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Bonding Interactions of a Molecular Pair of Tweezers with Transition Metals. Theoretical Study of Bis(η^2-alkyne) Complexes of Copper(I), Silver(I), and Gold(I)[1]

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Quantum chemical calculations at the DFT level of theory using the three-parameter fit of the potential B3LYP in conjunction with relativistic effective core potentials and large valence basis sets are reported for the model compounds [$Cl_2Ti(C{\equiv}CH)_2$]MCH_3 (M = Cu, Ag, Au), [$CuCH_3(HCCH)_n$] (n = 1, 2), and [$H_2X(C{\equiv}CH)_2$]$CuCH_3$ (X = Si, C). Theoretically predicted geometries and MCH_3 binding energies are given, and the nature of the binding interactions has been analyzed with the help of the NBO partitioning scheme and the topological analysis of the electron density distribution. The copper complex [$Cl_2Ti(C{\equiv}CH)_2$]-$CuCH_3$ has a much higher bond energy (D_e = 39.2 kcal/mol) than the analogous silver (D_e = 21.2 kcal/mol) and gold compound (D_e = 17.3 kcal/mol). There is significant metal → acetylide charge donation in the complexes, which induces strong Coulomb attraction between MCH_3 and the tweezer ligand. The role of the bridging TiY_2 moiety in the bisalkyne complexes is a twofold one. It serves to position the alkyne groups in a proper position for tricoordination around the group 11 metals, and it enhances the Lewis acidity of the ligands.

Introduction

The organometallic chemistry of group 11 transition metals copper, silver, and gold is presently an area where many new and spectacular achievements are reported. One example is the numerous nonclassical carbonyl complexes $M(CO)_n^+$ (M = Cu, Ag, Au) which have been isolated in the last years,[2] with stable $Cu(CO)_4^+$ as the latest success in the ongoing search for stable carbonyls.[3] Another example is the three-coordinated group 11 compounds, where a neutral monomeric species MR (M = Cu, Ag) is bonded in an η^2-fashion to both alkyne groups of [$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CSiMe_3)_2$] (Scheme 1).[4] The substituents R in [$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CSiMe_3)_2$]MR can be various groups such as halides, pseudohalides, alkanes, alkenes, alkynes, and aryls. The complexes are remarkably stable and include the first examples of room-temperature-stable methyl-, ethyl-, butyl-, and vinylcopper derivatives.[4a] This means that the metal−alkyne bonding interactions are particularly favorable in the three-coordinate complexes.

In the course of our theoretical investigations of group 11 organometallic compounds[5] we became interested in the bonding properties of the complexes [$(\eta^5\text{-}C_5H_4\text{-}SiMe_3)_2Ti(C{\equiv}CSiMe_3)_2$]MR. Although one of the previous studies included an EHT analysis of the bonding interactions, which gave some information about the nature of the metal−ligand bonds,[4a] several important aspects have not yet been addressed. The following questions still need to be answered and shall be addressed in this work. What are the metal−alkyne bond strengths in the complexes? What is the function of the bridging titanium group in the $Y_2Ti(C{\equiv}CR')$ bisalkenyl moiety? Is it only a spacer group, which can perhaps be replaced by suitable other moieties? Can a prediction be made for the yet unknown complexes with M = Au? What is the nature of the RM−bisalkyne bonds? Is the alkyne → M donation through the C≡C π orbitals important for the binding interaction, or is the back-donation from the metal into the π^* orbitals the dominant factor, as suggested from the EHT calculations?[4a]

To answer the questions, we carried out quantum chemical calculations using gradient-corrected density

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(1) Theoretical Studies of Organometallic Compounds. Part 36. Part 35: Reference 18.

(2) (a) Strauss, S. H. *Chemtracts-Inorg. Chem.* **1997**, *10*, 77. (b) Willner, H.; Aubke, F. *Angew. Chem.* **1997**, *109*, 2505; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2402. (c) Lupinetti, A. J.; Frenking, G.; Strauss, S. H. *Angew. Chem.* **1998**, *110*, 2229; *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2113.

