

# N-Heterocyclic Carbene, Silylene, and Germylene Complexes of MCl (M = Cu, Ag, Au). A Theoretical Study<sup>1</sup>

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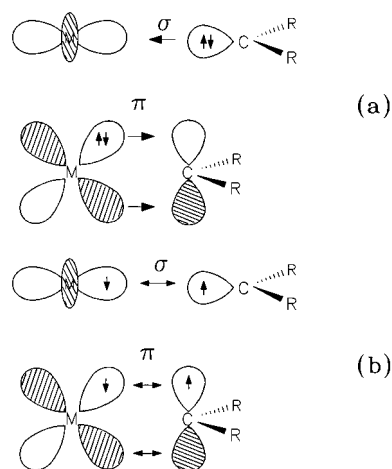
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Quantum chemical calculations at the MP2 level of theory using relativistic ECPs with large valence basis sets for the metals are reported for the complexes of CuCl, AgCl, and AuCl with the N-heterocyclic carbene imidazol-2-ylidene **1** and the related silylene **2** and germylene **3**. The metal–ligand bond dissociation energies are predicted at CCSD(T). The metal–carbene bonds are very strong. The strongest bond is predicted for **1**-AuCl, which has a bond strength  $D_e = 82.8$  kcal/mol. Even the silylene and germylene complexes have substantial bond energies between 37.4 and 64.1 kcal/mol for **2** and between 29.9 and 49.4 kcal/mol for **3**. The trend of the bond energies for the metal fragments is AuCl > CuCl > AgCl, and for the ligands it is **1** > **2** > **3**. The metal–ligand bonds have a strong ionic character which comes from the Coulomb attraction between the positively charged metal atom and the  $\sigma$ -electron pair of the donor atom. The covalent part of the bonding shows little  $\pi$ -back-bonding from the metal to the ligand. The aromaticity of the N-heterocyclic ligands is slightly enhanced in the metal complexes.

## Introduction

There are two types of transition metal compounds with a formal metal–carbon double bond, which are named after the persons who first synthesized them. Fischer-type carbene complexes<sup>2,3</sup> are compounds with a donor–acceptor bond between a low-valent metal fragment  $L_nM$  and a carbene ligand  $CR_1R_2$  where at least one of the ligands R carries a  $\pi$ -donor group.<sup>4</sup> The carbene ligand reacts typically with nucleophilic agents. The metal–ligand bonding in these compounds can be discussed in terms of the familiar Dewar–Chatt–Duncanson model<sup>6</sup> of synergistic  $R_2C \rightarrow ML_n$  donation and  $R_2C \leftarrow ML_n$  back-donation.<sup>7</sup> Schrock-type carbene complexes<sup>8,9</sup> have metals in a high oxidation state and carbene ligands which have usually alkyl groups or



**Figure 1.** Schematic representation of (a) donor–acceptor bonding in Fischer-type carbene complexes and (b) normal covalent bonding in Schrock-type carbene complexes (metallaalkylidenes).

hydrogen atoms as substituents. Although these definitions are not very precise, they have been found helpful to understand the different chemical behaviors of Fischer and Schrock carbene complexes. The carbene group of a Schrock carbene complex reacts usually with electrophilic reagents. It has been suggested that Schrock carbenes should better be considered as metallaalkylidenes  $L_nM=CR_2$ , which have a covalent double bond that is formally formed from a carbene ligand in a triplet state and a triplet metal fragment (Figure 1). This qualitatively different bonding situation, which explains the different chemical behaviors of the two classes of

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(4) Neither the oxidation state of the metal nor the nature of the carbene substituents is a safe criterion to establish if the compound is an alkylidene or a donor–acceptor complex. For example, the low-valent complex  $(PPh_3)_2Cl(NO)Os=CH_2$  reacts with a variety of electrophilic reagents, which is typical for alkylidenes (Schrock type) and not for donor–acceptor complexes (Fischer type).<sup>5</sup> Phenyl substituents at the carbene ligand are found for Fischer and for Schrock carbene complexes. The crucial difference between alkylidenes and donor–acceptor complexes is the electronic configuration at the metal.<sup>10,11,13</sup>

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carbene complexes,<sup>3,9</sup> was suggested in 1984 by Taylor and Hall.<sup>10a</sup> The same bonding picture was suggested by Carter and Goddard using GVB calculations.<sup>10b</sup> The first ab initio work which addressed the difference between Fischer and Schrock complexes was published by Nakatsuji et al.<sup>11</sup> A recent ab initio analysis of the calculated structures of typical Fischer and Schrock carbene complexes using the CDA method<sup>12</sup> supported the model of Taylor and Hall,<sup>10a</sup> although donor–acceptor type interactions were found for negatively charged high-valent (Schrock type) carbene complexes.<sup>13</sup> A similar distinction can also be made between the metal–carbon triple bonds of Fischer and Schrock carbyne complexes, although the differences are not as pronounced as those for the carbene complexes.<sup>14</sup>

Because of the different bonding situations in Fischer and Schrock type complexes, it is not surprising that for some transition metals only one type of carbene complexes is known experimentally, but not the other. For example, until recently only Schrock carbene complexes of titanium were known,<sup>15</sup> while Fischer carbene complexes of Ti could not be made. This is understandable because early transition metals do not have filled d orbitals which are necessary for the crucial  $R_2C \leftarrow ML_n$  back-donation of “classical” Fischer carbene complexes.<sup>16</sup> Further progress in the synthesis of carbene complexes was recently made following the successful isolation of the first stable carbene, i.e. the diadamantyl derivative of the imidazol-2-ylidene **1** reported by Arduengo et al.,<sup>17</sup> which revitalized the chemistry of transition metal complexes with this peculiar type of carbene ligand. Although Fischer-type complexes of **1** with  $Cr(CO)_5$  and  $Hg^{2+}$  were reported in 1968 by Öfele<sup>18</sup> and by Wanzlick et al.,<sup>19</sup> the full potential of this ligand, for which binding properties similar to those of electron-rich phosphanes were found,<sup>20</sup> was only recognized in the last few years.<sup>21</sup>

While typical carbene ligands in Fischer-type complexes are bonded to the metal fragment by significant  $R_2C \leftarrow ML_n$   $\pi$ -back-donation<sup>13,16</sup> similar to that for  $CO$ ,<sup>22,23</sup> the carbene ligand imidazol-2-ylidene **1** apparently binds only through  $R_2C \leftarrow ML_n$   $\sigma$ -donation, while  $\pi$ -back-donation is negligible. The analysis of the properties of transition metal complexes with **1** as ligand

suggests that it is a pure  $\sigma$ -donor.<sup>21,24</sup> 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  $N \rightarrow C_{\text{carbene}} \pi$ -donation, which leads to a highly filled  $p(\pi)$  orbital at the carbene carbon atom.<sup>25,26</sup> Unlike in classical Fischer carbene complexes, there is no need for  $R_2C \leftarrow ML_n$  back-donation to make the complex sufficiently stable to become isolated. The  $N-C-N$  4- $\pi$ -electron delocalization is the dominant factor for the stabilization of the unsaturated carbene **1**, which becomes additionally stabilized by aromatic 6- $\pi$ -electron delocalization.<sup>26</sup> This explains why the saturated analog of **1**, which has a  $CH_2-CH_2$  group instead of  $CH=CH$ ,<sup>27</sup> and later even the acyclic diaminocarbene  $((i\text{-Pr})_2N)_2C$  could be isolated.<sup>28</sup>

