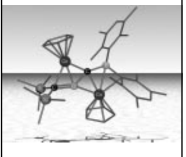
Compounds containing a planar-tetracoordinate carbon atom as analogues of planar methane



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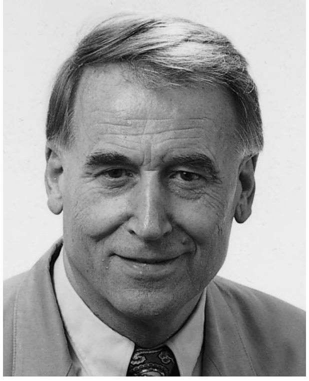
Over the past years the number of examples of compounds containing a planar-tetracoordinate carbon atom has increased. However, the presence of a carbon atom with a 360° sum of angles does not imply that the species is a derivative of planar methane; there must be an appropriate electronic stabilization. In the case of complexes 21a and 21b the central carbon atom is indeed stabilized by σ-donors and π-acceptors, as required for planar methane.

1 Introduction

One and a quarter centuries ago van't Hoff and LeBel[1] convinced the chemical community of the tetrahedral arrangement of the four hydrogen atoms around carbon in methane. According to calculations[2] planar CH_4 (**A**, X = X′ = H) has two two-center, two-electron (2c-2e) C–H bonds (X = H), one three-center, two-electron (3c-2e) bond (HCH; X′ = H) and a doubly occupied pπ orbital. To obtain the planar species an enthalpy of 150 kcal mol^{-1} needs to be overcome, which well exceeds the bond dissociation energy of the C–H bond. Therefore, achieving planar methane is unlikely. It should, however, be possible to stabilize a planar-tetracoordinate carbon (ptC) by incorporating substituents functioning as strong σ-donors and π-acceptors, which supply the lacking σ electron density and remove the energetically unfavorable π-electron density. This idea was first introduced and backed up with extended Hückel calculations by Hoffmann *et al.*,[2] who suggested that silyl or boryl groups might stabilize a ptC. Schleyer, Pople *et al.*[3] extended this concept to a variety of electropositive substituents expected to be capable of stabilizing a ptC in **A** (X = X′ = SiH_3, BH_2, Li). Their MO studies indicate that in 1,1-dilithiocyclopropane the lithium-substituted carbon atom favors a planar-tetracoordinate environment over a tetrahedral arrangement by 7 kcal mol^{-1}.

Over the past twenty years there have been a number of compounds reported having planar-tetracoordinate carbon atoms, and this area was reviewed recently by Erker *et al.*[4] The majority of examples belong to the class of π-stabilized carbon atoms with ptC as part of the π-system of an arene, as depicted in **B**, and of an olefin, as in **C**. In **B** the metal centers M and M′ are forced into the plane of the arene by interactions with the *ortho* substituents R. There is one example (see **3**) in which the metals M = M′ are directly bonded to the *ortho* carbon atoms of the ptC in benzene and bridged by a ligand L. The ptC in the olefinic compounds **C** is connected to the metal centers through a 3c-2e MCM′ bond. In addition, M binds through a 2c-2e bond to the other carbon atom of the double bond, and the metals are also bridged by a ligand L. Thus, two metal centers with chelating ability seem to be required for stabilization of a ptC in **B** and **C**. It is apparent that compounds with a ptC incorporated in a π-system do not need the stabilization pattern predicted[2] for compounds of type **A** (X = X′ = SiH_3, BH_2), as sufficient π-electron density is delocalized onto the arene or olefin moiety. In other words **B** and **C** are not stabilized as type **A** because there is no lone pair present in **B** and **C**.

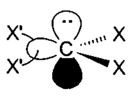
Walter Siebert studied chemistry at Philipps-Universität, Marburg, Germany, where he obtained his MSc degree in 1964 and earned his PhD with Max Schmidt in 1965. Having completed his Habilitation in the Chemistry Department at Julius-Maximilians-Universität, Würzburg, in 1971, he became Associate Professor at his Alma Mater, *Philipps-Universität in 1973. After rejecting a chair at the FU, Berlin, he moved to a full professorship at Ruprecht-Karls-Universität, Heidelberg in 1980. His research interests focus on boron heterocycles as ligands in sandwich, oligodecker, and polydecker complexes, on cluster chemistry, and on compounds containing a planar-tetracoordinate carbon atom.*



Walter Siebert

Anuradha Gunale, born in India (1968), completed her BA in chemistry at Northwestern University with Duward Shriver and her MSc degree at Indiana University with George Christou. In 1994 she began to work in the group of Walter Siebert at the University of Heidelberg, Germany, on compounds containing a planar-tetracoordinate carbon atom. She finished her PhD thesis in 1997.