(3) (a) Strauss, S. H. Reported at the 1998 ACS Spring National Meeting in Dallas. (b) Ivanov, S. V.; Miller, S. M.; Anderson, O. P.; Solntsev, K. A.; Strauss, S. H. Manuscript in preparation.

(4) (a) Janssen, M. D.; Köhler, K.; Herres, M.; Dedieu, A.; Smeets, W. J. J.; Spek, A. L.; Grove, D. M.; Lang, H.; van Koten, G. *J. Am. Chem. Soc.* **1996**, *118*, 4817. (b) Janssen, M. D.; Herres, M.; Zsolnai, L.; Spek, A. L.; Grove, D. M.; Lang, H.; van Koten, G. *Inorg. Chem.* **1996**, *35*, 2476. (c) Janssen, M. D.; Herres, M.; Zsolnai, L.; Grove, D. M.; Spek, A. L.; Lang, H.; van Koten, G. *Organometallics* **1995**, *14*, 1098. (d) Janssen, M. D.; Herres, M.; Spek, A. L.; Grove, D. M.; Lang, H.; van Koten, G. *J. Chem. Soc., Chem. Commun.* **1995**, 925. (e) Lang, H.; Herres, M.; Zsolnai, L. *Organometallics* **1993**, *12*, 5008.

(5) (a) Böhme, M.; Frenking, G.; Reetz, M. T. *Organometallics* **1994**, *13*, 4237. (b) Antes, I.; Frenking, G. *Organometallics* **1995**, *14*, 4263. (c) Antes, I.; Dapprich, S.; Frenking, G.; Schwerdtfeger, P. *Inorg. Chem.* **1996**, *35*, 2089. (d) Böhme, M.; Wagener, T.; Frenking, G. *J. Organomet. Chem.* **1996**, *520*, 31. (e) Boehme, C.; Frenking, G. *Organometallics* **1998**, *17*, 5801.

10.1021/om9809623 CCC: $18.00
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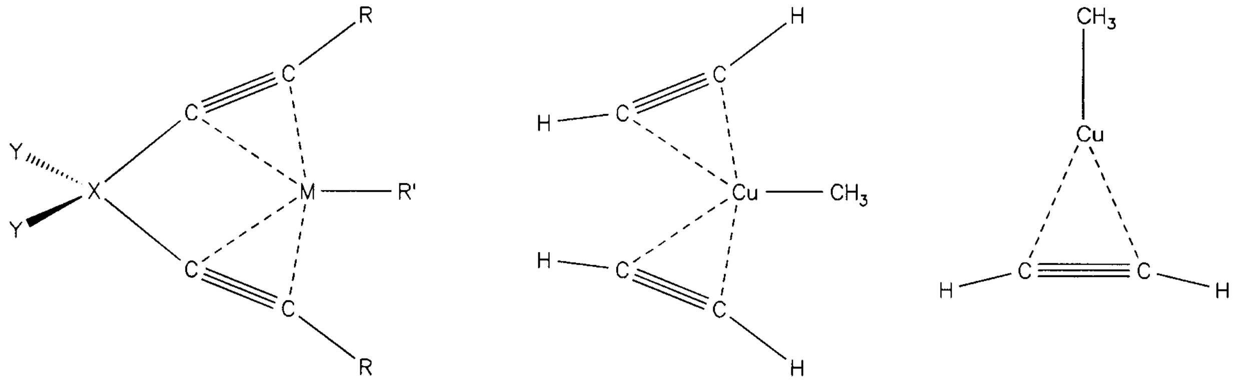
Scheme 1