The peculiar electronic structure of **1**, which causes it to behave as a  $\sigma$ -only donor, made it possible to prepare the first stable Fischer-type carbene complexes of titanium, among other transition metals.<sup>29</sup> *N,N*-Dimesityl derivatives of **1** were also employed to synthesize the first isolable carbene complexes of the late transition metals copper and silver.<sup>30</sup> Shortly afterward, the first X-ray structure analysis of a copper carbene complex with the related thiazolylidene ligand was reported.<sup>31</sup> While stable carbene complexes of gold were known for a long time,<sup>32</sup> the analogues of the lighter group 11 elements could not be isolated, although Cu and Ag are important catalysts in carbene chemistry.<sup>33</sup> Gold carbene complexes with **1** as ligand have also been prepared.<sup>34</sup> Because of the similar binding properties of **1** and electron-rich phosphanes, transition metal carbene complexes with imidazol-2-ylidene ligands are now being investigated as potential catalysts.<sup>21</sup>

The nature of the metal–ligand binding in carbene complexes of **1** has been deduced from the properties of the complexes, but no theoretical analysis of such compounds has yet been reported. Also, there are no data available for the bond strengths of carbene complexes of imidazol-2-ylidenes. A similar situation exists for the silylene and germylene analogues **2** and **3** of the carbene **1**, which were synthesized shortly after

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Arduengo reported his work.<sup>35,36</sup> Transition metal complexes of **2**<sup>37</sup> and **3**<sup>36</sup> have been isolated, and it was suggested, that **2** and **3** have little  $\pi$ -back-bonding. We decided to carry out quantum mechanical ab initio calculations of CuCl, AgCl, and AuCl complexes with **1–3** (R = H) as ligands. The synthesis of **1-CuCl**, **1-AgCl**, and **1-AuCl** was announced very recently, but we could not find a detailed report.<sup>21,29a</sup>

The following questions are addressed in our paper: (1) How strong are the **1-MCl** bonds? (2) What is the nature of the metal–ligand bond in the MCl complexes of **1**? (3) What are the differences in the metal–ligand bonding between the carbene complexes **1-MCl** and the silylene and germylene analogues **2-MCl** and **3-MCl**? (4) What predictions can be made about the stability of **2-MCl** and **3-MCl**?

## Methods

The geometries of the molecules were optimized at the MP2 level of theory<sup>38</sup> with the following basis sets. A 6-31G(d) basis set<sup>39</sup> was employed for the first-, second-, and third-row elements H, C, N, Si, and Cl. Quasi-relativistic ECPs were used for Ge and the transition metals Cu, Ag, and Au. The valence basis set for the 4s and 4p electrons of Ge has the same quality as the all-electron basis sets of the other main group elements, i.e. (31/31/1). It was optimized by the Stuttgart group.<sup>40</sup> The d-type polarization function of Ge has an exponent of  $\zeta = 0.246$ .<sup>41</sup> The small-core ECPs for the transition metals have a valence shell of triple- $\zeta$  quality (311111/22111/411).<sup>42</sup> To obtain more accurate binding energies, we carried out single-point energy calculations of the complexes **1-CuCl–3-AuCl** and the fragments **1–3** and MCl using coupled-cluster theory at the CCSD(T) level<sup>43</sup> with the same basis sets.

Inspection of the metal–ligand donor–acceptor interactions was performed using the charge-decomposition analysis (CDA).<sup>12</sup> In the CDA method, the (canonical, natural, or Kohn–Sham) molecular orbitals of the complex are expressed in terms of the MOs of appropriately chosen fragments. In the present case, the natural orbitals (NO) of the MP2 wave functions are formed in the CDA calculations as a linear combination of the MOs of **1–3** and the MCl fragment in the geometry of the complex. The orbital contributions are divided into three parts: (i) the mixing of the occupied MOs of **1–3** (**D**) and the unoccupied MOs of MCl ( $\sigma$ -donation **D**  $\rightarrow$  MCl); (ii) the mixing of the unoccupied MOs of **D** and the occupied MOs of MCl ( $\pi$ -back-donation **D**  $\leftarrow$  MCl); and (iii) the mixing of the occupied

MOs of **D** and the occupied MOs of MCl (repulsive polarization **D**  $\leftrightarrow$  MCl). A more detailed presentation of the method and the interpretation of the results is given in reference 12. Further examples where the CDA method was helpful to elucidate the binding in donor–acceptor complexes of transition metal complexes and main group elements have been published somewhere else.<sup>13,14,23,44</sup> The CDA calculations have been performed using the program CDA 2.1.<sup>45</sup>

The charge distribution in the compounds was calculated with the NBO partitioning scheme.<sup>46</sup> We also analyzed the bonding situation in the complexes with the help of the topological analysis of the electron density distribution.<sup>47</sup> The aromaticity in the free and complexed imidazol-2-ylidene ring was estimated via the NICS (Nuclear Independent Chemical Shift) procedure suggested by Schleyer et al.<sup>48</sup> The calculations have been carried out with the program packages Gaussian 94,<sup>49</sup> ACES II,<sup>50</sup> and Turbomole.<sup>51</sup>

## Geometries and Energies

Figure 2 shows the theoretically predicted geometries of the complexes **1-CuCl–3-AuCl** and the fragments **1–3**, CuCl, AgCl, and AuCl. There are no experimental geometries for **1-CuCl–3-AuCl** known to us, but a comparison of the theoretical structures with experimental geometries of related complexes indicates that the calculated values are quite accurate. The theoretically predicted Cu–C distance of **1-CuCl** (1.848 Å) is slightly shorter than the value found in the X-ray structure analysis of the thiazolyldiene analogue of **1-CuCl** (Cu–C = 1.888(6) Å).<sup>31</sup> The difference between calculated and experimental values may be due to the slightly different carbene ligand and to the fact that the experimental copper carbene complex is a weakly bonded dimer where the monomers are connected by long intermolecular Cu–Cl “bonds”. This could lead to slightly longer Cu–C distances. Also, the calculated Cu–Cl bond length of **1-CuCl** (2.077 Å) is somewhat shorter than the experimental value (2.122(2) Å).<sup>31</sup>

