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Theoretical Designs for Planar Tetracoordinated Carbon in Cu, Ag, and Au Organometallic Chemistry: A New Target for Synthesis

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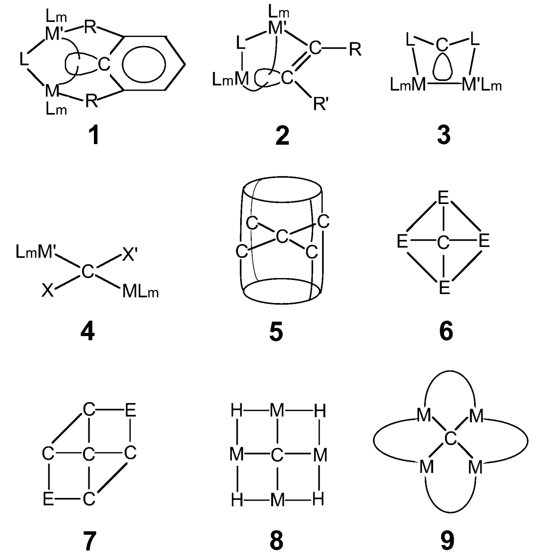
In the past 30 years, substantial efforts and progress have been made in the design and synthesis of molecules containing tetracoordinated planar carbon, by overcoming the inherent preference for tetrahedral bonding. As a result, we have studied 12 organometallic molecules containing group 11 elements (i.e., **M**–**X**; **M** = Cu, Ag, and Au and **X** = **I**, **II**, **III**, and **IV**) using density functional theory to determine whether the central carbon atom exists in a planar geometry. Our theoretical findings suggest that in such **M**–**X** species, bonding interactions between the central carbon and the coinage metal ligands and between the metal ligands (i.e., metallophilic attractions) are both important in favoring planar-tetracoordinated carbon compounds over the corresponding tetrahedral structures. The compounds studied in this work are seen as excellent targets for chemical synthesis.

The synthesis of compounds containing planar-tetracoordinated carbon (ptC)[1] that are stable enough to be isolated, investigated, and handled under ambient conditions has been a challenging research theme in both organic and inorganic chemistry for at least 30 years. A major reason for the widespread interest in this area is that frequent new findings continue to stimulate chemists' imaginations in designing fascinating and novel compounds with ptC. Several exhaustive and comprehensive reviews have appeared at different stages in the development of this research.[2] We examine those experimentally synthesized and theoretically proposed compounds containing a ptC atom and rationalize several models. The structural and electronic features are schematically depicted in **1**−**8** in Chart 1.[2h]

Chart 1



For compounds of type **1**, intramolecular chelation of both metal centers (M and M′) by the alkyl groups (R) encourages the aryl ligand and the metal atoms to lie in the same plane. Such molecules belong to the class of π-stabilized carbon atoms with ptC as part of the π system of the arene, as depicted in **1**. In **1**, the metal centers M and M′ are forced into the plane of the arene by interactions with the ortho substituent R. Consequently, the metal-bound phenyl carbon has a planar tetracoordinated environment.[3,4] Type **2** is a class

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of dimetallic compounds in which the ptC is stabilized by the interactions with both a transition (M′) and a main group (M) metal. The ptC in the olefinic compounds **2** 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 **2**. Compounds have been reported recently in which the ptC comprises part of a double bond.[5] Indeed, Erker et al. have reported more than 50 experimental examples of ptC compounds, which all belong to class **2**.[6] For compounds of type **3**, the coordination of the central carbon of the allene fragment to both metal atoms results in a planar tetracoordinated environment.[7] In the V-shaped L−C−L 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 L−C−L functions as a 4e donor, and one of the M−M′ π bonds interacts with the *empty* 2p orbital of the ptC. In class **4**, the metal centers could be asymmetrically bonded to the ptC. Such an asymmetric bonding would indicate that one center has better donor and weaker acceptor properties than the other, resulting in an electronic push/pull effect. This has been verified by recent experimental studies.[8]