1a X = Ti, Y = Cl, R = H, M = Cu, R' = Me
1b X = Ti, Y = Cp−SiMe$_3$, R = SiMe$_3$, M = Cu, R' = Me
2a X = Ti, Y = Cl, R = H, M = Ag, R' = Me
2b X = Ti, Y = Cp−SiMe$_3$, R = SiMe$_3$, M = Ag, R' = C$_6$H$_2$Me$_3$−2,4,6
3a X = Ti, Y = Cl, R = H, M = Au, R' = Me
6 X = Si, Y = H, R = H, M = Cu, R' = Me
7 X = C, Y = H, R = H, M = Cu, R' = Me

4

5

functional theory (DFT) at the B3LYP level for the model compounds [$Cl_2Ti(C{\equiv}CH)_2$]MCH_3 (M = Cu, Ag, Au) (**1a**−**3a**) shown in Scheme 1. The theoretical results of **1a** and **2a** may be compared with experimental values of the related compounds **1b** and **2b**. Because the substituted Cp ligands at Ti and the silyl substituents at the alkyne groups can be assumed to serve mainly as steric shields and should have little influence on the alkyne−M electronic interactions, we believe that **1a**−**3a** are suitable models to study the bonding situation of the real molecules. To investigate the role of the bridging titanium moiety, we calculated several other model compounds. First, structures **4** and **5** were calculated, which have no bridging groups at all. We optimized also the geometries of the complexes **6** and **7**, which have SiH_2 and CH_2 as bridging groups. The electronic structure of the compounds was examined with the help of the natural bond orbital (NBO) partitioning scheme[6] and the topological analysis of the electron density distribution.[7]

Methods

Two different basis set combinations A and B have been employed in this work. The moderate basis set A has an effective core potential (ECP) for Ti, Cu, Ag, and Au in conjunction with valence basis sets of DZP quality, i.e. (441/2111/*N*1) (*N* = 4, 3, 2 for first-, second-, and third-row TM elements).[8] Note that the ECPs for Ti and Cu are nonrelativistic, while the ECPs of Ag and Au include relativistic effects.[8] It has been found that relativistic effects can become important for the bond lengths and bond energies of copper compounds.[5c,9] An ECP with a valence basis set (31/311/1) has also been used for silicon and chlorine.[10] The exponents of the d-type polarization functions are $\zeta = 0.262$ for Si and $\zeta = 0.514$ for Cl.[11] Basis set combination A has 6-31G(d) basis sets for C and H.[12]

Significantly larger basis sets for the most relevant atoms have been used for the basis set combination denoted as B. Relativistically derived ECPs with (311111/22111/411) valence basis sets for Cu, Ti, Ag and (2111111/411/2111) for Au were employed for the metals.[13] Basis set B has TZP all-electron basis sets for C and H,[11] while the same ECPs with (31/311/1) basis sets for Si and Cl were employed as in A.

The geometries of all compounds were optimized using basis set B with the three-parameter fit of the functionals denoted B3LYP,[14] as given in the program Gaussian 94.[15] Initial geometry optimizations were carried out at the B3LYP level using basis set A. The B3LYP/A geometry optimizations were used for subsequent frequency calculations.[16] The geometry of the copper complex **1a** was also optimized at MP2/A in order

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

(7) Bader, R. F. W. *Atoms in Molecules: A Quantum Theory*; Oxford University Press: Oxford, 1990.

(8) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.

(9) (a) Pyykkö, P. *Chem. Rev.* **1988**, *88*, 563. (b) Barnes, L. A.; Rosi, M.; Bauschlicher, C. W. *J. Chem. Phys.* **1990**, *93*, 609.

(10) Bergner, A.; Dolg, M.; Küchle, W.; Stoll, H.; Preuss, H. *Mol. Phys.* **1993**, *80*, 1431.

(11) Andzelm, J.; Huzinaga, S.; Klobukowski, M.; Radzio, E.; Sakai, Y.; Tatekawi, H. *Gaussian Basis Sets for Molecular Calculations*; Elsevier: Amsterdam, 1984.