Anuradha Gunale



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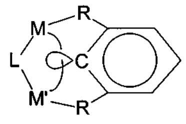

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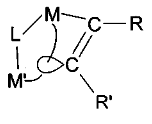

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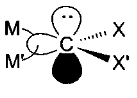

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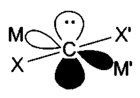

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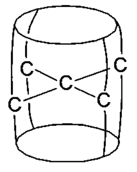


F

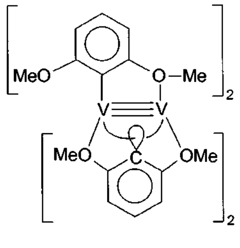
A second class of compounds with a ptC that should follow the structural and electronic features is schematically depicted in **A**, **D**, and **E**.[5] The latter two represent the *syn* and *anti* isomers of a singlet carbene stabilized by two σ-donor/π-acceptor groups X = X′ (*e.g.* BR_2) and two transition metal complex fragments M, M′. In **D** and **E** the metal centers could be symmetrically or asymmetrically bonded to the ptC. Asymmetric bonding would indicate that one center has better donor and weaker acceptor properties than the other, resulting in an electronic push/pull effect.

Another approach for the realization of a ptC is its incorporation into a hydrocarbon framework **F**, in which solely the steric forces are responsible for a ptC conformation. As examples of such compounds, fenestranes and more recently alkaplanes **F** have been investigated.[6,7] Octaplane has been calculated to have an unusually low ionization energy (*ca.* 5 eV) and a ptC in the radical cation.[7] The bonding in octaplane and its cation is similar to that in **A**: in the neutral molecule the HOMO is the doubly occupied pπ-like orbital, and the sp^2-hybridized ptC is involved in two 2c-2e C–C bonds and one 3c-2e CCC bond. The pπ orbital exhibits a slight deviation of the radial symmetry, which indicates that it is not a lone pair with pure p character, but is involved to a small extent in bonding with the neighboring C atoms. In contrast, the singly occupied MO (SOMO) of the radical cation shows no deviation.

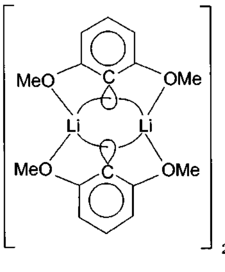
2 Planar-tetracoordinated carbon incorporated in a π system

Complexed arene

Cotton *et al.*[8] reported the crystal structure of **1**, in which four 1,3-dimethoxy-substituted phenyl groups coordinate to the triply bonded V_2 unit. Two of the phenyl rings are bonded through the *ipso* C atom and one MeO substituent to the V_2 unit, whereas the other two phenyl groups coordinate through both MeO groups. A 3c-2e VCV interaction of the *ipso*-C atom completes the planar tetracoordination first recognized by Keese *et al.*[9] The related 1,3-dimethoxy-2-lithiobenzene **2** also seems to have an *ipso* ptC. However, this compound proved to be a tetramer in the crystal,[10] in which two dimeric units of **2** are located on top of each other, and rotated with respect to each other by 90°. This indicates that the *ipso*-C atoms as well as the Li centers are actually pentacoordinated. The *ipso*-C atom in dimeric phenyllithium(tmeda) is tetrahedrally coordinated.[11] However, calculations by Schleyer *et al.* indicated a ptC for phenyllithium and cyclopropenyllithium.[12]



1



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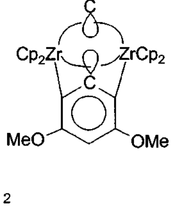
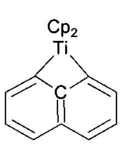


3

In the substituted benzene-1,3-biszirconium complex **3** reported by Buchwald *et al.*[13] the two Cp_2Zr moieties are bridged by a methyl group and both metals are in a bonding 3c-2e interaction with the carbon atom in the 2-position, which is a ptC stabilized by the aromatic π-system.