An alternative approach is based on using mechanical forces exerted by the surrounding ligands bound to the central carbon atom.[9] As examples of such compounds, a class of saturated polycyclic hydrocarbons, called alkaplanes (**5**), in which a central carbon locked in a nearly planar geometry as the result of steric constraints, has been investigated.[10] Nevertheless, in such mechanical schemes, it is difficult to overcome the enormous strain of a ptC in nonaromatic hydrocarbon cages without electronic assistance. As a result, a charge-compensation strategy has been employed to computationally design a family of neutral molecules with C(C)4-type ptCs.[11] An interesting approach for designing new ptC molecules is to focus on small five-atom species, the smallest molecule that can contain a central ptC atom, as shown in class **6**.[12] That is, planarity in these species is not enforced by their molecular architecture but rather by their intrinsic and unique electronic structure. It has been demonstrated that a general rule exists for achieving planarity in pentaatomic species composed of a central carbon atom and four second- or third-row ligand atoms. As a result, such species should possess 17 or 18 valence electrons, and several of them have been detected in the gas phase.[12] Further, Vela et al utilized ab initio calculations to show that alkaline metals can stabilize molecules containing ptC with a $C(C)_4$-type skeleton (class **7**), such as C_5^{2-}, C_5Li^-, and C_5Li_2, making them candidates for experimental detection.[13] Recently, on the basis of ab initio optimization results, it was reported that, in the form of the C-centered hydrometals M_4H_4C (see class **8**), carbon can be tetracoordinated by four metal ligands M (M = Cu, Ni) in perfect squares with four surrounding hydrogen atoms.[14]

It is these fascinating and imaginative results that have inspired this study. To the best of our knowledge, there have

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(4) A recent theoretical investigation indicated that the ptC in the bridging phenyl group should be described as a phenyl anion with the σ lone pair pointing towards the center of the metal−metal axis. This σ lone pair is stabilized by delocalization into metal d orbitals with predominantly metal−metal bonding character. See: Poumbga, C. N.; Benard, M.; Hyla-Kryspin, I. *J. Am. Chem. Soc.* **1994**, *116*, 8259.

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(6) The recent theoretical investigations indicated that in these compounds, there is no unfavorable p lone pair because the carbon is incorporated into an olefinic π bond. In contrast, the stability of such a planar arrangement is due mainly to the stabilization by σ interactions between carbon and the strong in-plane σ acceptor orbital at the metal. See: Gleiter, R.; Hyla-Kryspin, I.; Niu, S.; Erker, G. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 754.

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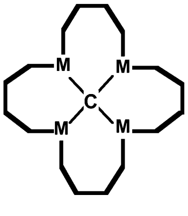
been only a limited number of planar methane derivatives synthesized containing four transition metal atoms. For instance, $C[AuP(\mathit{cyclo}\text{-}C_6H_{11})_3]_4$ from Schmidbaur and Steigelmann has been known for quite some time, but it was not structurally characterized.[15] However, in the complex anion $[\{I(OC)_3Re\}C\{Re(CO)_4\}_3]^-$, the carbon atom is at the center of a tetrahedrally distorted square of rhenium atoms.[16] The folding in the Re_4 ring of 42° was explained by repulsive interactions between ligands on adjacent metal atoms. In this work, we now report the computational discovery of a novel family of ptC molecules, the tetrametallamethanes (**9** in Chart 1), which utilize basically new electronic structural features, unprecedented in neutral molecules, to help planarize the central carbon coordination. Despite the numerous experimental as well as theoretical studies in the search for compounds that contain ptC,[2] we believe that a somewhat different approach and some new aspects emphasized here may supplement and make a significant contribution to this field.



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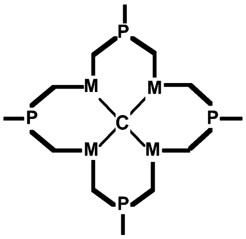

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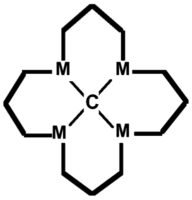

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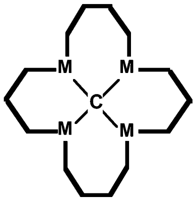

IV

Our design strategy is based on the skeletons **I**−**IV**, where the interstitial carbon atom is located in the center of a cyclic ring with four metal atoms (M) forming the M_4 plane. The d-block transition metal atoms that were used in this work are group 11 elements (the so-called "coinage metals"), that is, M = Cu, Ag, and Au. Various initial structures obtained at the B3LYP/LANL2DZ level were reoptimized at the B3LYP/BS2 level.[17−19] The structures of **Cu**−**X**, **Ag**−**X**, and **Au**−**X** (**X** = **I**, **II**, **III**, and **IV**) shown in Table 1 were characterized as equilibrium structures through B3LYP/LANL2DZ and B3LYP/BS2 frequency calculations. Cartesian coordinates for these stationary points are included in the Supporting Information. All of the calculations were performed with the Gaussian 03 program.[20]