(12) (a) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724. (b) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257. (c) Hariharan, P. C.; Pople, J. A. *Mol. Phys.* **1974**, *27*, 209. (d) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213. (e) Gordon, M. S. *Chem. Phys. Lett.* **1980**, *76*, 163.

(13) (a) Dolg, M.; Wedig, U.; Stoll, H.; Preuss, H. *J. Chem. Phys.* **1987**, *86*, 866. (b) Andrae, D.; Häussermann, U.; Dolg, M.; Stoll, H. *Theor. Chim. Acta* **1990**, *77*, 123. (c) Schwerdtfeger, P.; Dolg, M.; Schwarz, W. H. E.; Bowmaker, G. A.; Boyd, P. O. W. *J. Chem. Phys.* **1989**, *91*, 1762.

(14) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(15) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomberts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, I.; Stewart, J. J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*; Gaussian Inc.: Pittsburgh, PA, 1995.

to compare the changes in the geometry at different levels of theory B3LYP/A, MP2/A, and B3LYP/B. Unless otherwise noted, B3LYP/B geometries are used for the discussion.

For the topological analysis of the electron density distribution we used the programs SADDLE, GRID, SCHUSS, CPLOT, and BADERCAT.[17]

Geometries and Bond Energies

Figure 1 shows the optimized structures of the calculated compounds **1a**−**7**. Table 1 gives theoretical and experimental interatomic distances and angles for the titanium-bridged metal−alkyne complexes **1**−**3**. Bond lengths and angles of the corresponding frequent molecules are listed in Table 2. Table 3 gives the geometries of the model compounds **4**−**7** and the alkyne ligands.

Table 1 shows that the calculated geometries of **1a** at B3LYP/A, MP2/A, and B3LYP/B are not very different, except for the nonbonding interatomic distance between Ti and Cu. The differences are not very important, however, and the good agreement between the B3LYP/A value for **1a** and the experimental value for **1b** may be fortuitous, because the potential energy surface about the Ti−Cu equilibrium distance is very flat (see below).

Comparison of the calculated geometries for **1a** and **2a** with the experimental results of **1b** and **2b** shows generally a good agreement. The calculated Ti−C_1 distances (2.000 Å for **1a** and 2.012 Å for **2a**) are shorter than the experimental values for **1b** (2.075 Å) and **2b** (2.090 Å), which is probably due to the presence of Cl in the model compounds instead of η^5-$C_5H_4SiMe_3$. More important for the present study are the geometry data which are directly related to the metal−alkyne binding interactions. The Cu−$C_{1/2}$ distances of **1a** (2.115 and 2.061 Å) are in good agreement with the experimental values for **1b** (2.076 and 2.080 Å). Slightly longer Ag−$C_{1/2}$ bond lengths are calculated for **2a** (2.342 and 2.336 Å) than observed for **2b** (2.270 and 2.305 Å). To study theoretically the influence of the metal−$C_{1/2}$ distances on the calculated structures, we optimized the geometry of **1a**, with the Cu−$C_{1/2}$ bond lengths being constrained to the experimental values (**1a′**, Table 1). The energy difference between **1a** and **1a′** is only <0.1 kcal/mol, although the Ti−C nonbonding distance changes by 0.048 Å. Table 1 shows that the constraints on the Cu−$C_{1/2}$ distances have little influence on the other bond lengths and bond angles. The calculated M−CH_3 distances of the free MCH_3 compounds given at B3LYP/B are in good agreement with previous theoretical work.[5b,22]