Poumbga, Bénard, and Hyla-Kryspin[14] studied compounds **1** and **3** by extended Hückel, *ab initio* Hartree–Fock, and CI calculations. It was pointed out that the ptC is part of the π-system and bears a minus charge ($\sigma^4\pi^1$ configuration). Donation of σ-electron density into empty d orbitals with metal–metal bonding character occurs. Here again, the mode of stabilization is not that in **A**.

In the naphthalene derivatives **4** and **5** the Ti–C9 distance in **4** [2.442(7) Å)][15] and the B–C9 distance in **5** [2.045(5) Å)][16] are shorter than the sum of the van-der-Waals radii, and it may seem that a ptC is present (especially in the case of **4**). However, on the basis of orbital symmetry there is no bonding interaction between Ti or B and the bridging carbon atom C9.



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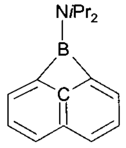

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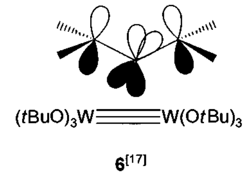
Complexed allene and analogues

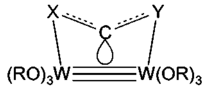
Chisholm *et al.*[17] reported the ditungsten allene complex **6**, in which the central carbon atom of the allene has the coordination characteristics of a ptC. The bonding of the allene to the W_2 unit is unique (see formula drawing of **6**).[17] In the V-shaped C_3 ligand three 2p orbitals form bonding, nonbonding, and antibonding combinations, and the central carbon atom has an empty p orbital orthogonal to the three 2p combinations. The allene functions as a 4e donor, and one of the W_2 π bonds interacts with the *empty* 2p orbital of the ptC.

The complexes **7** obtained from $W_2(OR)_6$ and the allene analogues[18] X=C=Y (X = Y = N–R, X = O, Y = N–Ph) have been described, in which the central atom is a planar-tetracoordinate carbon.

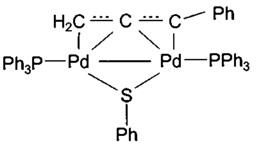
Related to **6** and **7** are the complexes **8** and **9**. In the allenyldipalladium complex **8**[19] the Pd centers with formally d^8 configuration are directly connected through a 2c-2e Pd–Pd bond. The ptC is bonded to both Pd centers [Pd–C 2.361(2),



6[17]



7 X = Y = N-R
X = O; Y = N-Ph



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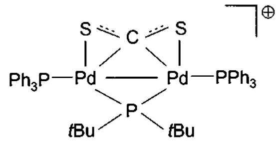
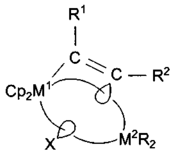


9

2.431(3) Å], and the C_3 unit is almost linear (173.2°). In **9**[20] the ptC is nearly symmetrically bonded to the Pd atoms [Pd–C 2.280(7), 2.331(9) Å], and the CS_2 ligand is in the plane defined by the Pd atoms and the bridging phosphorous atom.

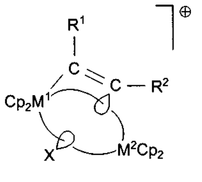
Complexed olefins and analogues

The essential features of olefin complexes **10–12**[21] are that the ptC is part of the C=C double bond and that one of its sp^2 hybrid orbitals is involved in a 3c-2e bond with both metal centers. The bonding in complexes **10** and **11** may be compared with the familiar electronic situation in B_2H_6, where two 3c-2e bonds hold the two BH_3 molecules together. Here the metal centers are electronically connected through the two 3c-2e bonds M^1CM^2 and M^1XM^2. Complexes **10** and **12** are different in that only one 3c-2e bond is present in **12** (M^1CAl), and the bridging chlorine atom is involved in two 2c-2e bonds.