The calculated bond lengths of **1-AgCl** are in nearly perfect agreement with the experimental values for the

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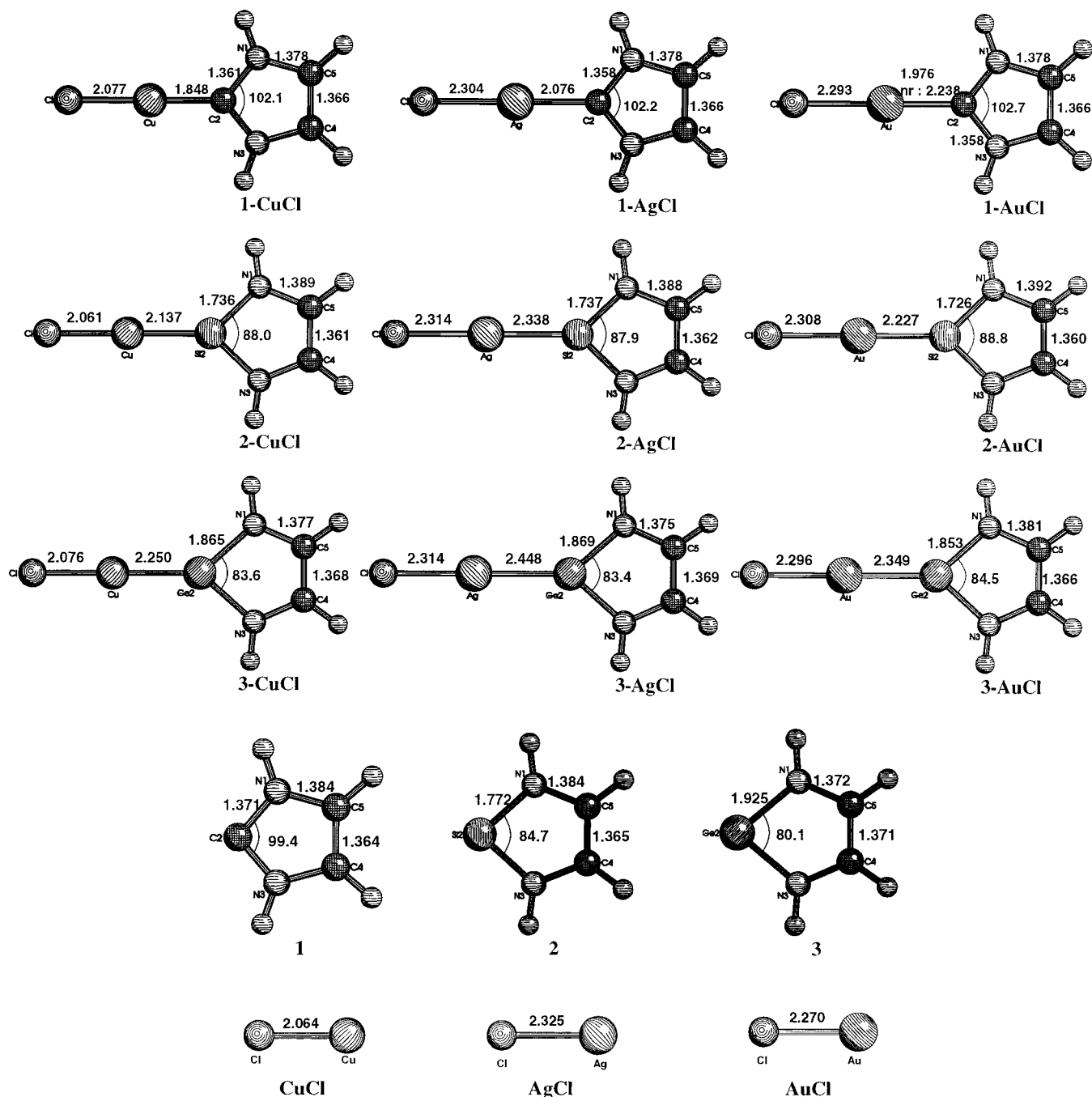
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**Figure 2.** Optimized geometries of the compounds at the MP2 level. Bond lengths are given in angstroms; angles, in degrees.

homoleptic bis(carbene) complex  $1_2\text{Ag}^+$ , which has *N*-mesityl groups in **1**.<sup>30</sup> The distances are Ag–C = 2.076 Å (exp 2.067(4) and 2.078(4) Å), C2–N1 = 1.358 Å (exp 1.352(6)–1.360(6) Å), N1–C5 = 1.378 Å (exp 1.390(6)–1.399(6) Å), and C4–C5 = 1.366 Å (exp 1.329(7)–1.330(7) Å). The calculations predict that the Au–C bond of the gold complex **1-AuCl** (1.976 Å) should be clearly *shorter* than the Ag–C bond of **1-AgCl** (2.076 Å). This is in agreement with experimental values. The experimentally observed Au–C distance of the substituted analogue of **1-AuCl** where the substituents at nitrogen are R = benzyl and R' = benzoyl is 1.97(1) Å, which is in perfect agreement with our calculated value.<sup>34c</sup> Slightly longer Au–C bond lengths between 1.99 Å and 2.027 Å (average) have been reported for related bis(carbene) complexes of gold  $1_2\text{Au}^+$  with

different substituents at the carbene ligands.<sup>34a,b,d</sup> Thus, the calculated geometries of the carbene complexes of **1** with CuCl, AgCl, and AuCl should be quite reliable. Although there are no experimental data available to judge the accuracy of the theoretical geometries of the silylene and germylene complexes **2-MCl** and **3-MCl**, we think that they should also be close to the correct values.

The calculated values for the free ligands **1–3** have been discussed previously.<sup>26</sup> They are in good agreement with experimental results for *N*- and *C*-substituted analogues.<sup>17,35,36,53</sup> We wish to point out the changes in