The theoretical Cu−CH_3 distance of model compound **1a** (1.966 Å) is also in perfect agreement with the experimental value for **1b**. Theory and experiment agree nicely about the changes of the fragment geometries (Table 2) when the metal−alkyne complexes are formed. The C≡C distance of $[Y_2Ti(C_2H)_2]$ (1.215 Å calc; 1.203 and 1.214 Å expt[4e]) becomes longer by ~0.03 Å in the copper complexes **1a** (1.246 Å) and **1b** (1.247 Å) and in the silver complexes **2a** (1.239 Å) and **2b** (1.24 Å). The smaller C≡C elongation that is calculated for **2a** than for **1a** is a hint that the metal−alkyne interactions in the silver complex might be weaker than in the copper complex. The calculated C≡C distance of the gold complex **3a** (1.249 Å) is even slightly longer than in **1a**. However, it will be shown below that the C≡C distances are not a reliable measure for the metal−alkyne bond strengths. Note that the Ti−C_1 bond lengths in the complexes **1**, **2a**, and **3a** remain nearly the same as in the free ligand, while the M−CH_3 bond lengths become significantly longer in **1a** and **3a** but only slightly longer in **2a** (Tables 1, 2).

The calculations predict that the linear or nearly linear Ti−C≡C and C≡C−H moieties of $[Cl_2Ti(C_2H)_2]$ become bent in the metal−alkyne complexes. The calculated bond angles of **1a** (Ti−C≡C 159.8°, C≡C−H = 158.8°) and **2a** (Ti−C≡C = 165.1°, C≡C−H = 162.7°) are in excellent agreement with the experimental values for **1b** (Ti−C≡C = 163.7°, C≡C−H = 158.5°) and **2b** (Ti−C≡C = 166.6°, C≡C−H = 162.9°). It follows that the calculated geometries of **1a**−**3a** may safely be used to analyze the metal−alkyne bonding of the isolated compounds **1b** and **2b** and the yet unknown complex **3b**.

Table 1 gives also the theoretically predicted bond dissociation energies of **1a**−**3a** yielding MCH_3 and $[Cl_2Ti(C_2H)_2]$. The calculations predict that the copper complex **1a** has significantly stronger metal−alkyne bonds (D_e = 39.2 kcal/mol) than the silver analogue **2a** (D_e = 21.2 kcal/mol). This is in agreement with experimental observations. Reaction of bis(η^2-alkyne) complexes of silver with Cu(I) compounds produces bis(η^2-alkyne) complexes of copper, while the reverse reaction does not occur.[4a] A perhaps unexpected result concerns the Au−alkyne bond dissociation energy. The calculations predict that **3a** has even *weaker* metal−alkyne bonds (D_e = 17.3 kcal/mol) than **2a**. This seems surprising, because the C≡C and M−CH_3 distances in **3a** were elongated more than in **1a** and **2a** (Tables 1, 2). Also, the general trend of bond strengths among analogous complexes of Cu(I), Ag(I), and Au(I) is usually Au > Cu > Ag; that is, gold complexes are frequently the most stable species. For example, the calculated metal−CO bond strength of $[M(CO)]^+$ shows the order (in kcal/mol) Au(38.5) > Cu(32.9) > Ag(22.0).[18] The same order is predicted for the first CO dissociation energy of the

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[16] The geometries of the complexes have been optimized with the c_s symmetry constraint. Vibrational frequency calculations gave one imaginary frequency with a very small absolute number which corresponds to the rotation of the M−CH_3 group. Relaxation of the c_s symmetry constraint and rotation of the methyl group gives negligible changes in energy and geometry.

[17] Biegler-König, F. W.; Bader, R. F. W.; Ting-Hua, T. *J. Comput. Chem.* **1982**, *3*, 317.

