The Significance of π Interactions in Group 11 Complexes with N-Heterocyclic Carbenes[†]

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The nature of the chemical bond in mixed carbene−halogen complexes (**1**)TMX (X = F−I) and bis(carbene) complexes $(\mathbf{1})_2\mathrm{TM}^+$ of group 11 metals (TM = Cu, Ag, Au) with imidazol-1-ylidene (**1**) as ligand has been investigated at the BP86 level of theory using an energy decomposition analysis (EDA). The metal−carbene bonds are mainly held together by classical electrostatic attraction, which contributes >65% of the binding interactions. The metal−carbene bonds are very strong. In the bis(carbene) complexes, the N-heterocyclic carbene ligand **1** is bonded even more strongly than in the mixed carbene−halogen complexes. In the bis(carbene) complexes, orbital interactions are slightly more important than in the mixed carbene−halogen complexes but the covalent contribution is always <35% of the total attractive interaction. The orbital interaction part of the bonding has only ∼20% π back-bonding. The calculated data are not very different from previous EDA results for the Fischer carbene complex $(\mathrm{CO})_5\mathrm{W{-}C(OH)_2}$. The EDA results suggest that $\mathrm{R_2C} \leftarrow \mathrm{ML}_n$ π back-donation in complexes with N-heterocyclic carbenes is not substantially smaller than in classical Fischer carbene complexes bearing two π donor groups R.

Introduction

N-heterocyclic carbenes are widely used as ligands in inorganic and organometallic chemistry. They form complexes with early and late transition metals and also with main-group elements, where they bind as both Lewis acids and Lewis bases. In homogeneous catalysis a new class of catalysts has recently been developed with N-heterocyclic carbenes instead of organophosphine ligands.[1] N-heterocyclic carbenes can be used for a large variety of reactions of high synthetic interest, such as 1,2-migration reactions, dimerizations, and cycloaddition reactions.

Transition-metal carbene complexes are usually divided into two groups, according to the qualitative nature of the metal−carbon bond. Fischer type carbene complexes are compounds with a donor−acceptor bond between a low-valent metal fragment and a carbene ligand $\mathrm{CR_1R_2}$, where at least one of the substituents R carries a π-donor group.[2] Formally, the metal−ligand bonding results from synergistic $\mathrm{R_2C} \rightarrow \mathrm{ML}_n$ σ donation and $\mathrm{R_2C} \leftarrow \mathrm{ML}_n$ π back-donation. In contrast, Schrock type carbene complexes are usually formed from metals in a high oxidation state and carbene ligands with alkyl groups or hydrogen atoms as substituents.[3] It has been suggested that Schrock type carbene complexes should be considered as metal alkylidenes $\mathrm{L}_n\mathrm{M{-}CR_2}$, which have a covalent double bond that results formally from the interaction of a triplet carbene with a triplet metal fragment. Recent theoretical studies of the bonding situation using charge and energy decomposition analyses support the bonding models for Fischer and Schrock complexes.[4]

Unlike typical Fischer type carbenes, imidazol-2-ylidene (**1**) apparently binds through $\mathrm{R_2C} \rightarrow \mathrm{ML}_n$ σ donation only, while $\mathrm{R_2C} \leftarrow \mathrm{ML}_n$ π back-donation is negligible. The analysis of the properties of TM complexes with **1** as a ligand suggests that it is generally a pure σ donor.[5] This is understandable, because theoretical studies of the electronic structure of **1** showed that the main reason for its high kinetic stability is the strong $\mathrm{N} \rightarrow \mathrm{C}_{\mathrm{carbene}}$ π donation, which leads to a highly filled p(π) orbital at the carbene carbon atom.[6] Thus, there is no

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[†] Theoretical Studies of Organometallic Compounds. 52. Part 51: Frunzke, J.; Loschen, C.; Frenking, G. *J. Am. Chem. Soc.* **2004**, *126*, 3642.

[‡] Philipps-Universität Marburg.

[§] Budapest Technical University.

[1] Herrmann, W. A. *Angew. Chem.* **2002**, *114*, 1342; *Angew. Chem., Int. Ed.* **2002**, *41*, 1290.

[2] Recent reviews: (a) Sierras, M. A. *Chem. Rev.* **2000**, *100*, 3591. (b) de Meijere, A.; Schirmer, H.; Deutsch, M. *Angew. Chem.* **2000**, *112*, 4124; *Angew. Chem., Int. Ed.* **2000**, *39*, 3964. (c) Barluenga, J.; Flórez, J.; Fañanás, F. J. *J. Organomet. Chem.* **2001**, *624*, 5.

[3] Schrock, R. R. *Chem. Rev.* **2002**, *102*, 145.

[4] (a) Jacobsen, H.; Schreckenbach, G.; Ziegler, T. *J. Phys. Chem.* **1994**, *98*, 11406. (b) Jacobsen, H.; Ziegler, T. *Organometallics* **1995**, *14*, 224. (c) Ehlers, A. W.; Dapprich, S.; Vyboishchikov, S. F.; Frenking, G. *Organometallics* **1996**, *15*, 105. (d) Jacobsen, T.; Ziegler, T. *Inorg. Chem.* **1996**, *35*, 775. (e) Fröhlich, N.; Pidun, U.; Stahl, M.; Frenking, G. *Organometallics* **1997**, *16*, 442. (f) Frenking, G.; Pidun, U. *J. Chem. Soc., Dalton Trans.* **1997**, 1653. (g) Torrent, M.; Durán, M.; Solá, M. *Organometallics* **1998**, *17*, 1492. (h) Vyboishchikov, S. F.; Frenking, G. *Chem. Eur. J.* **1998**, *4*, 1428. (i) Beste, A.; Krämer, O.; Gerhard, A.; Frenking, G. *Eur. J. Inorg. Chem.* **1999**, 2037. (j) Frenking, G. *J. Organomet. Chem.* **2001**, *635*, 9. (k) Cases, M.; Frenking, G.; Duran, M.; Solá, M. *Organometallics* **2002**, *21*, 4182. (l) Lein, M.; Szabó, A.; Kovács, A.; Frenking, G. *Faraday Discuss.* **2003**, *124*, 365. (m) Fernández, I.; Cossío, F. P.; Arrieta, A.; Lecea, B.; Mancheño, J.; Sierra, M. A. *Organometallics* **2004**, *23*, 1065.

[5] Herrmann, W. A.; Köcher, C.; *Angew. Chem.* **1997**, *109*, 2257; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2162.