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**Table 1. Calculated Total Energies  $E_{\text{tot}}$  and Bond Dissociation Energies  $D_e$  at the MP2 and CCSD(T) Levels**

molecule	no.	MP2		CCSD(T)	
		$E_{\text{tot}}^b$	$D_e^c$	$E_{\text{tot}}^b$	$D_e^c$
ClCu-C <sub>3</sub> H <sub>4</sub> N <sub>2</sub>	<b>1-CuCl</b>	-881.82621	76.3	-881.81571	67.4
ClAg-C <sub>3</sub> H <sub>4</sub> N <sub>2</sub>	<b>1-AgCl</b>	-831.43702	61.2	-831.55675	56.5
ClAu-C <sub>3</sub> H <sub>4</sub> N <sub>2</sub>	<b>1-AuCl</b>	-820.16515	88.6	-820.21972	82.8
ClAu-C <sub>3</sub> H <sub>4</sub> N <sub>2</sub> , nr <sup>a</sup>	<b>1-AuCl</b>	-816.14887	49.5		
ClCu-SiC <sub>2</sub> H <sub>4</sub> N <sub>2</sub>	<b>2-CuCl</b>	-1132.87953	52.7	-1132.87475	45.1
ClAg-SiC <sub>2</sub> H <sub>4</sub> N <sub>2</sub>	<b>2-AgCl</b>	-1082.49675	41.5	-1082.62086	37.4
ClAu-SiC <sub>2</sub> H <sub>4</sub> N <sub>2</sub>	<b>2-AuCl</b>	-1071.22414	68.5	-1071.28741	64.1
ClCu-GeC <sub>2</sub> H <sub>4</sub> N <sub>2</sub>	<b>3-CuCl</b>	-847.61307	39.5	-847.60915	35.1
ClAg-GeC <sub>2</sub> H <sub>4</sub> N <sub>2</sub>	<b>3-AgCl</b>	-797.23619	33.0	-797.35907	29.9
ClAu-GeC <sub>2</sub> H <sub>4</sub> N <sub>2</sub>	<b>3-AuCl</b>	-785.95309	53.5	-786.01130	49.4

<sup>a</sup> Calculation with nonrelativistic ECP. <sup>b</sup> Atomic units. <sup>c</sup> kcal/mol.

the fragment geometries of **1–3** and MCl in the complexes. Figure 2 shows that the ring internal angles at the donor atoms of **1–3** (C, Si, Ge) become larger in the complexes and that the bond lengths X–N (X = C, Si, Ge) in the complexes are smaller than in the free ligands. This is in agreement with experimental observations for the carbene complexes. For example, the N1–C2–N3 angle of **1**<sub>2</sub>Ag<sup>+</sup> with *N*-mesityl groups in **1** is 104.2° (average value) and the C2–N1/3 distance is 1.356 Å (average value).<sup>30</sup> The N1–C2–N3 angle is larger and the C2–N1/3 bond is shorter than those in the free carbene. The trend of the changes in the M–Cl distances when one compares the complexes with free MCl is interesting. The Au–Cl distance becomes longer in the complexes and the Ag–Cl bond becomes shorter, while the Cu–C bond of the complexes is longer in **1-CuCl** and **3-CuCl** but slightly shorter in **2-CuCl** (Figure 2). This indicates that the metal–ligand interactions are probably determined by more than one factor. This will be discussed below.

Table 1 shows the calculated total energies and metal–ligand bond dissociation energies. We did not correct the theoretical bond energies for basis set superposition errors because previous studies have shown that uncorrected CCSD(T) values using valence basis sets similar to those in this work give highly accurate ( $\pm 3$  kcal/mol) dissociation energies for electronically saturated transition metal complexes.<sup>44f,54,55</sup> The CCSD(T) values shown in Table 1 indicate that the **1-MCl** complexes have very strong metal–carbene bonds. The theoretically predicted metal–carbene bond energy for **1-AuCl** ( $D_e = 82.8$  kcal/mol) is even higher than the calculated value for the classical Fischer complex (CO)<sub>5</sub>W–CH(OH) ( $D_e = 75.0$  kcal/mol).<sup>13</sup> This is remarkable because the metal–carbene interactions of **D-MCl** have little **D** ← MCl  $\pi$ -back-donation, which is generally believed to be essential for the stability of Fischer-type complexes. It becomes clear that transition metal donor–acceptor complexes with carbene ligands can have very strong bonds even when the **D** ← MCl  $\pi$ -back-donation is negligible.

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**Table 2. Results of the CDA Calculations at MP2: **D** → MCl Donation  $d$ , **D** ← MCl Back-donation  $b$ , Ratio  $d/b$ , and **D** ↔ MCl Repulsive Polarization  $r$** 

molecule	no.	$d$	$b$	$d/b$	$r$
ClCu-C <sub>3</sub> H <sub>4</sub> N <sub>2</sub>	<b>1-CuCl</b>	0.538	0.081	6.64	-0.128
ClAg-C <sub>3</sub> H <sub>4</sub> N <sub>2</sub>	<b>1-AgCl</b>	0.446	0.046	9.70	-0.131
ClAu-C <sub>3</sub> H <sub>4</sub> N <sub>2</sub>	<b>1-AuCl</b>	0.396	0.091	4.35	-0.273
ClCu-SiC <sub>2</sub> H <sub>4</sub> N <sub>2</sub>	<b>2-CuCl</b>	0.740	0.156	4.74	-0.114
ClAg-SiC <sub>2</sub> H <sub>4</sub> N <sub>2</sub>	<b>2-AgCl</b>	0.714	0.162	4.41	-0.053
ClAu-SiC <sub>2</sub> H <sub>4</sub> N <sub>2</sub>	<b>2-AuCl</b>	0.622	0.286	2.17	-0.066
ClCu-GeC <sub>2</sub> H <sub>4</sub> N <sub>2</sub>	<b>3-CuCl</b>	0.693	0.106	6.54	-0.100
ClAg-GeC <sub>2</sub> H <sub>4</sub> N <sub>2</sub>	<b>3-AgCl</b>	0.490	0.094	5.21	-0.059
ClAu-GeC <sub>2</sub> H <sub>4</sub> N <sub>2</sub>	<b>3-AuCl</b>	0.527	0.168	3.14	-0.126

The calculated  $D_e$  values show for the metals the order Au > Cu > Ag. This is in agreement with the general trend for the bond strengths of the first, second, and third TM rows.<sup>54</sup> The same trend is calculated for the silylene and germylene complexes of MCl (Table 1). The trend for the bond strengths of the carbene, silylene, and germylene metal complexes is C > Si > Ge. However, even the germylene complex **3-AuCl** is predicted to have a rather high bond dissociation energy,  $D_e = 49.4$  kcal/mol. It follows that transition metal complexes of silylene **2** and germylene **3** have strong donor–acceptor bonds. The MP2 values for the metal–ligand bond energies are always higher than the CCSD(T) values, but they show the same trend. This behavior has been found before,<sup>54</sup> and the use of the much less expensive MP2 method was suggested to estimate CCSD(T) values for bond energies using an isostructural correction scheme.<sup>56</sup>

### Analysis of the Bonding Situation

Table 2 shows the CDA results for the complexes. The most important result is the finding that the **D** → MCl (**D** = **1**, **2**, **3**) donation is always significantly larger than the **D** ← MCl back-donation. We wish to emphasize that the absolute values for the donation and back-donation are not important; relevant is the  $d/b$  ratio. The **1** ← MCl back-donation in the carbene complexes is negligible, particularly in the silver complex **1-AgCl**. The CDA results confirm the previous suggestion that **1** is a pure  $\sigma$ -donor.<sup>21,24</sup> The somewhat lower  $d/b$  ratio of the gold complex **1-AuCl** indicates some **1** ← AuCl back-donation. This can be explained with the effect of relativity, which leads to a contraction of the s and p orbitals but to more diffuse d and f orbitals.<sup>57</sup> Relativistic effects are particularly strong in gold compounds.<sup>57,58</sup> The extent of **1** ← MCl back-donation is significantly smaller than in typical Fischer carbene complexes such

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(61) The reader should not confuse the atomic charge distribution with the dipole moment of CO. Carbon monoxide has a very low dipole moment (0.11 D), with the negative end at the carbon side.<sup>62</sup> The measured dipole moment is the resulting vector along the C–O axis from the 3-dimensional charge distribution, which has a significant concentration at oxygen in the  $\pi$ -region. The charge distribution of the  $\sigma$ -symmetric HOMO of CO, which has its largest extension at the more diffuse carbon end, overcompensates, because of its shape, the higher charge concentration at the more compact oxygen atom.