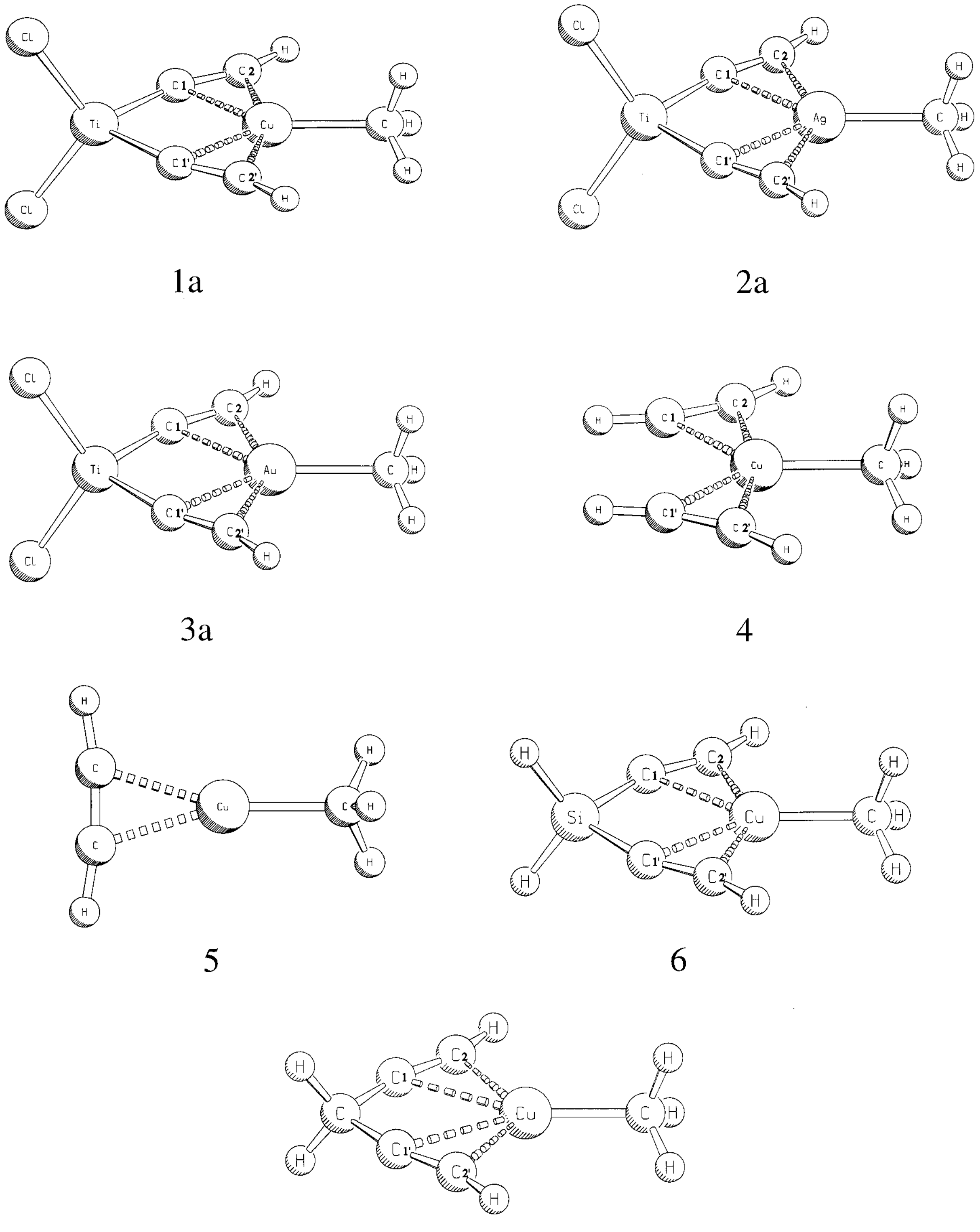
[18] Lupinetti, A. J.; Jonas, V.; Thiel, W.; Frenking, G.; Strauss, S. H. *Chem. Eur. J.*, submitted for publication.

[19] This has been discussed in more detail in ref 18.

[20] Cremer, D.; Kraka, E. *Angew. Chem.* **1984**, *96*, 612; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 627.