[6] (a) Heinemann, C.; Müller, T.; Apeloig, Y.; Schwarz, H. *J. Am. Chem. Soc.* **1996**, *118*, 2023. (b) Boehme, C.; Frenking, G. *J. Am. Chem. Soc.* **1996**, *118*, 2039.

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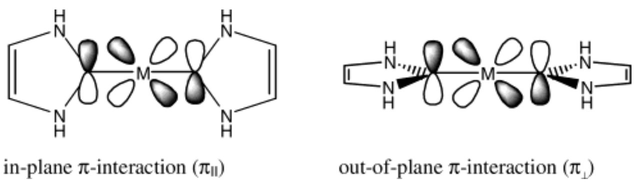
need for $R_2C\leftarrow ML_n$ π back-donation to stabilize the complex for isolation.

The nature of the chemical bond between a transition metal and a carbene ligand was investigated theoretically soon after the first stable TM carbene complex was reported in 1964.[7] However, the metal−ligand bonding in complexes of N-heterocyclic carbenes such as **1** has not been investigated until Frenking and Boehme published the results of a charge decomposition analysis in 1998.[8] In this work, a strong ionic character was suggested for the metal−ligand bond, which comes from the Coulomb attraction between the positively charged metal atom and the σ electron pair ot the donor atom. The analysis of the orbital interactions gave little π back-bonding from the metal to the ligand. The electron delocalization in N-heterocyclic carbenes and their complexes with $Cr(CO)_5$ have also been investigated in a combined experimental and theoretical study by Scherer and co-workers.[9] Theoretical studies of the electronic structure of transition metal complexes with N-heterocyclic carbene ligand have recently been carried out by other groups.[10]

For main group compounds with N-heterocyclic carbenes, significant π back-donation was found theoretically.[11−13] The bonding of phosphinidenes with N-heterocyclic carbenes results from a dative bond formed by the nucleophilic carbene carbon atom with some back- bonding arising from the P valence space which creates a partial double bond character.[11] The level of π back-donation could be correlated with the π donating ability of the substituents on the nitrogen atom.[12] A donor−acceptor interaction with a substantial π back-bonding of the carbenoid moiety was also suggested in the case of CH_2, SiH_2, PH, and S.[13]

Bis(carbene) complexes were investigated of group 10 and group 11 metals.[14−16] There is no agreement as to the degree of π back-bonding with the group 10 metals. While some π interaction was suggested for bis(carbene) complexes of nickel(0) and platinum(0),[14] the complexes of group 11 metals were suggested to be purely σ bonded. Recently, however, a significant amount of π interaction between group 11 metals and carbene ligands was suggested on the basis of structural data.[17,18] Furthermore, Meyer and co-workers carried out density functional calculations of the experimentally investigated complex $[(TIME^{Me})_2Ag_3]^{3+}$. They concluded from visual inspection of the contour line diagram of molecular orbitals that there exists significant π-bonding interaction within the Ag−carbene unit of the $[(TIME^{Me})_2Ag_3]^{3+}$ cation. Visual inspection only is, however, not sufficient to draw conclusions about the strength of σ and π contributions to the metal−ligand bond in terms of interaction energy. The question about the energy contributions of σ and π orbital interactions can be addressed quantitatively using the energy decomposition analysis (EDA) of Morokuma[19] and Ziegler.[20] The advantage of the EDA method is that it gives not only the strength of the covalent (orbital) interactions but also the classical electrostatic (Coloumb) binding. We used the EDA method in recent investigations for a systematic analysis of the metal−ligand interactions in transition-metal complexes.[21,22] We decided to address the question about the strength of the π orbital interactions in group 11 complexes with N-heterocyclic carbene ligands using the EDA approach. In doing so, we have to distinguish between an in-plane π interaction ($\pi_{\parallel}$), which is unimportant for the question of π back-donation, and an out-of-plane π interaction ($\pi_{\perp}$). In-plane and out-of-plane π interactions are illustrated in Chart 1.

Chart 1



in-plane π-interaction ($\pi_{\parallel}$) out-of-plane π-interaction ($\pi_{\perp}$)

In this paper, the following questions are adressed: (i) What is the nature of metal−ligand bonding in the group 11 complexes of imidazol-2-ylidene (**1**)? (ii) What is the difference in metal−ligand bonding in the carbene complexes (**1**)TMCl and the bis(carbene) complexes $(\mathbf{1})_2TM^+$? (iii) What is the amount of $\pi_{\perp}$ bonding between the metal and the imidazol-2-ylidene ligand?

Computational Details

The calculations were performed at the DFT level of theory using the exchange functional of Becke[23] in conjunction with the correlation functional of Perdew[24] (BP86). Scalar relativistic effects have been considered using the zero-order regular approximation[25] (ZORA). Uncontracted Slater-type orbitals were employed as basis functions for the SCF calculations.[26]

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(7) Maasböl, A.; Fischer, E. O. *Angew. Chem.* **1964**, *76*, 645; *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 580.

(8) Boehme, C.; Frenking, G. *Organometallics* **1998**, *17*, 5801.

(9) Tafipolsky, M.; Scherer, W.; Öfele, K.; Artus, G.; Pedersen, B.; Herrmann, W. A.; McGrady, G. S. *J. Am. Chem. Soc.* **2002**, *124*, 5865.

(10) (a) Weskamp, T.; Kohl, F. J.; Hieringer, W.; Gleich, D.; Herrmann, W. A. *Angew. Chem.* **1999**, *111*, 2573; *Angew. Chem., Int. Ed.* **1999**, *38*, 2416. (b) Schwarz, J.; Böhm, V. P. W.; Gardiner, M. G.; Grosche, M.; Herrmann, W. A.; Hieringer, W.; Raudaschl-Sieber, G. *Chem. Eur. J.* **2000**, *6*, 1773. (c) Lee, M.-T.; Hu, C.-H. *Organometallics* **2004**, *23*, 976.

(11) Frison, G.; Sevin, A. *J. Phys. Chem. A* **1999**, *103*, 10998.

(12) Frison, G.; Sevin, A. *J. Organomet. Chem.* **2002**, *643*−*644*, 105.

(13) Frison, G.; Sevin, A. *J. Chem. Soc., Perkin Trans. 2* **2002**, 1692.

(14) Arduengo, A. J., III.; Gamper, S. F.; Calabrese, J. C.; Davidson, F. *J. Am. Chem. Soc.* **1994**, *116*, 4391.

(15) Green, J. C.; Scurr, R. G.; Arnold, P. L.; Cloke, F. G. N. *Chem. Commun.* **1997**, 1963.

