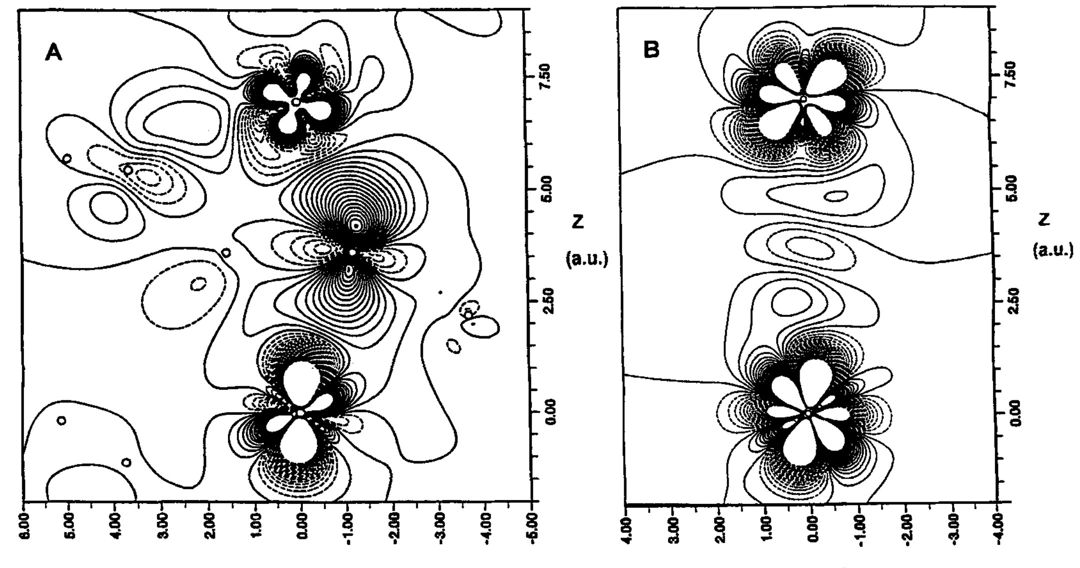

Figure 4. Deformation density plots obtained by subtracting the density generated by a superposition of molecular fragments [{CpCo}$_2$] (**10**) and **9b** from the ab initio molecular density of **6b**. A) *yz* plane; B) *xz* plane. Bold lines for zero contour, solid lines for positive contours (electron density accumulation), and dotted lines for negative contours (electron density depletion). Contour interval: 0.05 e Å$^{-3}$.

NAOs (a″) shows that Co 1 can be characterized as a good σ donor and good π acceptor, but that Co 2 has σ-acceptor and π-donor properties (Table 1). Thus, the bonding between Co 1 and the ptC atom in **6b** has an unconventional character and that with Co 2 shows typical features of a metal–carbene bond. Furthermore, the Co 2–ptC bond length of 1.887 Å falls within the range for a Co=C double bond;[36] the Co 1–ptC distance of 2.008 Å is much longer. In the σ plane, electron density is transferred from Co 1 through the ptC atom to Co 2 while, in the perpendicular plane, π electron density reorganizes in the opposite direction. This situation is clearly illustrated in the deformation density maps computed from the ab initio wavefunctions derived for the ground state of **6b** and the molecular fragments $[\{CpCo\}_2]$ and **9b** (Figure 4, page 297).

In order to investigate the postulated bonding interactions between a duryl ligand and the Co 1 atom, based on NMR and X-ray experiments,[20] and to see what role aromatic substitution on boron plays in the stabilization of the complex, calculations were carried out on the model compound **6c**, in which $R^3$ is a phenyl group. **6c** has $C_1$ symmetry and the $BH(C_6H_5)$ group is rotated by 30° out of the *yz* plane. The calculations predict that the stabilization manner of the ptC atom in **6c** is the same as in the parent complex **6b**, with the exception of one additional interaction appearing in **6c**. The LUMO of **6c** has an admixture of the π* orbital of the phenyl group with large p components on the *ipso* and *ortho* carbon atoms (Figure 5). With respect to the cobalt levels, the LUMO of **6c** behaves as an acceptor orbital and back-bonding from Co 1 to the π* orbital of the phenyl group is possible. Compared to the model ligand **9c**, the electron density associated with the phenyl group increases in **6c** by 0.08 e while that of Co 1 decreases by 0.07 e with respect to **6b**. This interaction contributes to an extra stabilization of **6c** and could be responsible for the experimentally observed short $Co1-C_{ipso}$ bond distance. Furthermore, attempts to synthesize an analogous complex with alkyl, rather than aryl, substitution on boron failed. In this case only a mononuclear complex could be isolated.[37]

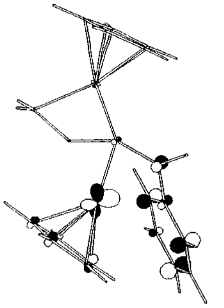
Figure 5. LUMO of **6c**.

## Conclusions

The electronic configuration of the ptC (C 2: $\sigma^{2.978}\pi^{1.501}$) of the free diborylcarbene **9b** ligand is different from that of planar methane (C: $\sigma^2\pi^2$). Further stabilization of the ptC atom is achieved through electron density reorganization due to the interactions with the metal dimer fragment. In **6b** the electronic configuration for the ptC is $\sigma^{3.944}\pi^{1.356}$ and the manner of stabilization is the same as that suggested by Hoffmann et al. for planar methane-like molecules. The accumulation of σ electron density at the ptC atom of **6b** does indeed play a role, as it is greater than the depletion of π electron density. The bonding between the ptC atom and the Co 2 atom has normal metal–carbene bond character, but that with the Co 1 atom displays unconventional character with Co 1 → ptC σ donation and ptC → Co 1 π back-donation. The σ electron density flows from Co 1 through the ptC to Co 2 and the π electron density reorganizes in the opposite direction. The overall stabilization of complexes **6** is achieved by this push–pull effect.

In looking for an analogue of the $CH_4^{2+}$ dication, $[\{(C_5H_5)Ni\}_2(\mu\text{-}CR^1_2BCBR^2R^3)]^{2+}$ presents itself as a possibility. Future attempts will be made to synthesize this complex either directly from **8** or by exchanging the CpCo fragments in **6** with the isolobal $CpNi^+$. Although $[\{AuP(c\text{-}C_6H_{11})_3\}_4C]$ (Schmidbaur et al.[38]) is assumed to be tetrahedral, its strong Lewis basicity[39a] may be an indication of a planar structure, in accordance with the Hoffmann model. On the other hand, the isolobal relationship between H and $Ph_3PAu$ suggests that twofold oxidation of tetragold methane could lead to a $CH_4^{2+}$ analogue with a ptC. The complex cations $[(AuPPh_3)_4(\mu^4\text{-}CR)]^{n+}$ (R = H, $n = 1$;[39a] R = Me, $n = 1$;[39b] R = S(O)Me$_2$, $n = 2$[39c]) containing a hypercoordinate carbon center have been synthesized and structurally characterized. They can be viewed as donor–acceptor compounds between a nucleophile and $[(AuPPh_3)_4C]^{2+}$.

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