[21] (a) Frenking, G.; Koch, W.; Gauss, J.; Cremer, D. *J. Am. Chem. Soc.* **1988**, *11*, 8007. (b) Koch, W.; Frenking, G.; Gauss, J.; Cremer, D.; Collins, J. R. *J. Am. Chem. Soc.* **1987**, *109*, 5917. (c) Gobbi, A.; Frenking, G. *J. Am. Chem. Soc.* **1993**, *115*, 2362. (d) Gobbi, A.; Frenking, G. *J. Am. Chem. Soc.* **1994**, *116*, 9275. (e) Stegmann, R.; Frenking, G. *Can. J. Chem.* **1996**, *74*, 801. (f) Pidun, U.; Frenking, G. *Organometallics* **1995**, *14*, 5325. (g) Veldkamp, A.; Frenking, G. *Chem. Phys. Lett.* **1994**, *226*, 11. (h) Vyboishchikov, S. F.; Frenking, G. *Chem. Eur. J.* **1998**, *4*, 1428. (i) Vyboishchikov, S. F.; Frenking, G. *Chem. Eur. J.* **1998**, *4*, 1439.

[22] (a) Bauschlicher, C. W.; Langhoff, S. R.; Partridge, H.; Barnes, L. A. *J. Chem. Phys.* **1989**, *91*, 2399. (b) Sodupe, M.; Bauschlicher, C. W.; Lee, T. J. *Chem. Phys. Lett.* **1992**, *189*, 266. (c) Sosa, C.; Andzelm, J.; Elkin, B. C.; Wimmer, E.; Dobbs, K. D.; Dixon, D. A. *J. Phys. Chem.* **1992**, *96*, 6630.



1a 2a 3a 4 5 6 7

Figure 1. Optimized structures of the molecules. For geometrical data see Tables 1 and 3.

dicarbonyls $[M(CO)_2]^+$. However, the calculations of the tricarbonyls $[M(CO)_3]^+$ predict a sequence Cu > Ag > Au.[18] This is in agreement with the order for the metal–alkyne bond strength of **1a**–**3a**, which are also tricoordinated compounds. The change in the order of the bond strengths has been explained with loss of covalent bonding in tricoordinated group 11 complexes, which is particularly strong for gold compounds.[18] The calculations show clearly that the C≡C bond lengths in the complexes **1a**–**3a**, which are the results of attractive *and* repulsive interactions between MCH_3 and the bisalkyne ligands, are not a reliable indicator of the final metal–alkyne bond *strengths*. As shown below, this is because the nature of the binding interactions of the different atoms Cu, Ag, and Au is not the same.

To investigate the role of the bridging TiY_2 unit in the bis(η^2-alkyne) complexes, we calculated the complexes $[(C_2H_2)_2CuCH_3]$ (**4**) and $[(C_2H_2)CuCH_3]$ (**5**), which have two and one free acetylene ligands, respectively. Table 3 shows that the calculated C≡C bond length of free acetylene (1.196 Å) is elongated in **4** by 0.032 Å and in **5** by 0.019 Å. The copper–alkyne bond dissociation

Table 1. Calculated and Experimental Molecular Geometries[a] of the Complexes and Theoretically Predicted Bond Energies of the Titanium Complexes[b]