(16) Arduengo, A. J., III; Dias, H. V. R.; Calabrese, J. C.; Davidson, F. *Organometallics* **1993**, *12*, 3405.

(17) Tulloch, A. A. D.; Danopoulos, A. A.; Kleinhenz, S.; Light, M. E.; Hursthouse, M. B.; Eastham, G. *Organometallics* **2001**, *20*, 2027.

(18) Hu, X.; Tang, Y.; Gantzel, P.; Meyer, K. *Organometallics* **2003**, *22*, 612.

(19) (a) Morokuma, K. *J. Chem. Phys.* **1971**, *55*, 1236. (b) Kitaura, K.; Morokuma, K. *Int. J. Quantum Chem.* **1976**, *10*, 325.

(20) Ziegler, T.; Rauk, A. *Theor. Chim. Acta* **1977**, *46*, 1.

(21) (a) Diefenbach, A.; Bickelhaupt, F. M.; Frenking, G. *J. Am. Chem. Soc.* **2000**, *122*, 6449. (b) Uddin, J.; Frenking, G. *J. Am. Chem. Soc.* **2001**, *123*, 1683. (c) Chen, Y.; Frenking, G. *Dalton* **2001**, 434. (d) Lein, M.; Frunzke, J.; Timoshkin, A.; Frenking, G. *Chem. Eur. J.* **2001**, *7*, 4155. (e) Doerr, M.; Frenking, G. *Z. Allg. Anorg. Chem.* **2002**, *628*, 843. (f) Frenking, G.; Wichmann, K.; Fröhlich, N.; Grobe, J.; Golla, W.; Le Van, D.; Krebs, B.; Läge, M. *Organometallics* **2002**, *21*, 2921. (g) Frunzke, J.; Lein, M.; Frenking, G. *Organometallics* **2002**, *21*, 3351. (h) Loschen, C.; Voigt, K.; Frunzke, J.; Diefenbach, A.; Diedenhofen, M.; Frenking, G. *Z. Allg. Anorg. Chem.* **2002**, *628*, 1294. (i) Rayón, V. M.; Frenking, G. *Chem. Eur. J.* **2002**, *8*, 4693. (j) Esterhuysen, C.; Frenking, G. *Theor. Chem. Acc.* **2004**, *111*, 381. (k) Esterhuysen, C.; Frenking, G. *Chem. Eur. J.* **2003**, *9*, 3518.

(22) Frenking, G.; Wichmann, K.; Fröhlich, N.; Loschen, C.; Lein, M.; Frunzke, J.; Rayón, V. M. *Coord. Chem. Rev.* **2003**, *238*−*239*, 55.

(23) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.

(24) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822.

(25) (a) Snijders, J. G. *Mol. Phys.* **1978**, *36*, 1789. (b) Snijders, J. G.; Ross, P. *Mol. Phys.* **1979**, *38*, 1909.

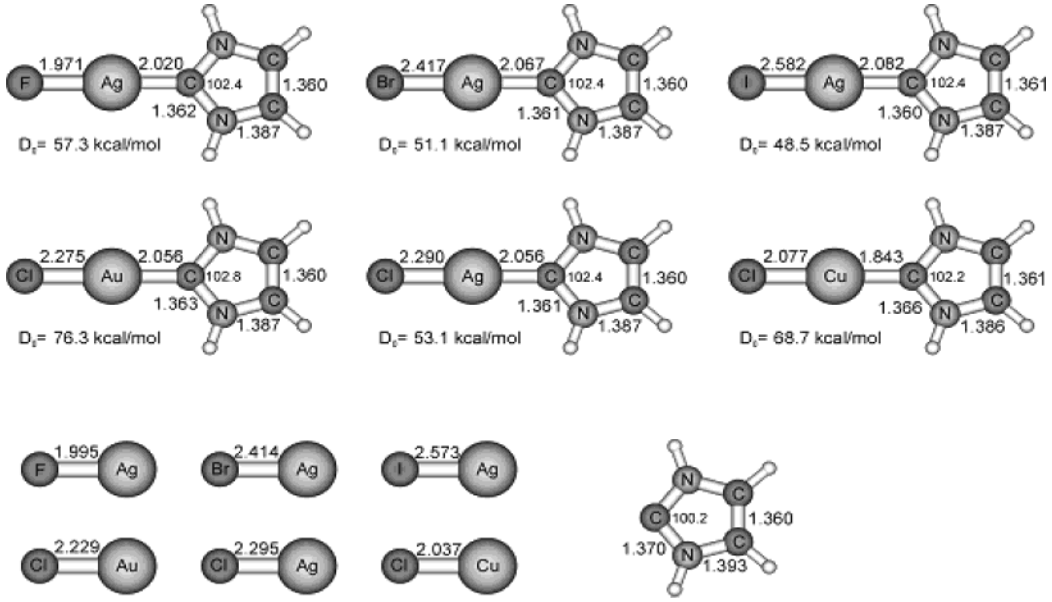

Figure 1. Optimized geometries and dissociation energies at BP86/TZ2P. Bond lengths are given in Å, angles in degrees, and energies in kcal/mol. The D_o values refer to dissociation of one imidazol-1-ylidene ligand **1**.

The basis sets used are of triple-ζ quality augmented by two sets of polarization functions, and a frozen-core approximation was not used. The calculations were carried out with the program package ADF 2003.01.[27] The geometries have been optimized, and the nature of the stationary points was investigated by calculating the vibrational frequencies. The (**1**)TMX compounds and the $(\mathbf{1})_2\mathrm{TM}^+$ compounds with two perpendicular rings are minima on the potential energy surface, while the planar $(\mathbf{1})_2\mathrm{TM}^+$ compounds each have one (very small) imaginary frequency.