**Table 3. Results of the NBO Partitioning Scheme: Population of the  $\pi$ -Symmetric p Orbital of X (X = C, Si, Ge)  $p_{\pi}(X)$ , Charges of Atom X  $q(X)$ , of Metal M  $q(M)$ , and of the MCl Fragment  $q(MCl)$ , and Wiberg Bond Indices  $P(M-X)$  and  $P(X-N)$** 

molecule	no.	$p_{\pi}(X)$	$q(X)$	$q(M)$	$q(MCl)$	$P(M-X)$	$P(X-N)$
ClCu-C <sub>3</sub> H <sub>4</sub> N <sub>2</sub>	<b>1-CuCl</b>	0.84	-0.02	0.54	-0.16	0.451	1.206
ClAg-C <sub>3</sub> H <sub>4</sub> N <sub>2</sub>	<b>1-AgCl</b>	0.83	-0.01	0.54	-0.18	0.405	1.218
ClAu-C <sub>3</sub> H <sub>4</sub> N <sub>2</sub>	<b>1-AuCl</b>	0.86	0.04	0.38	-0.24	0.591	1.202
ClCu-SiC <sub>2</sub> H <sub>4</sub> N <sub>2</sub>	<b>2-CuCl</b>	0.59	1.00	0.48	-0.23	0.612	0.780
ClAg-SiC <sub>2</sub> H <sub>4</sub> N <sub>2</sub>	<b>2-AgCl</b>	0.60	0.98	0.50	-0.22	0.513	0.788
ClAu-SiC <sub>2</sub> H <sub>4</sub> N <sub>2</sub>	<b>2-AuCl</b>	0.59	1.11	0.32	-0.33	0.762	0.775
ClCu-GeC <sub>2</sub> H <sub>4</sub> N <sub>2</sub>	<b>3-CuCl</b>	0.65	0.88	0.49	-0.21	0.489	0.790
ClAg-GeC <sub>2</sub> H <sub>4</sub> N <sub>2</sub>	<b>3-AgCl</b>	0.67	0.84	0.53	-0.19	0.410	0.794
ClAu-GeC <sub>2</sub> H <sub>4</sub> N <sub>2</sub>	<b>3-AuCl</b>	0.64	0.98	0.32	-0.30	0.620	0.788
C <sub>3</sub> H <sub>4</sub> N <sub>2</sub>	<b>1</b>	0.67	0.06				1.120
SiC <sub>2</sub> H <sub>4</sub> N <sub>2</sub>	<b>2</b>	0.54	0.87				0.747
GeC <sub>2</sub> H <sub>4</sub> N <sub>2</sub>	<b>3</b>	0.63	0.78				0.744
CuCl				0.71			
AgCl				0.74			
AuCl				0.54			

**Table 4. Results of the Topological Analysis of the Electron Density Distribution: Electron Density at the Bond Critical Point  $\rho_c$  ( $\text{\AA}^{-3}$ ), Laplacian of the Electron Density at the Bond Critical Point  $\nabla^2\rho_c$  ( $\text{\AA}^{-5}$ ), and Energy Density at the Bond Critical Point  $H_c$  ( $\text{au}/\text{\AA}^3$ )**

molecule	no.	$\rho_c$			$\nabla^2\rho_c$			$H_c$		
		M-Cl	M-X	X-N	M-Cl	M-X	X-N	M-Cl	M-X	X-N
ClCu-C <sub>3</sub> H <sub>4</sub> N <sub>2</sub>	<b>1-CuCl</b>	0.688	0.882	2.100	9.368	11.076	-14.283	-0.185	-0.338	-3.461
ClAg-C <sub>3</sub> H <sub>4</sub> N <sub>2</sub>	<b>1-AgCl</b>	0.564	0.713	2.111	6.500	7.914	-13.611	-0.137	-0.236	-3.492
ClAu-C <sub>3</sub> H <sub>4</sub> N <sub>2</sub>	<b>1-AuCl</b>	0.652	1.000	2.128	6.173	7.900	-15.329	-0.207	-0.497	-3.524
ClCu-SiC <sub>2</sub> H <sub>4</sub> N <sub>2</sub>	<b>2-CuCl</b>	0.687	0.627	0.797	9.337	1.482	16.906	-0.182	-0.282	-0.254
ClAg-SiC <sub>2</sub> H <sub>4</sub> N <sub>2</sub>	<b>2-AgCl</b>	0.547	0.552	0.796	6.512	0.942	16.891	-0.124	-0.236	-0.254
ClAu-SiC <sub>2</sub> H <sub>4</sub> N <sub>2</sub>	<b>2-AuCl</b>	0.624	0.732	0.815	6.224	-2.657	17.397	-0.182	-0.500	-0.265
C <sub>3</sub> H <sub>4</sub> N <sub>2</sub>	<b>1</b>			1.997			-9.106			-3.247
SiC <sub>2</sub> H <sub>4</sub> N <sub>2</sub>	<b>2</b>			0.729			14.795			-0.222