10

M^1 = Ti, Zr, Hf; R^1, R^2 = Alkyl, Aryl, $SiMe_3$
M^2R_2 = BEt_2, Al*i*Bu_2, $AlMe_2$, $AlEt_2$, $GaMe_2$
X = Me, Et, C_2Me, C_2Ph, C_2*c*Hex



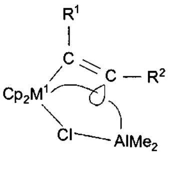
11

M^1, M^2 = Zr, Hf
R^1 = Me, Et, Pr, Ph, Bz
R^2 = Me; X = C≡C–R

Erker *et al.*[4,21] have reported more than 50 examples of ptC compounds of types **10–12**, which all belong to class **C**. In these compounds there is no unfavorable p-lone pair as the carbon atom is incorporated (*vide supra*) into an olefinic π-bond. Therefore examples of class **C** cannot be stabilized according to the Hoffmann model[2] for planar methane (**A**) and its derivatives (**D**, **E**).

In compounds of the type **10–12** the sp^2 carbon atom is involved with one of its sp^2 hybrid orbitals in a 3c-2e bonding to two metals (M^1, M^2). Gleiter, Hyla-Kryspin *et al.*[22] have studied complexes of type **11** by *ab initio* and extended Hückel methods and found that the stabilization of the ptCs in the d^0 complexes depends on the presence of an in-plane acceptor orbital at M^1 and that the delocalization of the π-electron density of the ptC does not play any role.

The structural alternatives for the compounds **10–12** are the classical heterocyclic structures with the planar-tetracoordinate environment at carbon being represented as trigonal planar. Compounds of the types **10** and **11** have been studied with respect to their isomerization. It was found that their conventional structures **13** and **14** are > 30 kcal mol^{-1} and *ca.* 12–14 kcal mol^{-1} less stable than **10** and **11**, respectively.



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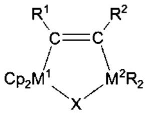
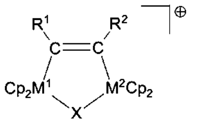


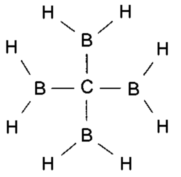
13 M^1 = Zr, M^2 = B, Al, Ga



14 M^1 = M^2 = Zr

3 Derivatives of planar-tetracoordinate methane

Although the all-boron substituted compounds $C[B(OR)_2]_4$[23] have been known for quite some time, the methyl derivative (R = CH_3) has only recently been structurally characterized. In the case of $C(BCl_2)_4$, the possibility of planar tetracoordination was considered from the beginning. Schleyer, Pople *et al.*[3a] have carried out MO calculations on the structures and stabilities of the geometric isomers of tetraborylmethane **15** and on the spiro-cyclic compound **16** which indicate that the latter could be a candidate for a stabilized ptC; the tetrahedral environment is preferred by only 6 kcal mol^{-1}.[3a] We have tried to prepare compound **17**, however with no success.



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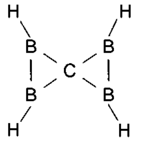

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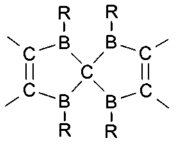

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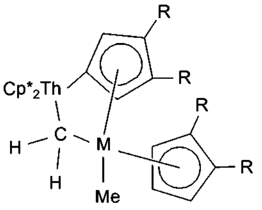
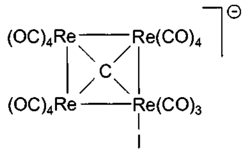
An example of a compound with a ptC is the methane dication CH_4^{2+}, which has been observed in the gas phase.[24] According to a comparison of the measured and calculated ionization energies, an "anti-van't Hoff–LeBel" isomer of CH_4^{2+} is formed when an electron is removed from the tetrahedral methane monocation.[25] High-level *ab initio* calculations by Wong and Radom[26] show that the structure of CH_4^{2+} of lowest energy has C_{2v} symmetry (and not D_{4h}, as for square-planar methane with four H–C–H bonds of 90°) with two short and two long C–H bonds.[26] This dication is therefore a complex between CH_2^{2+} and molecular hydrogen.