The bonding interactions between the molecular fragments A and B of the transition-metal compounds have been analyzed with the energy decomposition scheme implemented in the ADF program package and based on the EDA method of Morokuma and Ziegler. The bond dissociation energy between two fragments is partitioned into several contributions which can be identified as physically meaningful quantities. $\Delta E = -D_e$ is partitioned into the two major components ΔE_{prep} and ΔE_{int}:

$$\Delta E = \Delta E_{\mathrm{prep}} + \Delta E_{\mathrm{int}} \tag{1}$$

ΔE_{prep} is the energy which is necessary to promote the fragments A and B from their equilibrium geometry and electronic state to the geometry and electronic state they have in the compound AB. ΔE_{int} is the instantaneous interaction energy between the two fragments in the molecule. This quantity is the focus of the present work. The interaction energy ΔE_{int} can be divided into three main components:

$$\Delta E_{\mathrm{int}} = \Delta E_{\mathrm{elstat}} + \Delta E_{\mathrm{Pauli}} + \Delta E_{\mathrm{orb}} \tag{2}$$

$\Delta E_{\mathrm{elstat}}$ gives the electrostatic interaction energy between the fragments calculated with the frozen electron density of A and B in the geometry of the complex. $\Delta E_{\mathrm{Pauli}}$ gives the repulsive interactions between the fragments which are caused by the fact that two electrons with the same spin cannot occupy the same region in space. This term comprises the four-electron destabilizing interactions between occupied orbitals. It is calculated by enforcing the Kohn−Sham determinant of the molecule AB, which results from superimposing fragments A and B, to be orthonormal through antisymmetrization and renormalization. The stabilizing orbital interaction term ΔE_{orb} is calculated in the final step of the EDA calculations when the Kohn−Sham orbitals relax to their optimal form. ΔE_{orb} can be further partitioned into contributions from orbitals belonging to different irreducible representations of the point group of the molecule. According to the symmetry of the irreducible representations, it is possible to distinguish between σ, π, and δ contributions to the orbital interaction energy. Details about the EDA method are described in the literature.

Results and Discussion

This section is organized as follows. First, we discuss the geometries and bond dissociation energies of the silver compounds (**1**)AgX with X = F, Cl, Br, I and of the compounds with chlorine ligands (**1**)TMCl with TM = Cu, Ag, Au. Next, we discuss the results for the $[(\mathbf{1})_2\mathrm{TM}]^+$ (TM = Cu, Ag, Au) compounds. Then we present the results of the energy decomposition analysis, first for the (**1**)AgX and the (**1**)TMCl compounds and then for the $[(\mathbf{1})_2\mathrm{TM}]^+$ complexes. We employed two different analyses for the bis(carbene) compounds with perpendicular orientations of the carbene rings. First, we partitioned the complexes into one $[(\mathbf{1})\mathrm{TM}]^+$ fragment and one molecule **1** as another fragment, and in a second analysis the bonding was analyzed in terms of interactions between two molecules of **1** and the TM cation. To distinguish between in-plane and out-of-plane π contributions to the bonding energy, we will then show the results of the EDA calculations for the planar $[(\mathbf{1})_2\mathrm{TM}]^+$ (TM = Cu, Ag, Au) molecules, using the second fragmentation scheme with one fragment of two carbenes and a TM cation.

Geometries and Bond Dissociation Energies. Figure 1 shows the calculated geometries of the halogen complexes (**1**)AgX and (**1**)TMCl, the TMX compounds, and imidazol-2-ylidene **1**. The calculated structure of **1** is in good agreement with experimental results for N- and C-substituted analogues.[16−18,28] The structure of the carbene ring changes only slightly upon binding to the metal. The bonding angle at the $\mathrm{C}_{\mathrm{carbene}}$ atom widens

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[26] Snijders, J. G.; Baerends, E. J.; Vernooijs, P. *At. Nucl. Data Tables* **1982**, *26*, 483.

[27] (a) Bickelhaupt, F. M.; Baerends, E. J. *Rev. Comput. Chem.* **2000**, *15*, 1. (b) te Velde, G.; Bickelhaupt, F. M.; Baerends, E. J.; Fonseca Guerra, C.; van Gisbergen, S. J. A.; Snijders, J. G.; Ziegler, T. *J. Comput. Chem.* **2001**, *22*, 931.

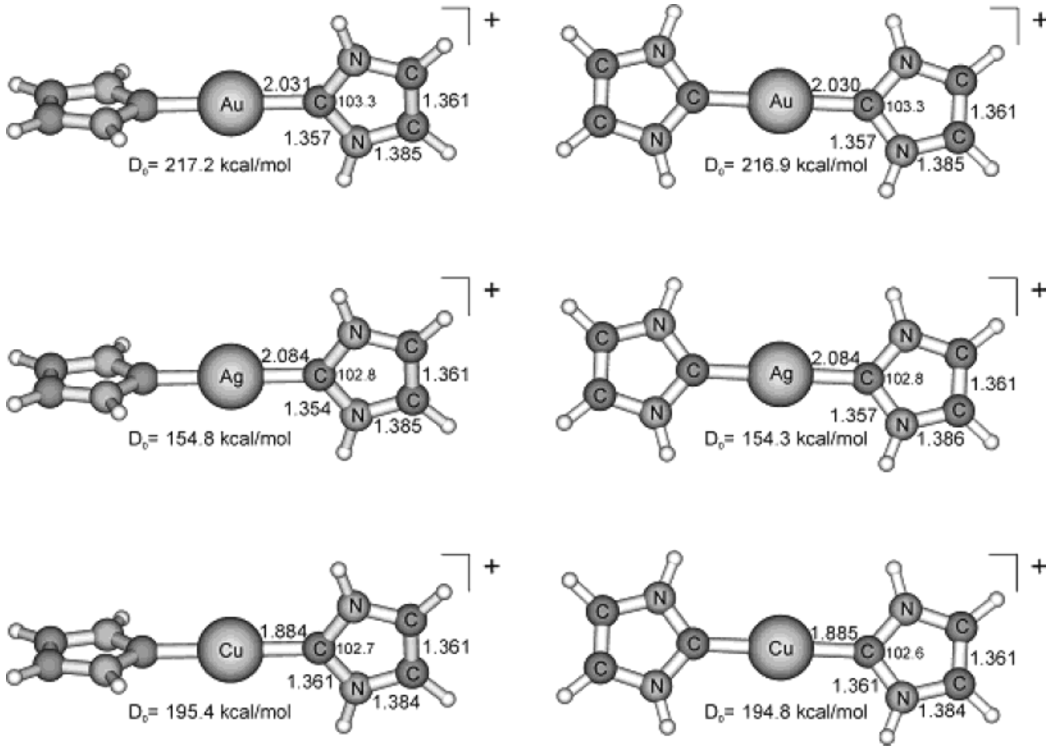

Figure 2. Optimized geometries and dissociation energies at BP86/TZ2P. Bond lengths are given in Ångstroms, angles in degrees, energies in kcal/mol. The D_o values refer to dissociation of two imidazol-1-ylidene ligands **1**.

by 2−3°, and the $C_{carbene}$−N bond length shortens by up to 0.01 Å, as does the $C_{C=C}$−N bond length. The C═C bond distance remains unchanged. This is in agreement with experimental observations for metal complexes of this type of carbene. The changes in the TM−X distances vary. The Ag−Cl and Ag−F bond distances are shorter in the carbene complex than in the free compounds, while the Ag−Br and Ag−I bond distances are longer in the complexes. The differences are smaller for the Ag−Cl and Ag−Br distances than for the Ag−F and Ag−I distances. While the Ag−Cl distance decreases slightly in the complex, both the Cu−Cl and Au−Cl distances are about 0.04 Å longer in the complex than in the free compounds.