Calculated vibrational frequencies for the **Cu**−**X**, **Ag**−**X**, and **Au**−**X** species reveal that all of these ptC structures are true minima on the potential energy surface. As one can see in Table 1, the calculated $M-C_{ptC}$ bond lengths in the **Cu**−**X**, **Ag**−**X**, and **Au**−**X** model structures are in the range of 1.868−1.889 Å, 2.064−2.071 Å, and 2.089−2.066 Å, respectively. These bond lengths are apparently shorter than the sum of van der Waals radii for Cu−C (2.050 Å), Ag−C (2.217 Å), and Au−C (2.184 Å), respectively.[21] This suggests that these model compounds have significant coinage-metal−central-carbon interactions, which, in turn, can stabilize the whole system (vide infra). Besides, the reason for such short bond distances mentioned above is presumably attributed to the small size of the central cavities provided by the skeletons **I**−**IV**.[22] The supporting evidence comes from the fact that the central cavities in the frameworks **III** and **IV** are slightly too small to accommodate the central quaternary carbon in an energy surface minimum. Indeed, our theoretical calculations shown in Table 1 indicate that the central carbon is about 0.1−0.5 Å above an exactly planar arrangement for **M**−**III** and **M**−**IV** (**M** = Cu, Ag, and Au) species. As a result, **M**−**III** and **M**−**IV** molecules contain a nearly but not exactly ptC atom. Conversely, the extension of the cavity in models **I** and **II** seems to allow accommodation of the carbon atom within the plane of the cavity and, thus, preserve the planar structure for both model molecules. Indeed, our theoretical calculations indicate that exact planarity at the

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Table 1. Molecular Parameters, NBO Charges, Electronic Configurations on ptC, Koopmans' Ionization Potentials (IP), and the Energy Difference between Singlet and Triplet (ΔE_{st}) for **Cu−X**, **Ag−X**, and **Au−X** (**X** = **I**, **II**, **III**, and **IV**) Model Molecules[a,b]

model	**I**	**II**	**III**	**IV**
Cu−C_{ptC} (Å)	1.889	1.886	1.868	1.880
Cu−Cu (Å)	2.671	2.667	2.642	2.733, 2.570
d (Å)[c]	0.0	0.0	0.0	0.1
charge	Cu: +0.8767 C_{center}: −1.618	Cu: +0.9067 C_{center}: −1.500	Cu: +0.8768 C_{center}: −1.566	Cu: +0.8767 C_{center}: −1.607
C_{ptC} configuration	$[He]2s^{1.65}$ $2p_x^{1.48}2p_y^{1.49}2p_z^{0.973}$	$[He]2s^{1.66}$ $2p_x^{1.442}p_y^{1.442}p_z^{0.934}$	$[He]2s^{1.66}$ $2p_x^{1.412}p_y^{1.412}p_z^{1.07}$	$[He]2s^{1.66}$ $2p_x^{1.442}p_y^{1.462}p_z^{1.03}$
IP (eV)	6.106	6.332	5.994	6.150
ΔE_{st} (kcal/mol)	+31.06	+19.12	+14.61	+33.10
Ag−C_{ptC}(Å)	2.071	2.064	2.070	2.068
Ag−Ag (Å)	2.935	2.915	2.859	2.988, 2.816
d (Å)[c]	0.1	0.1	0.4	0.2
charge	Ag: +0.7740 C_{center}: −1.314	Ag: +0.8301 C_{center}: −1.246	Ag: +0.7867 C_{center}: −1.357	Ag: +0.7852 C_{center}: −1.607
C_{ptC} configuration	$[He]2s^{1.70}$ $2p_x^{1.30}2p_y^{1.30}2p_z^{0.985}$	$[He]2s^{1.69}$ $2p_x^{1.35}2p_y^{1.35}2p_z^{0.830}$	$[He]2s^{1.68}$ $2p_x^{1.39}2p_y^{1.39}2p_z^{0.878}$	$[He]2s^{2.00}$ $2p_x^{1.34}2p_y^{1.35}2p_z^{0.973}$
IP (eV)	5.940	6.201	5.823	5.932
ΔE_{st} (kcal/mol)	+14.21	+7.544	+7.251	+15.86
Au−C_{ptC}(Å)	2.079	2.066	2.089	2.075
Au−Au (Å)	2.940	2.922	2.864	2.983, 2.847
d (Å)[c]	0.0	0.0	0.5	0.2
charge	Au: +0.7414 C_{center}: −1.330	Au: +0.7850 C_{center}: −1.178	Au: +0.7225 C_{center}: −1.212	Au: +0.7428 C_{center}: −1.315
C_{ptC} configuration	$[He]2s^{1.63}$ $2p_x^{1.36}2p_y^{1.36}2p_z^{0.956}$	$[He]2s^{1.63}$ $2p_x^{1.33}2p_y^{1.33}2p_z^{0.858}$	$[He]2s^{1.66}$ $2p_x^{1.28}2p_y^{1.28}2p_z^{0.958}$	$[He]2s^{1.63}$ $2p_x^{1.35}2p_y^{1.30}2p_z^{0.994}$
IP (eV)	6.280	6.480	5.986	6.190
ΔE_{st} (kcal/mol)	+29.52	+15.40	+10.98	+24.68