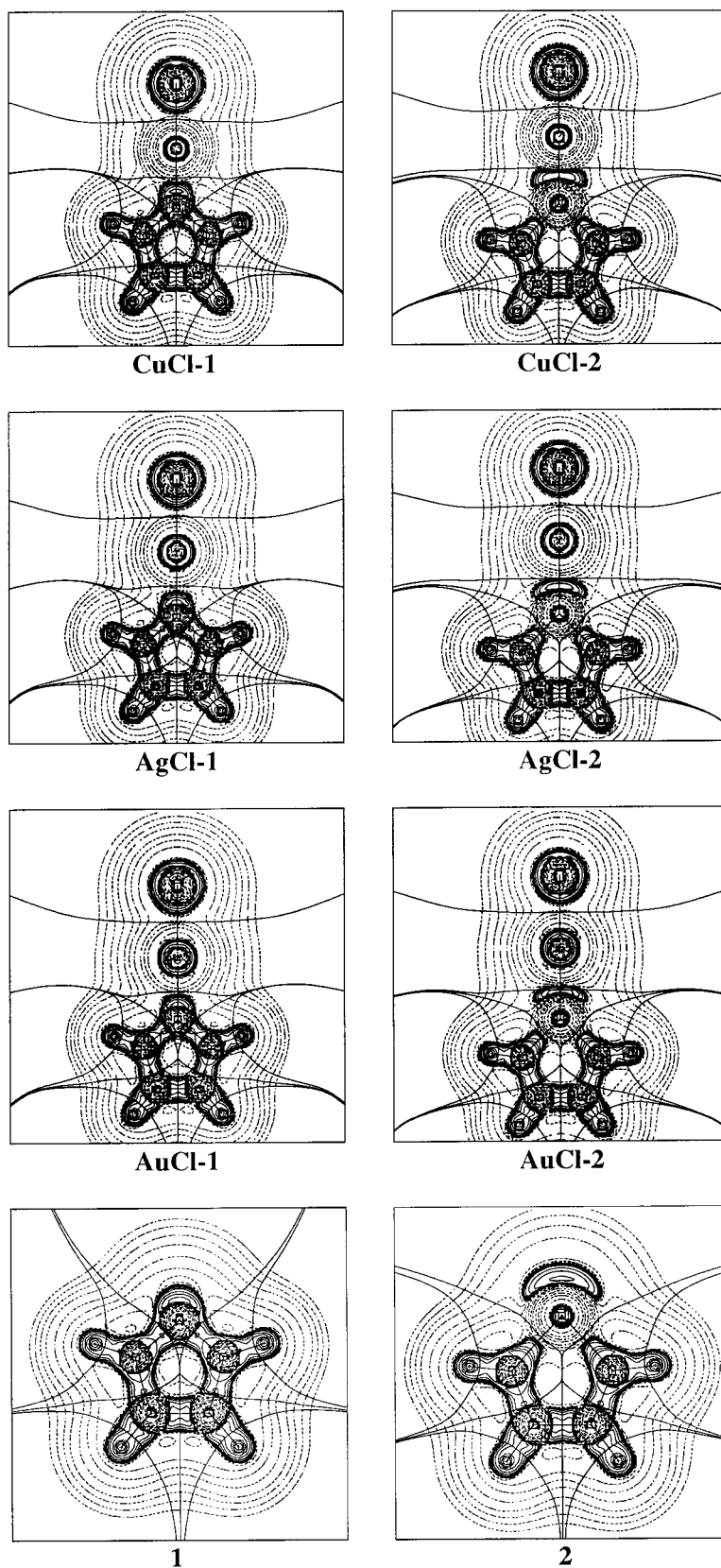
as (CO)<sub>5</sub>W(CRR') with R, R' = H, F, OH, which have  $d/b$  ratios between 1.11 and 2.36.<sup>13</sup> The values for **1-MCl** are between 4.35 and 9.70 (Table 2). The influence of **D**  $\leftarrow$  MCl back-donation becomes somewhat stronger in the silylene and germylene complexes, but the **D**  $\rightarrow$  MCl donation remains the dominant term. Thus, the M-C, M-Si, and M-Ge bonding in the complexes **D-MCl** can be sketched as for the Fischer carbene complexes shown in Figure 1a, but with the  $\sigma$ -donor contribution as the most important factor.

Table 3 shows the results of the NBO partitioning scheme and the Wiberg bond indices. The carbon atom of the free carbene ligand **1** is nearly neutral, while Si and Ge in **2** and **3** carry large positive charges. Table 3 shows also that the  $p(\pi)$  population of the donor atom X = C, Si, Ge is enhanced in the complexes compared to the free ligands. The increase is particularly strong in the carbene complexes but less so in the silylene and germylene analogues. The additional  $p(\pi)$  charge is not due to X  $\leftarrow$  MCl back-donation, but rather to stronger N  $\rightarrow$  X  $\pi$ -donation in the ligands. This becomes obvious from the bond orders for the X-N bond, which are higher in the complexes than in the free ligands. The X  $\rightarrow$  MCl  $\sigma$ -donation causes the donor atoms X to become more electron deficient, which in turn induces stronger N  $\rightarrow$  X  $\pi$ -donation. This explains the shortening of the X-N bonds in the complexes. Further proof that the X-N bond shortening is an indirect effect of the X  $\rightarrow$  M  $\sigma$ -donation comes from the change in the geometry when a proton is attached to the carbene carbon atom of **1**. The N-C<sub>carbene</sub> bond length of **1H**<sup>+</sup> at MP2/6-31G(d) is 1.339 Å, which is 0.032 Å shorter than that in **1**.<sup>52</sup>

We investigated the alteration in the electronic structure of the donor ligands **1** and **2** and the metal fragments MCl when the complexes **1-MCl** and **2-MCl** are formed<sup>63</sup> with the help of the topological analysis of the electron density distribution,<sup>47</sup> in order to estimate the ionic or covalent character of the donor-acceptor bonds. It was found that the energy density at the bond critical point of a chemical bond  $H_c$  indicates nicely the nature of the bonding interactions. A covalent bond has strongly negative values for  $H_c$ , while closed-shell interactions between ions and in van der Waals complexes have  $H_c$  values which are zero or even positive.<sup>59</sup> Figure 3 shows the Laplacian distribution of the complexes and the ligands **D** in the molecular plane. The area of charge concentration ( $\nabla^2\rho(\mathbf{r}) < 0$ , solid lines) at the donor atoms pointing toward the metal atoms, which indicates the donor electron pair, is somewhat distorted in the complexes as the results of the binding interactions. Visual inspection of Figure 3 shows that the distortion is less in the silver complexes than in the copper and gold complexes. This indicates that the silver compounds have a more ionic metal-ligand bond than the copper and gold compounds. This is supported by the calculated values of the energy densities at the bond critical points for the metal-ligand bonds (Table 4). The  $H_c$  values for the **D-AgCl** bonds are less negative than those for the copper and gold analogues. A comparison of the absolute values for  $H_c$  underlines the significantly ionic character of the M-Cl, M-X, and Si-N bonds compared to the C-N bond (Table 4). A somewhat higher covalent character is found for the Au-X bonds

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(63) The germanium complexes have not been analyzed because the ECP at Ge may lead to erroneous results for the topological analysis of the electron density distribution.



**Figure 3.** Contour line diagrams of the Laplacian distribution  $\nabla^2\rho(\mathbf{r})$  of the copper and silver complexes of **1** and **2** and the free ligands **1** and **2**. Dashed lines indicate charge depletion ( $\nabla^2\rho(\mathbf{r}) > 0$ ); solid lines indicate charge concentration ( $\nabla^2\rho(\mathbf{r}) < 0$ ). The solid lines connecting the atomic nuclei are the bond paths, and the solid lines separating the atomic nuclei indicate the zero-flux surfaces in the molecular plane.

than for Cu–X and Ag–X. It follows that the metal–ligand bonds in **D-MCl** are largely ionic, but the covalent contributions are not negligible.