Figure 1 also shows the calculated metal−carbene bond dissociation energies of the (**1**)TMX compounds. The metal−carbene bonds are quite strong. For the silver complexes with the different halogen ligands, the bond dissociation energies do not differ much. The Ag−(**1**) bond is strongest in the complex with the fluorine ligand (57.3 kcal/mol) and weakest in the complex with iodine (48.5 kcal/mol). The silver−carbene dissociation energies, albeit still quite high, are the lowest dissociation energies of the investigated complexes. The gold−carbene dissociation energy in (**1**)AuCl is much higher (76.3 kcal/mol), as is the copper−carbene dissociation energy in (**1**)CuCl (68.7 kcal/mol) compared with the silver homologues. The values of our calculated bond dissociation energies agree well with previous MP2 and CCSD(T) energy calculations.[8] The order of the calculated D_e values for the metals is Au > Cu > Ag. This trend is in agreement with the general trend for the bond strengths of the first, second, and third TM rows.[29]

Figure 2 shows the calculated structures of the bis(carbene) complexes $[(\mathbf{1})_2TM]^+$ (TM = Cu, Ag, Au). We investigated two structural isomers of $[(\mathbf{1})_2TM]^+$, one with a perpendicular arrangement of the carbene rings and the other with a coplanar arrangement of the rings. The structures with perpendicular carbene rings are minima on the potential energy surfaces, while the planar structures are marginally higher in energy ($\Delta E \leq 0.5$ kcal/mol), having one imaginary frequency with very small absolute values. The small energy differences between the planar and perpendicular structures could be taken as evidence that the π-contribution to the metal−ligand bonding is negligible. The energy decomposition analysis which is given below shows that this assumption is not justified.

The changes of the ring structure in the $[(\mathbf{1})_2TM]^+$ complexes are more pronounced than in the (**1**)TMCl complexes. The angle at the $C_{carbene}$ atom widens by almost 3°, and the $C_{carbene}$−N bond length shortens by ~0.01 Å, as does the $C_{C=C}$−N bond length. Apart from the rotation of the carbene rings about the Ag−C bonding axis, the geometrical data of the two structures of the bis(carbene) complexes are quasi-identical. The bond dissociation energies for the dissociation of one carbene ligand are also shown in Figure 2. The values of 69.2 ($(\mathbf{1})_2Ag$), 82.4 ($(\mathbf{1})_2Cu$) and 88.5 kcal/mol ($(\mathbf{1})_2Au$) are even higher than for the (**1**)TMCl complexes. Again, the dissociation energies decrease in the order Au > Cu > Ag. The bond dissociation energies for the fragmentation of both metal−carbene bonds into a metal cation

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[28] (a) Guerret, O.; Solé, S.; Gornitzka, H.; Teichert, M.; Trinquier, G.; Bertrand, G. *J. Am. Chem. Soc.* **1997**, *119*, 6668. (b) Wang, H. M. J.; Lin, I. J. B. *Organometallics* **1998**, *17*, 972. (c) Wang, H. M. J.; Chen, C. Y. L.; Lin, I. J. B. *Organometallics* **1999**, *18*, 1216.

[29] Frenking, G.; Antes, I.; Boehme, M.; Dapprich, S.; Ehlers, A.; Jonas, V.; Neuhaus, A.; Otto, M.; Stegmann, R.; Veldkamp, A.; Vyboyshchikov, S. F. In *Reviews in Computational Chemistry*; Lipkowitz, K. B., Boyd, D. B., Eds.; VCH: New York, 1996; Vol. 8, p 63.

Table 1. Energy Decomposition Analysis of the Mixed Carbene−Halogen Complexes (1)-TMX at the BP86/TZ2P Level Using the Carbene Ligand 1 and TMX as Fragments[a]

	(**1**)AgF	(**1**)AgCl	(**1**)AgBr	(**1**)AgI	(**1**)CuCl	(**1**)AuCl
ΔE_{int}	−57.9	−53.6	−51.7	−49.0	−69.5	−77.5
$\Delta E_{\mathrm{Pauli}}$	138.0	127.9	125.7	123.8	126.7	211.3
$\Delta E_{\mathrm{elstat}}{}^{b}$	−153.1	−141.7	−138.2	−134.2	−150.0	−218.6
	(78.2)	(78.1)	(77.9)	(77.7)	(76.4)	(75.7)
$\Delta E_{\mathrm{orb}}{}^{b}$	−42.8	−39.3	−39.2	−38.6	−46.2	−70.2
	(21.8)	(21.9)	(22.1)	(22.3)	(23.6)	(24.3)
$\Delta E_{\mathrm{a_1}}{}^{c}$	−29.8	−28.6	−28.5	−28.7	−28.7	−50.2
	(69.6)	(71.9)	(72.8)	(74.3)	(62.0)	(71.5)
$\Delta E_{\mathrm{a_2}}{}^{c}$	−0.2	−0.2	−0.2	−0.2	−0.1	−0.3
	(0.5)	(0.6)	(0.6)	(0.6)	(0.2)	(0.4)
$\Delta E_{\mathrm{b_1}}{}^{c}$	−4.2	−3.6	−3.4	−3.2	−5.2	−6.5
	(9.7)	(9.0)	(8.8)	(8.3)	(11.2)	(9.3)
$\Delta E_{\mathrm{b_2}}{}^{c}$	−8.6	−7.3	−7.0	−6.5	−12.3	−13.2
	(20.1)	(18.4)	(17.8)	(16.8)	(26.6)	(18.8)
$\Delta E_{\sigma}{}^{c}$	−29.8	−28.6	−28.5	−28.7	−28.7	−50.2
	(69.6)	(71.9)	(72.8)	(74.3)	(62.0)	(71.5)
$\Delta E_{\pi(\parallel)}{}^{c}$	−4.2	−3.6	−3.4	−3.2	−5.2	−6.5
	(9.7)	(9.0)	(8.8)	(8.3)	(11.2)	(9.3)
$\Delta E_{\pi(\perp)}{}^{c}$	−8.6	−7.3	−7.0	−6.5	−12.3	−13.2
	(20.1)	(18.4)	(17.8)	(16.8)	(26.6)	(18.8)
ΔE_{prep}	0.6	0.5	0.6	0.5	0.8	1.2
ΔE ($-D_{\mathrm{e}}$)	−57.3	−53.1	−51.1	−48.5	−68.7	−76.3
$-D_{\mathrm{o}}$	−55.4	−51.4	−49.5	−47.0	−66.9	−74.5

[a] Energies are given in kcal/mol; the symmetry is C_{2v} in all cases. [b] Values in parentheses give the percentage of the total attractive interactions $\Delta E_{\mathrm{elstat}} + \Delta E_{\mathrm{orb}}$. [c] Values in parentheses give the percentage of the total orbital interactions ΔE_{orb}.