[a] All at the B3LYP/BS2 (singlet) level of theory, see the text. [b] The triplet energy was obtained from the vertical energy at the singlet geometry. $\Delta E_{st} = E_{triplet} - E_{singlet}$. [c] "d" stands for the distance between the ptC and the M_4 plane.

central quaternary carbon atom is achieved for both **M−I** and **M−II** molecules.

Additionally, as shown in Table 1, in **Cu−X**, **Ag−X**, and **Au−X** model compounds, the metal−metal distances within the rings lie in the range of 2.73−2.57, 2.99−2.82, and 2.98−2.85 Å for M = Cu, Ag, and Au, respectively. These values are somewhat longer than those in the bulk metals (i.e., 2.56, 2.89, and 2.90 Å for Cu−Cu, Ag−Ag, and Au−Au, respectively)[23a] but are, nonetheless, in the range where "metallophilic"[23,24] attractions may occur. Namely, the M···M interactions provide a significant contribution to their stability. As a consequence, the geometry is as predicted from the metallophilicity concept: small M−CptC−M angles (∼90°) and short intramolecular M···M contacts in the **Cu−X**, **Ag−X**, and **Au−X** model molecules clearly lead to a dramatic stabilization of these planar configurations over the corresponding tetrahedral forms.

Table 2. Bond Lengths and Energy Differences (ΔE in kcal/mol) between Tetrahedral (T_d) and Planar (D_{4h}) Structures of CM_4 (M = Cu, Ag, and Au) at B3LYP/BS2 + ZPE[a]

	T_d	D_{4h}
CCu_4		
C−Cu (Å)	1.837	1.829
ΔE (kcal/mol)	0.0	22.41
NIMAG	0	2[b]
CAg_4		
C−Ag (Å)	2.061	2.059
ΔE (kcal/mol)	0.0	25.99
NIMAG	0	2[c]
CAu_4		
C−Au (Å)	2.006	2.040
ΔE (kcal/mol)	0.0	65.69
NIMAG	0	1[d]

[a] NIMAG gives the number of imaginary frequencies. [b] 74.9i (B2u) and 547i (A2u) cm^{-1}. The former leads to the tetrahedral structure, whereas the latter leads to the pyramidal structure. [c] 57.4i (B2u) and 958i (A2u) cm^{-1}. The former leads to the tetrahedral structure, whereas the latter leads to the pyramidal structure. [d] 187i (B2u) cm^{-1}, which leads to the tetrahedral structure.

Natural bond orbital (NBO) analyses[25] indicate that, in the **Cu−X**, **Ag−X**, and **Au−X** molecules, there is considerable electron transfer from the surrounding metal atoms to the more electronegative carbon center, a clear manifestation of the ionic characteristics existing in the metal−CptC interactions. As demonstrated in Table 1, for instance, the **Cu−I** molecule has atomic charges of +0.876 and −1.62 *e* for Cu and CptC, respectively, the atomic charges of **Ag−I** are +0.774 and −1.31 *e* for Ag and CptC, respectively, and the Au and CptC of the **Au−I** species carry the atomic charges of +0.741 and −1.33 *e*, respectively. Accordingly, the substantial stability of these **Cu−X**, **Ag−X**, and **Au−X** molecules studied in this work is partially due to a high degree of ionic character in the bonding between the central carbon and its surrounding coinage metals.

As one can see in Table 2, our B3LYP/BS2 calculations verify that the planar D_{4h} form of the parent CCu_4, CAg_4, and CAu_4 molecules are 22, 26, and 66 kcal/mol less stable

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(23) One of the metallophilic interactions is the famous "aurophilic" attraction. For the leading review, see: (a) Pyykko, P. *Chem. Rev.* **1997**, *97*, 597. (b) Scherbaum, F.; Grohmann, A.; Huber, B.; Kruger, C.; Schmidbaur, H. *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1544. (c) Schmidbaur, H. *Gold Bull.* **1990**, *23*, 11. (d) Schmidbaur, H. *Chem. Soc. Rev.* **1995**, 391.