We evaluated the change in the aromaticity from the free to the complexed ligands **1–3**. Recent theoretical studies showed that the high stability of **1–3** is mainly

**Table 5. Results of the NICS Calculations at RHF/TZ**

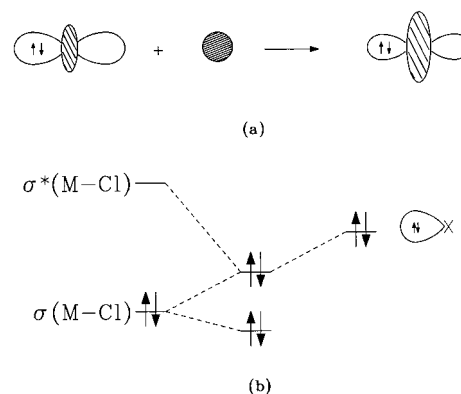
molecule	no.	NICS	molecule	no.	NICS
ClCu–C <sub>3</sub> H <sub>4</sub> N <sub>2</sub>	<b>1-CuCl</b>	-14.2	C <sub>3</sub> H <sub>4</sub> N <sub>2</sub>	<b>1</b>	-13.7
ClCu–SiC <sub>2</sub> H <sub>4</sub> N <sub>2</sub>	<b>2-CuCl</b>	-10.4	SiC <sub>2</sub> H <sub>4</sub> N <sub>2</sub>	<b>2</b>	-10.2
ClCu–GeC <sub>2</sub> H <sub>4</sub> N <sub>2</sub>	<b>3-CuCl</b>	-11.3	GeC <sub>2</sub> H <sub>4</sub> N <sub>2</sub>	<b>3</b>	-10.8

due to N–X–N delocalization, which gains additional support from aromatic stabilization through the 6- $\pi$ -electron delocalization in the ring.<sup>25,26</sup> The degree of aromaticity might become higher in the **D-MCl** complexes because the N  $\rightarrow$  X  $\pi$ -donation is larger in the complexes than in the free ligands. This could lead to enhanced ring delocalization. Indeed, the NMR chemical spectra of the bis(carbene) complexes **1**<sub>2</sub>M<sup>+</sup> (M = Cu, Ag) with *N*-mesityl groups showed a substantial downfield shift for the imidazole ring protons compared to those of the free ligands, which could mean a higher degree of delocalization in the complexed imidazole rings.<sup>30</sup> We investigated the degree of aromaticity in free and CuCl-complexed **1–3** using the calculated NICS (nuclear independent chemical shift) values, which were introduced by Schleyer as a measure for aromaticity.<sup>48</sup> The values for the silver and gold complexes should be very similar and, therefore, have not been calculated.

It has been shown that classical aromatic compounds such as benzene and pyridine have strongly negative chemical shifts at the center of the ring, while antiaromatic compounds have positive shifts. Nonaromatic compounds have chemical shifts of about 0 ppm. Table 5 shows our calculated NICS values at the center of the rings. The NICS values for **1–3** may be compared with the calculated value of the cyclopentadienyl anion C<sub>5</sub>H<sub>5</sub><sup>-</sup> (-14.3 ppm), which may serve as comparison for a five-membered-aromatic compound.<sup>48</sup> The data given in Table 5 indicate that ligands **1–3** have a significantly aromatic character, which becomes only slightly enhanced, however, in the **D-CuCl** complexes.

### Discussion

The results presented above make it possible now to answer the questions which were posed in the Introduction. The metal–carbene, –silylene, and –germylene bonds are very strong; they can even be stronger than in typical Fischer-type complexes. The topological analysis of the metal–carbene bond in **D-MCl** suggests that it has a strong ionic character. This seems to be surprising, since the carbene carbon atom carries only a negligible partial charge in the free ligand and in the complex, and Si and Ge carry even positive partial charges (Table 3). We refer to the bonding between positively charged metal atoms M<sup>+</sup> and CO in M<sup>+</sup>–CO complexes, which is quite strong for M<sup>+</sup> = Cu<sup>+</sup>, Ag<sup>+</sup>, and Au<sup>+</sup> (between 22 and 38 kcal/mol) although the carbon atom of CO is *positively* charged.<sup>60,61</sup> A bonding analysis has shown that even the H–CO<sup>+</sup> bond in the formyl cation has ca. 50% ionic character.<sup>60a</sup> The reasons for the ionic contribution are the interactions between the positively charged atoms M<sup>+</sup> and the  $\sigma$ -electron lone pair at the carbon atom of CO, which is directed toward M<sup>+</sup>. The center of the lone-pair charge concentration is in closer proximity to M<sup>+</sup> than to the carbon nucleus, which yields net charge attraction rather than charge repulsion. Since the carbene lone-pair electron in **1** is



**Figure 4.** (a) Schematic illustration showing the mixing of the empty s and occupied d<sub>z</sub><sup>2</sup> orbitals of the metal, which leads to less charge repulsion with ligands coming along the z axis. (b) Diagram of the orbital interaction between the donor lone-pair orbital of atom X (X = C, Si, Ge) of **D** and the M–Cl orbitals. The influence of mixing with the occupied d<sub>z</sub><sup>2</sup> orbital (see text) is not shown.

more diffuse than in CO because of the different hybridization (only 22% p in CO, but 48% p in **1**), the Coulomb attraction in carbene complexes is even higher. The weaker bonds of the silylene and germylene complexes are partly due to the larger distances between the metal atoms and the lone-pair electrons at Si and Ge.