Table 2. Energy Decomposition Analysis of the Bis(carbene) Complexes $(1)_2$TM$^+$ (Perpendicular Structure) at the BP86/TZ2P Level Using One Carbene Ligand 1 and (1)TM$^+$ as Fragments[a]

	$(\mathbf{1})_2$Cu$^+$	$(\mathbf{1})_2$Ag$^+$	$(\mathbf{1})_2$Au$^+$
ΔE_{int}	−83.7	−70.1	−91.0
$\Delta E_{\mathrm{Pauli}}$	111.9	114.7	175.6
$\Delta E_{\mathrm{elstat}}{}^{b}$	−146.2	−140.5	−197.7
	(74.7)	(76.0)	(74.1)
$\Delta E_{\mathrm{orb}}{}^{b}$	−49.5	−44.3	−68.9
	(25.3)	(24.0)	(25.9)
$\Delta E_{\mathrm{a_1}}{}^{c}$	−33.0	−32.1	−51.3
	(66.7)	(72.5)	(74.4)
$\Delta E_{\mathrm{a_2}}{}^{c}$	−0.6	−0.7	−0.8
	(1.3)	(1.6)	(1.1)
$\Delta E_{\mathrm{a_1}}{}^{c}$	−5.0	−7.7	−11.1
	(10.2)	(17.3)	(16.1)
$\Delta E_{\mathrm{a_2}}{}^{c}$	−10.8	−3.8	−5.8
	(21.8)	(8.6)	(8.4)
$\Delta E_{\sigma}{}^{c}$	−33.0	−32.1	−51.3
	(66.7)	(72.5)	(74.4)
$\Delta E_{\pi(\parallel)}{}^{c}$	−5.0	−3.8	−5.8
	(10.2)	(8.6)	(8.4)
$\Delta E_{\pi(\perp)}{}^{c}$	−10.8	−7.7	−11.1
	(21.8)	(17.3)	(16.1)
ΔE_{prep}	1.3	0.9	2.5
ΔE ($-D_{\mathrm{e}}$)	−82.4	−69.2	−88.5
$-D_{\mathrm{o}}$	−80.3	−67.0	−86.5

[a] Energies are given in kcal/mol; the symmetry is D_{2d} in all cases. [b] Values in parentheses give the percentage of the total attractive interactions $\Delta E_{\mathrm{elstat}} + \Delta E_{\mathrm{orb}}$. [c] Values in parentheses give the percentage of the total orbital interactions ΔE_{orb}.

and a two-ring fragment are much higher. The D_e values are 195.4, 154.8, and 217.2 kcal/mol for the perpendicular structures of the $[(\mathbf{1})_2\mathrm{Cu}]^+$, $[(\mathbf{1})_2\mathrm{Ag}]^+$, and $[(\mathbf{1})_2\mathrm{Au}]^+$ complexes, respectively, and they differ only by ≤0.5 kcal/mol from the dissociation energies of the planar bis(carbene) complexes.

Energy Decomposition Analysis. Table 1 presents the results of the EDA calculations of the (**1**)AgX (X = F−I) and (**1**)TMCl (TM = Cu, Ag, Au) complexes.

The largest contributions to the ΔE_{int} values come always from the electrostatic interaction term $\Delta E_{\mathrm{elstat}}$, which contributes >75% to the binding energy, while the orbital term contributes <25%. The strength of the interactions in the (**1**)AgX complexes decreases in the order F > Cl > Br > I. The effect of the metal on the TM−carbene bond is larger than the effect of the halogen ligand. For the variation of the metal in the (**1**)TMCl complexes one observes the typical V-like trend for the dissociation energies of TM = Cu, Ag, Au. Note that the absolute values of $\Delta E_{\mathrm{Pauli}}$, $\Delta E_{\mathrm{elstat}}$, and ΔE_{orb} for the gold complex are much larger than for the copper and silver homologues.

ΔE_{orb} can be split up into contributions coming from orbitals of different irreducible representations. The molecular symmetry is C_{2v}, yielding orbitals which belong to a_1, a_2, b_1, and b_2 irreducible representations. With our choice of the mirror planes, b_2 orbitals are in-plane $\pi_{\parallel}$ orbitals and b_1 orbitals are out-of-plane $\pi_{\perp}$ orbitals. The a_2 representation has δ symmetry. a_1-symmetric orbitals have mainly σ symmetry, although there are a few orbitals having δ symmetry. Assuming that the energy contribution from the a_1 (δ) orbitals is very small—of the same magnitude as the energy contribution from the a_2 orbitals—we can specify σ, in-plane $\pi_{\parallel}$, and out-of-plane $\pi_{\perp}$ energy contributions to the orbital symmetry. The total σ, $\pi_{\parallel}$, and $\pi_{\perp}$ contributions to the orbital interaction are listed in Table 1. By far the largest contributions come from σ orbitals, and the in-plane $\pi_{\parallel}$ contributions account for one-third of the total π interaction. The out-of-plane $\pi_{\perp}$ energy contributions constitute ≤20% of the orbital interaction energy in the silver and gold complexes. The latter term is slightly larger in the case of (**1**)CuCl, where the $\pi_{\perp}$ interactions contribute 26.6% to the orbital interactions. Given that the total orbital interaction accounts only for 22−25% of the attractive interaction, this is a rather small contribution, although it is not negligible compared to the σ interaction.