There has only been a limited number of methane derivatives containing transition metals. $C[AuP(cyclo\text{-}C_6H_{11})_3]_4$ from Schmidbaur *et al.*[27] has been known for quite some time, but it was not structurally characterized. Although this compound was assumed to have a tetrahedral geometry—a prediction that is substantiated by the presence of the bulky phosphane ligands, which might prevent the angle of 109° between the Au centers from decreasing towards 90°—the strong Lewis basicity[28] may indicate a planar structure in which, in accordance with the Hoffmann model, the filled p orbital perpendicular to the molecular plane is available for attack by an electrophile. In analogy to the methane dication, oxidation of tetragoldmethane may lead to a metal-containing derivative of CH_4^{2+}. The complex cations $[(AuPPh_3)_4(\mu^4\text{-}CR)]^{n+}$ (R = H, n = 1;[28] R = Me, n = 1;[29] R = S(O)Me_2, n = 0[30]) have been isolated and characterized. They have a distorted square-pyramidal structure in which the central carbon atom is substituted with four basal gold atoms and the apical substituent R, and can therefore be viewed as donor–acceptor complexes[5] between a nucleophile (H^-, CH_3^-) and $[C(AuPPh_3)_4]^{2+}$.

In compound **18**, synthesized by Marks *et al.*,[31] the presence of a ptC for the bridging methylene group has been proposed in the transition state of a dynamic process. This is supported by extended Hückel calculations, and would imply that this is the first planar dimetallamethane derivative to be investigated, but a reversible metal–CH_2 bond cleavage is also a possible mechanism. A carbidotetrarhenium cluster[32] could be regarded



18 a: M = Hf, R = H
b: M = Zr, R = H, Me



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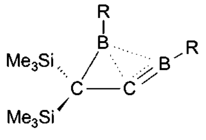
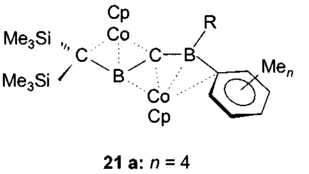
as an example of a tetrametallamethane. However, in the complex anion $[\{I(OC)_3Re\}C\{Re(CO)_4\}_3]^-$ (**19**) the carbon atom is at the center of a tetrahedrally distorted square of rhenium atoms. The folding in the Re_4 ring of 42° is explained by repulsive interactions between ligands on adjacent metals.

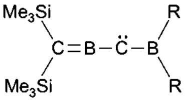
We have investigated the complexation chemistry of the nonclassic boriranylideneboranes **20**.[33–35] Upon treatment with two equivalents of $[Co(C_5H_5)(C_2H_4)_2]$, **20a**, **b** react with cleavage of the ring C–C bond and migration of the aryl substituent R from one boron atom to the other to provide **21a** and **21b**. The boriranylideneboranes have been transformed into chain structures which can be considered as the complex-stabilized diborylcarbenes **21a**, **b**.



20 a: R = Dur
b: R = Mes



21 a: *n* = 4
b: *n* = 3



22 a,b
22 c: $H_2C{=}B{-}\ddot{C}{-}BH_2$

Crystals of **21a** that were suitable for an X-ray structure analysis were obtained. Microcrystals of the mesityl derivative **21b** could also be grown and studied with an image plate (IPDS, Stoe), although they were poor in quality. The refinement of the weak-intensity data yielded a structure similar to that of **21a**, but did not allow the discussion of any structural details. The crystal structure of **21a** shows a planar tetracoordinated carbon atom (sum of angles 359.9°) coordinated by four electropositive centers and with short B–C bond lengths (Fig. 1). However, this coordination geometry is not sufficient for a compound to be a derivative of planar methane. The bonding situation must also be in agreement with the description presented by Hoffmann *et al.*[2]

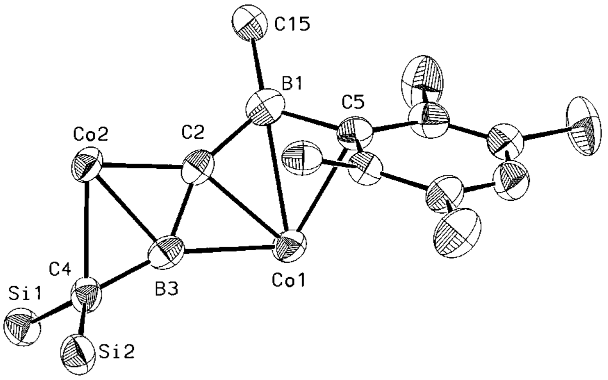


Fig. 1 Ortep representation of the central framework of **21a**. Selected bond lengths and angles: C4–B3 1.483(10), B3–C2 1.474(9), C2–B1 1.522(10), B1–C5 1.601(10), Co1–C5 2.180(7), Co1–B1 2.276(6), Co1–C2 2.009(6), Co1–B3 2.081(8), Co2–C4 2.114(6), Co2–B3 1.973(7), Co2–C2 1.887(6); B1–C2–B3 150.3(6), B1–C2–Co1 78.9(4), B1–C2–Co2 139.0(5), B3–C2–Co1 71.5(4), B3–C2–Co2 70.7(4), C2–B3–C4 138.0(6); (see also ref. 35).