Which orbitals at the metal side are involved in the covalent part of the metal–carbene bonding in **D-MCl**, which has little **D** ← MCl back-bonding and mainly **D** → MCl σ-donation? The metal cations Cu<sup>+</sup>–Au<sup>+</sup> have an s<sup>0</sup>d<sup>10</sup> electron configuration, but the s orbital is partly filled in MCl because of the M<sup>+</sup>–Cl<sup>-</sup> bond. The next-lowest-lying empty orbitals at the metal are the set of p orbitals. Table 6 shows the occupation of the valence s, d, and p orbitals at the metal in MCl and in the complexes. It becomes obvious that the metal s orbital in MCl is only slightly filled, the d orbitals are occupied, and the p orbitals are vacant. Note that the d<sub>z</sub><sup>2</sup> orbital is slightly less occupied than the other d orbitals. The most important difference between the **D-MCl** complexes and free MCl is the *increase* in the s population and the further *decrease* in the d<sub>z</sub><sup>2</sup> orbital population. The valence p orbitals of the metals remain empty. It follows that the metal p orbitals are not involved in the metal–carbene bonds. The non-negligible covalent part of this bond is formed by donation of the carbene lone-pair electrons into the lowly occupied metal s orbital. This accounts for the significant increase of the M(s) population (Table 6). At the same time, there is a small decrease in the population of the metal d<sub>z</sub><sup>2</sup> orbital. Note that there is no further charge transfer from the metal to chlorine when the **D-MCl** bond is formed, except for the gold complexes, where relativistic effects are probably responsible for the small Au → Cl charge transfer. It follows that the population decrease of the metal d<sub>z</sub><sup>2</sup> orbital is rather caused by the Coulomb repulsion with the carbene lone-pair electrons. This repulsion increases the energy of the metal d<sub>z</sub><sup>2</sup> orbital and hence facilitates the mixing with the valence s orbital. This is graphically shown in Figure 4a.<sup>64</sup> The competition for the empty metal s orbital between donation from Cl<sup>-</sup> and the carbene lone pair should lead to a longer M–Cl bond. The smaller population of the metal d<sub>z</sub><sup>2</sup> orbital, on the



**Table 6. Populations of the d, s, and p Metal Valence Orbitals in MCl and in the Complexes**

molecule	no.	d <sub>xy</sub>	d <sub>xz</sub>	d <sub>yz</sub>	d <sub>x<sup>2</sup>-y<sup>2</sup></sub>	d <sub>z<sup>2</sup></sub>	s	p <sub>x</sub>	p <sub>y</sub>	p <sub>z</sub>
ClCu-C <sub>3</sub> H <sub>4</sub> N <sub>2</sub>	<b>1-CuCl</b>	1.97	1.92	1.95	1.97	1.80	0.66	0.02	0.02	0.01
ClAg-C <sub>3</sub> H <sub>4</sub> N <sub>2</sub>	<b>1-AgCl</b>	1.99	1.96	1.97	1.99	1.84	0.61	0.02	0.02	0.01
ClAu-C <sub>3</sub> H <sub>4</sub> N <sub>2</sub>	<b>1-AuCl</b>	1.99	1.91	1.95	1.99	1.72	0.95	0.02	0.02	0.01
ClCu-SiC <sub>2</sub> H <sub>4</sub> N <sub>2</sub>	<b>2-CuCl</b>	1.97	1.92	1.92	1.97	1.88	0.64	0.03	0.03	0.02
ClAg-SiC <sub>2</sub> H <sub>4</sub> N <sub>2</sub>	<b>2-AgCl</b>	1.99	1.95	1.95	1.99	1.91	0.59	0.02	0.02	0.01
ClAu-SiC <sub>2</sub> H <sub>4</sub> N <sub>2</sub>	<b>2-AuCl</b>	1.99	1.91	1.92	1.99	1.84	0.90	0.02	0.02	0.01
ClCu-GeC <sub>2</sub> H <sub>4</sub> N <sub>2</sub>	<b>3-CuCl</b>	1.97	1.93	1.94	1.97	1.88	0.60	0.03	0.03	0.01
ClAg-GeC <sub>2</sub> H <sub>4</sub> N <sub>2</sub>	<b>3-AgCl</b>	1.99	1.96	1.96	1.99	1.91	0.54	0.02	0.02	0.01
ClAu-GeC <sub>2</sub> H <sub>4</sub> N <sub>2</sub>	<b>3-AuCl</b>	1.99	1.93	1.94	1.99	1.83	0.87	0.03	0.03	0.01
ClCu	<b>CuCl</b>	1.97	1.97	1.97	1.97	1.90	0.31	0.02	0.02	0.01
ClAg	<b>AgCl</b>	1.99	1.99	1.99	1.99	1.96	0.24	0.02	0.02	0.01
ClAu	<b>AuCl</b>	1.99	1.98	1.98	1.99	1.86	0.55	0.02	0.02	0.01

other hand, results also in less Coulomb repulsion with the occupied orbitals of Cl<sup>-</sup>. Indeed, both bond elongation and bond shortening are observed in the different complexes, depending on which effect dominates (Figure 2). We wish to point out that the same effect of reduced Coulomb repulsion is responsible for the fact that the second carbonyl ligand in M<sup>+</sup>(CO)<sub>n</sub> (M<sup>+</sup> = Cu<sup>+</sup>, Ag<sup>+</sup>, Au<sup>+</sup>) is *more strongly* bonded than the first CO.<sup>60b</sup> The first bond of the metal cation to a ligand facilitates the approach of the second ligand. Thus, the covalent part of the metal bonding in **D-MCl** has the pattern of the familiar 4-electron-3-center interaction as shown in Figure 4b, with the important additional role of the d<sub>z<sup>2</sup></sub> orbital, which contributes to the M-Cl and **D-MCl** bonding (not shown in Figure 4b). The data in Table 6 show that the changes in the metal orbital population in the silylene and germylene complexes have the same trend as that in the carbene complexes.

### Summary and Conclusion

The binding interactions between the N-heterocyclic carbenes, silylenes, and germylenes **1-3** and the metal chlorides MCl yield very strong bonds. The strongest bond is predicted for the gold complex **1-AuCl**, which has a higher bond dissociation energy ( $D_e = 82.8$  kcal/mol) than the classical Fischer complex (CO)<sub>5</sub>W-

(64) A similar reasoning was previously suggested by Siegbahn to explain the trends in transition metal-ligand bond strength: (a) Siegbahn, P. E. M. *Theor. Chim. Acta* **1993**, *86*, 219. (b) Siegbahn, P. E. M.; Blomberg, M. R. A.; Svensson, M. *J. Am. Chem. Soc.* **1993**, *115*, 4191. (c) Siegbahn, P. E. M. *J. Am. Chem. Soc.* **1994**, *116*, 7722.

CH(OH) ( $D_e = 75.0$  kcal/mol). The trend of the metal-ligand bond strengths in **D-MCl** shows for the ligands **D** the order carbene > silylene > germylene and for the metals Au > Cu > Ag. The most important change of the ligand geometries is the shortening of the N-X<sub>donor</sub> (X = C, Si, Ge) bonds, which indicates stronger N → X<sub>donor</sub> π-donation. The ligand ← metal π-back-donation in the complexes is small, much smaller than in classical Fischer carbene complexes. The **D-MCl** bonds are largely due to Coulombic attraction between the positively charged metal atoms and the lone-pair electrons at the ligand donor atoms, but there are also significant covalent interactions. The covalent contribution to the **D-MCl** bonding arises from donation of the donor lone-pair electrons to the M-Cl σ\* orbital, which is mainly a metal sd<sub>z<sup>2</sup></sub>-hybridized orbital. The weak aromaticity of the N-heterocyclic ligands increases only slightly when they become bonded to MCl.

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