For the perpendicular structure of $(\mathbf{1})_2\mathrm{TM}^+$ we employed two fragmentation schemes. First, we analyzed the dissociation of only one carbene ligand in order to allow for a comparison to the (**1**)TMCl complexes. Then we analyzed a fragmentation scheme into two carbenes and a TM cation in order to investigate the total σ and π bonding more closely. The second fragmentation scheme is also used for the planar structure of the bis(carbene) complexes. The results of the EDA calculations for the dissociation of one carbene ligand are shown in Table 2. As for the (**1**)TMCl complexes, the dissociation energies decrease in the order Au > Cu > Ag. In absolute values, Pauli, electrostatic, and orbital interactions are comparable in the copper and silver bis(carbene) complexes, while they are much higher in the gold compound. The proportion of orbital interactions to the total attractive interaction varies from 24% to 26% and is thus marginally higher than in the (**1**)TMCl compounds. The molecular symmetry of the perpendicular structure of $(\mathbf{1})_2\mathrm{TM}^+$ is D_{2d}, but for the EDA calculations the symmetry is reduced to C_{2v}, because the fragment with the lowest symmetry determines the

Table 3. Energy Decomposition Analysis of the Bis(carbene) Complexes $(\mathbf{1})_2\mathrm{TM}^+$ (Perpendicular Structure) at the BP86/TZ2P Level Using One Carbene Ligand 1 and $(\mathbf{1})\mathrm{TM}^+$ as Fragments[a]

	$(\mathbf{1})_2\mathrm{Cu}^+$	$(\mathbf{1})_2\mathrm{Ag}^+$	$(\mathbf{1})_2\mathrm{Au}^+$
ΔE_{int}	−203.8	−161.3	−224.8
$\Delta E_{\mathrm{Pauli}}$	219.9	226.4	348.8
$\Delta E_{\mathrm{elstat}}{}^{b}$	−290.0	−274.4	−389.4
	(68.4)	(70.8)	(67.9)
$\Delta E_{\mathrm{orb}}{}^{c}$	−133.7	−113.4	−184.2
	(31.6)	(29.2)	(32.1)
$\Delta E_{\mathrm{a1}}{}^{c}$	−71.8	−66.4	−122.0
	(53.7)	(58.5)	(66.2)
$\Delta E_{\mathrm{a_2}}{}^{c}$	−1.0	−0.9	−0.9
	(0.7)	(0.7)	(0.5)
$\Delta E_{\mathrm{b_1}}{}^{c}$	−0.9	−1.4	−1.8
	(0.7)	(1.3)	(1.0)
$\Delta E_{\mathrm{b_2}}{}^{c}$	−20.4	−16.3	−19.9
	(15.3)	(14.3)	(10.8)
$\Delta E_{\mathrm{e}}{}^{c}$	−39.6	−28.5	−39.6
	(29.6)	(25.1)	(21.5)
$\Delta E_{\sigma}{}^{c}$	−92.3	−82.6	−141.9
	(69.0)	(72.9)	(77.0)
$\Delta E_{\pi}{}^{c}$	−39.6	−28.5	−39.6
	(29.6)	(25.1)	(21.5)
ΔE_{prep}	8.4	6.5	7.6
$\Delta E\ (-D_{\mathrm{e}})^{d}$	−195.4	−154.8	−217.2
$-D_{\mathrm{o}}{}^{d}$	−191.4	−151.2	−213.3

[a] Energies are given in kcal/mol; the symmetry is D_{2d} in all cases. [b] Values in parentheses give the percentage of the total attractive interactions $\Delta E_{\mathrm{elstat}} + \Delta E_{\mathrm{orb}}$. [c] Values in parentheses give the percentage of the total orbital interactions ΔE_{orb}. [d] The dissociation energy refers to the reaction $(\mathbf{1})_2\mathrm{TM}^+ \rightarrow \mathrm{TM}^+ + 2\ \mathbf{1}$.

overall symmetry. Thus, the orbital interaction can be split up into contributions of σ and in-plane and out-of-plane π symmetry, similar to the case for the (**1**)TMCl compounds. The copper complex $(\mathbf{1})_2\mathrm{Cu}^+$ has the highest (22%) relative amount of out-of-plane $\pi_\perp$ interaction. In the silver and gold complexes, the out-of-plane $\pi_\perp$ orbitals contribute only 17% and 16% to the orbital interaction term, respectively.

The perpendicular and planar structures were then investigated using the fragmentation into a TM$^+$ cation and a fragment consisting of two carbene ligands. The values for $\Delta E_{\mathrm{Pauli}}$, $\Delta E_{\mathrm{elstat}}$, and ΔE_{orb} are virtually the same for the planar and perpendicular forms. The largest difference is 1.0 kcal/mol for the electrostatic interaction of the gold compounds. The D_{e} values for the dissociation of both carbene ligands are shown in Table 3 (perpendicular structures) and Table 4 (planar structures). The D_{e} values are much higher than for the dissociation of only one ligand, but they show the same V-like trend as before, decreasing in the order Au > Cu > Ag. The attractive forces are dominated by electrostatic interactions $\Delta E_{\mathrm{elstat}}$. ΔE_{orb} contributes ~30% to the attractive interactions. Only the planar structure allows for a separation of the orbital interaction ΔE_{orb} in σ and in-plane $\pi_{\|}$ and out-of-plane $\pi_\perp$ interactions. The molecular symmetry of the planar structure is D_{2h}. Orbitals from the $\mathrm{a_{1g}}$ and $\mathrm{b_{2u}}$ irreducible representations mostly have σ symmetry, although there are very few δ orbitals in the $\mathrm{a_{1g}}$ representation. More δ orbitals come from the $\mathrm{a_{1u}}$ and $\mathrm{b_{2g}}$ irreducible representations. $\mathrm{b_{1g}}$ and $\mathrm{b_{3u}}$ orbitals belong to in-plane $\pi_{\|}$ symmetry, while $\mathrm{b_{1u}}$ and $\mathrm{b_{3g}}$ indicate out-of-plane $\pi_\perp$ orbitals. The total σ, $\pi_{\|}$, and $\pi_\perp$ contributions to the orbital interaction are listed in Table 4. The largest part of ΔE_{orb} come from σ orbitals,[30] and the in-plane $\pi_{\|}$ contributions account for one-third of the total π interaction. The energy resulting from δ orbital interactions is negligible. Thus, the out-of-plane $\pi_\perp$ interactions contribute ≤21% to the orbital interaction energies.