Hyla-Kryspin, Gleiter *et al.*[5] have studied the electronic stabilization of this unusual configuration by extended Hückel and *ab initio* SCF calculations. In the simplified system, in which all substituents were replaced by hydrogen atoms, the complex **21c** was built up from the cobalt dimer fragment $[Co(C_5H_5)]_2$ and the bridging diborylcarbene ligand $H_2C{=}B{-}C{-}BH_2$ (**22c**). It was determined that the electronic structure of **22c** is similar to that of planar methane. The HOMO is mainly localized on the ptC and is almost purely 2pπ in character. The low-lying LUMO is an out-of-phase combination of the in-plane 2p orbitals, and it has the correct symmetry to accept σ-electron density from the CoCp dimer fragment. This indicates that the features of the electronic situation for the free diborylcarbene **22c** are similar to those of planar methane. However, the energetics are already a bit better: according to a natural population analysis, the electron density at the ptC in free diborylcarbene **22c** is $\sigma^{2.978}\pi^{1.501}$, as compared to $\sigma^2\pi^2$ in planar methane.[2] In other words, with respect to planar methane, the energetically unfavorable π-electron density has been decreased, and there is additional electron density for bonding in the σ plane.

Upon complexation, an additional shift in electron density takes place, and the final electronic configuration at the ptC in **21c** is $\sigma^{3.944}\pi^{1.356}$. The in-plane σ-electron density increases from 2.978 to 3.944e, and the out-of-plane π-electron density decreases from 1.501 to 1.356e. Thus, in **21c** the overall stabilization manner of the ptC corresponds to that predicted by Hoffman *et al.*[2] as required for realizing this unusual geometry: **21c** is a derivative of planar methane.

Since the natural charge on the ptC increases from −0.482 in **22c** to −1.310 in **21c**, a net shift of electron density takes place from the $Co(C_5H_5)$ units to the bridging diborylcarbene ligand upon complexation. In total, the two cobalt atoms are donors with respect to the ptC, but their in-plane and out-of-plane interactions have different character. According to an analysis of the occupancies of the in-plane and out-of-plane natural atomic orbitals, Co1 is a strong σ-donor (decrease from 5.007 to 4.157 upon complexation) and a strong π-acceptor (increase from 2.968 to 3.886), whereas Co2 is best described as a weak σ-acceptor (increase from 5.007 to 5.206) and a moderate π-donor (decrease from 2.970 to 2.340). Therefore, σ-electron density is transferred from Co1 through the ptC atom to Co2, whereas π-electron density moves in the opposite direction in the plane perpendicular to that of the four substituents on the ptC. This push/pull interaction is responsible for the stabilization of the ptC.

4 Conclusions

Over the past years the number of examples of compounds containing a planar-tetracoordinate carbon atom has increased. The confirmation of the presence of this now not so unusual geometry has for the most part come from crystal structure analyses. However, the presence of a carbon atom with a 360° sum of angles does not imply that the species is a derivative of planar methane. Theoretical calculations are required to determine the nature of the interactions in the system. In most cases investigated, the mode of stabilization is different from that predicted for planar CH_4. Very often the delocalization of π-electron density does not play a role in stabilization of the geometry, as sufficient density is already distributed into the π-system of the arene or olefin (as with **3**, **6**, and **10**–**13**). In the case of **2**, which has often been listed as a compound containing a ptC, the carbon atom is in reality coordinated by five atoms, and not four.

Another point of interest is that there are few purely organic species that come into question (for example, the octaplanes), and most examples involve transition metal complexes. Therefore, the interaction of the orbitals of carbon with those of metals must be particularly well suited to stabilizing a ptC.

Compounds **21a** and **21b** are the first analogues of planar methane to be structurally characterized and investigated. It is hoped that further examples can be found, and trends recognized for the factors required to obtain this still very rare species.

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