(24) Pyykko, P.; Li, J.; Runeberg, N. *Chem. Phys. Lett.* **1994**, *218*, 133.

(25) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *J. Chem. Rev.* **1988**, *88*, 899.

than their corresponding normal tetrahedral T_d structures, respectively. This shows that an additional large-ring effect is needed to achieve the ptC arrangement. In addition, frequency analyses indicate that the planar species **I**−**IV** without the central carbon atom are all second-order saddle points.[26] Accordingly, our theoretical findings suggest that it is the introduction of a carbon atom at the central cavity of frameworks **I**−**IV** and the subsequent formation of four equivalent M−CptC interactions as well as the intramolecular metallophilic attractions that play a crucial role in maintaining planarity in the **Cu**−**X**, **Ag**−**X**, and **Au**−**X** compounds.

One striking feature of the electronic structures of the **Cu**−**X**, **Ag**−**X**, and **Au**−**X** molecules is the highest occupied molecular orbital (HOMO), which is basically a p-type lone pair orbital localized on the central quaternary carbon atom, perpendicular to the M_4 plane. As seen in Table 1, for example, the C_{ptC} atoms in **Cu**−**I**, **Ag**−**I**, and **Au**−**I** species have the electronic configurations $[He]2s^{1.65}2p_x^{1.48}p_y^{1.49}p_z^{0.973}$, $[He]2s^{1.70}2p_x^{1.30}p_y^{1.30}p_z^{0.985}$, and $[He]2s^{1.63}2p_x^{1.36}p_y^{1.36}p_z^{0.956}$, respectively. It should be mentioned that these observations are consistent with the findings of previous investigations[1,10] that the ptC in planar methane has a pure lone pair of $2p_z$ electrons and there is considerable electron transfer from the four hydrogen atoms to the central carbon atom. Moreover, such electronic structures of the **Cu**−**X**, **Ag**−**X**, and **Au**−**X** model compounds also are responsible for their low Koopmans' ionization potentials (IPs). As given in Table 1, the IPs of the **Cu**−**X**, **Ag**−**X**, and **Au**−**X** species fall in the ranges of 6.0−6.3, 5.8−6.2, and 6.5−6.0 eV, respectively. These values are surprisingly similar to those of benzene (6.7 eV) and naphthalene (5.8 eV),[11] whereas the lowest experimental value for a neutral saturated hydrocarbon is 7.1 eV for tetra-*tert*-butyltetrahedrane.[27] We have also examined the lowest energy triplet state at the singlet geometry. As shown by the ΔE_{st} ($= E_{triplet} - E_{singlet}$ for **Cu**−**X**, **Ag**−**X**, and **Au**−**X** species) values in Table 1, all of the singlet states are significantly more stable than the corresponding triplets.

In conclusion, our work presents the first theoretical evidence that a ptC atom can be localized at the centers of perfect squares surrounded by four coinage metal atoms. Also, we calculate that planar geometries can be favored over the corresponding tetrahedral structures in the presence of four strong equivalent $M-C_{ptC}$ interactions with high degrees of ionic character and metallophilic bonding interactions among the ligand coinage metal atoms. It is expected that the molecules studied in this work will soon be synthesized in a stable form and open a new area of ptC chemistry. We eagerly await experimental evidence to confirm our predictions.

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Supporting Information Available: Cartesian coordinates for **Cu**−**X**, **Ag**−**X**, and **Au**−**X** (**X** = **I**, **II**, **III**, and **IV**). This material is available free of charge via the Internet at http://pubs.acs.org.

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(26) For example, the B3LYP/BS2 frequency calculations for the **Au**−**I**, **Au**−**II**, **Au**−**III**, and **Au**−**IV** species without the central carbon atom suggest that they all are second-order saddle points with two imaginary frequencies of (75i, 55i), (196i, 141i), (135i, 43i), and (136i, 39i) cm^{-1}, respectively.

(27) (a) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem., Ref. Data* **1988**, *17*, 1. (b) Heilbronner, E.; Jones, T. B.; Krebs, A.; Maier, G.; Malsch, K.-D.; Pocklington, J.; Schmelzer, A. *J. Am. Chem. Soc.* **1980**, *102*, 564.