Table 4. Energy Decomposition Analysis of the Bis(carbene) Complexes $(\mathbf{1})_2\mathrm{TM}^+$ (Planar Structure) at the BP86/TZ2P Level Using Two Carbene Ligands $(\mathbf{1})_2$ and TM$^+$ as Fragments[a]

	$(\mathbf{1})_2\mathrm{Cu}^+$	$(\mathbf{1})_2\mathrm{Ag}^+$	$(\mathbf{1})_2\mathrm{Au}^+$
ΔE_{int}	−203.7	−161.3	−224.9
$\Delta E_{\mathrm{Pauli}}$	219.1	226.1	349.8
$\Delta E_{\mathrm{elstat}}{}^{b}$	−289.1	−274.0	−389.9
	(68.4)	(70.7)	(67.9)
$\Delta E_{\mathrm{orb}}{}^{b}$	−133.7	−113.4	−184.7
	(31.6)	(29.3)	(32.1)
$\Delta E_{\mathrm{a_{1g}}}{}^{c}$	−71.8	−67.0	−123.2
	(53.7)	(59.1)	(66.7)
$\Delta E_{\mathrm{b_{1g}}}{}^{c}$	−8.6	−6.6	−9.5
	(6.4)	(5.8)	(5.1)
$\Delta E_{\mathrm{b_{2g}}}{}^{c}$	−0.9	−1.4	−1.8
	(0.7)	(1.3)	(1.0)
$\Delta E_{\mathrm{b_{3g}}}{}^{c}$	−16.9	−11.0	−15.9
	(12.6)	(9.7)	(8.6)
$\Delta E_{\mathrm{a_{1u}}}{}^{c}$	−0.9	−0.9	−0.9
	(0.7)	(0.7)	(0.5)
$\Delta E_{\mathrm{b_{1u}}}{}^{c}$	−10.8	−8.3	−11.0
	(8.1)	(7.3)	(6.0)
$\Delta E_{\mathrm{b_{2u}}}{}^{c}$	−20.5	−15.7	−19.0
	(15.3)	(13.8)	(10.3)
$\Delta E_{\mathrm{b_{3u}}}{}^{c}$	−3.2	−2.6	−3.5
	(2.4)	(2.3)	(1.9)
$\Delta E_{\sigma}{}^{c}$	−92.3	−82.7	−142.2
	(69.0)	(72.9)	(77.0)
$\Delta E_{\pi(\|)}{}^{c}$	−11.8	−9.2	−13.0
	(8.8)	(8.1)	(7.0)
$\Delta E_{\pi(\perp)}{}^{c}$	−27.7	−19.3	−27.0
	(20.7)	(17.0)	(14.6)
ΔE_{prep}	8.9	7.0	8.0
$\Delta E\ (-D_{\mathrm{e}})^{d}$	−194.8	−154.3	−216.9
$-D_{\mathrm{o}}{}^{d}$	−191.0	−150.9	−204.7

[a] Energies are given in kcal/mol; the symmetry is D_{2h} in all cases. [b] Values in parentheses give the percentage of the total attractive interactions $\Delta E_{\mathrm{elstat}} + \Delta E_{\mathrm{orb}}$. [c] Values in parentheses give the percentage of the total orbital interactions ΔE_{orb}. [d] The dissociation energy refers to the reaction $(\mathbf{1})_2\mathrm{TM}^+ \rightarrow \mathrm{TM}^+ + 2\ \mathbf{1}$.

The strength of the out-of-plane $\pi_\perp$ interactions in the planar structures of $(\mathbf{1})_2\mathrm{TM}^+$ seems surprising, considering the very small energy differences (≤5 kcal/mol) between the planar and perpendicular forms. The negligible rotational barrier can be explained by the contribution of the in-plane $\pi_{\|}$ contributions to the metal−ligand interactions. The EDA results in Tables 3 and 4 show that the sum of $\pi_{\|} + \pi_\perp$ interactions in the planar forms have nearly the same strength as the π bonding in the perpendicular forms.

The results of the EDA calculations of the group 11 complexes with N-heterocyclic carbenes may be compared with a recent study of the Fischer carbene complex $(\mathrm{CO})_5\mathrm{W{-}C(OH)_2}$.[4l] The EDA values for the latter complex indicate that the attractive interactions come from 67.3% electrostatic bonding and 32.7% covalent bonding. The latter term has 23.5% out-of-plane $\pi_\perp$ interactions ($\mathrm{b_1}$ orbitals). A comparison with the results of (**1**)TMX given in Table 1 shows that the relative contributions of the overall orbital interactions

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(30) Note that we used the sum of $\mathrm{a_{1g}}$ and $\mathrm{b_{2u}}$ irreducible representations for the energy coming from σ orbitals.

and the $\pi_{\perp}$ contribution to ΔE_{orb} in (**1**)TMX are smaller than in $(CO)_5W-C(OH)_2$ but the difference is not very large. The nature of the metal–carbene bonding is qualitatively not very different for the two cases. The EDA results suggest that $R_2C \leftarrow ML_n$ π back-donation in complexes with N-heterocyclic carbenes is not substantially smaller than in Fischer carbene complexes which have two π donor groups R. We want to point out that the influence of the π donation of R on the $R_2C \leftarrow ML_n$ π back-donation is very large. The EDA result for $(CO)_5W-C(OH)_2$ showed that the orbital term contributes 38.8% to the attractive interaction and the out-of-plane $H_2C \leftarrow W(CO)_5$ $\pi_{\perp}$ interactions (48.5%) are now stronger than the $H_2C \rightarrow W(CO)_5$ σ donation (46.2%).[4m]

Summary and Conclusion

The imidazol-2-ylidene ligand (**1**) is strongly bonded to the group 11 metals in the compounds (**1**)TMX and $[(\mathbf{1})_2TM]^+$. The strongest bonds are calculated for the gold complexes and the weakest for the silver complexes. In the silver halogen complexes, the trend for the metal–carbene bond strengths follows the order F > Cl > Br > I. The energy decomposition analysis indicates that **1** is more electrostatically than covalently bonded to the metals. The electrostatic term $\Delta E_{\mathrm{elstat}}$ contributes 68–78% to the attractive interactions.[31] Thus, according to the EDA model, the metal–carbene bonds are more covalent than electrostatic. In the bis(carbene) complexes, the orbital interactions are slightly more important than in the (**1**)TMX complexes. The out-of-plane $\pi_{\perp}$ interactions contribute ~20% to the total orbital interaction. The EDA results suggest that $R_2C \leftarrow ML_n$ π back-donation in complexes with N-heterocyclic carbenes is not substantially smaller than in Fischer carbene complexes bearing two π donor groups R.

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[31] This does not mean that the metal–ligand bond has a strong ionic character. Large electrostatic contributions may also be found in nonpolar bonds, such as in N_2. For a discussion of this point see refs 21j and 22.