		1a						
variable	**1b** expt[c]	B3LYP/A	MP2/A	B3LYP/B	**1a′**[d] B3LYP/B	**2b** expt[c]	**2a** B3LYP/B	**3a** B3LYP/B
Ti−Cl		2.196	2.189	2.197	2.198		2.194	2.195
$Ti-C_1$	2.0752(16)	2.000	2.015	2.000	1.999	2.090(8)	2.012	2.012
C_1-C_2	1.247(3)	1.256	1.279	1.246	1.244	1.24(1)	1.239	1.249
C_2-H		1.074	1.076	1.068	1.067		1.067	1.068
$M-C_{Me}$	1.966(2)	1.966	1.973	1.966	1.970	2.099(5)	2.134	2.122
$C_{Me}-H_1$		1.095	1.093	1.090	1.090		1.088	1.088
$C_{Me}-H_{2/3}$		1.094	1.091	1.088	1.088		1.087	1.087
Ti···M	2.9645(5)	2.950	2.838	2.898	2.850	3.104(7)	3.105	3.073
$M\cdots C_1$	2.0763(16)	2.148	2.056	2.115	2.0763	2.270(9)	2.342	2.337
$M\cdots C_2$	2.0802(18)	2.085	2.031	2.061	2.0802	2.305(9)	2.336	2.294
Cl−Ti−Cl		117.2	120.4	117.4	117.6		116.8	116.4
$C_1-Ti-C_{1'}$	88.89(6)	93.5	92.8	93.7	93.2	94.0(3)	97.9	99.0
$Ti-C_1-C_2$	163.70(14)	160.6	159.1	159.8	162.0	166.6(6)	165.1	162.1
$C_1-C_2-H(Si)$[e]	158.51(16)	158.7	154.9	158.8	161.2	162.9(7)	162.7	158.3
$M-C_{Me}-H_1$		107.2	105.3	107.3	107.4		107.9	108.1
$M-C_{Me}-H_{2/3}$		109.8	109.1	110.2	110.2		109.2	109.6
$C_1\cdots M\cdots C_{1'}$		85.4	90.4	87.2	89.4		80.8	81.8
$C_2\cdots M\cdots C_{2'}$		154.3	163.3	156.6	159.3		142.2	144.3
D_e				39.2			21.2	17.3
D_0				40.8			21.7	18.2

[a] Bond lengths in angstroms, bond angles in degrees. [b] Alkyne−MCH_3 bond dissociation energies D_e (ZPE corrected values D_0) in kcal/mol. [c] X-ray data from ref 4a. [d] Constrained at the experimental $M-C_1/C_2$ values of **1d**. [e] C_1-C_2-Si in **1b** and **2b**.

Table 2. Optimized Molecular Geometries[a] of the Fragments of Complexes 1a−3a

	$[TiCl_2(C_2H)_2]$				
variable	expt[b]	B3LYP/B	CuMe B3LYP/B	AgMe B3LYP/B	AuMe B3LYP/B
Ti−Cl		2.183			
$Ti-C_1$	2.124(5) 2.103(5)	1.998			
C_1-C_2	1.214(6) 1.203(9)	1.215			
C_2-H		1.064			
$M-C_{Me}$			1.898	2.114	2.049
$C_{Me}-H$			1.088	1.085	1.085
Cl−Ti−Cl		113.2			
$C_1-Ti-C_{1'}$	102.8(2)	106.5			
$Ti-C_1-C_2$	178.2(5) 175.8(4)	179.3			
$C_1-C_2-H^c(Si)$	178.3(5) 174.8(4)	180.0			
$M-C_{Me}-H$			108.1	107.2	106.8

[a] Bond lengths in angstroms, bond angles in degrees. [b] Ref 4e. [c] C_1-C_2-Si in the experimental structure.

energies of **4** (D_e = 20.0 kcal/mol) and **5** (17.4 kcal/mol) are significantly lower than in **1a**. It is interesting to note that addition of a second acetylene ligand to **5** results in a marginal energy gain (2.6 kcal/mol). It seems highly unlikely that Cu(I) complexes with two unbridged alkyne ligands can be isolated. Copper(I) complexes with one alkyne ligand may become observable under appropriate conditions, however.

The results for **4** and **5** point to the decisive role of the TiY_2 moiety in the bis(η^2-alkyne) complexes. The question remains if the TiY_2 group serves only as a bridge and possibly a steric shield, or if electronic interactions play a role for the stabilization of the complexes. How stable are bis(η^2-alkyne) complexes of Cu(I) with groups other than TiY_2 as bridging ligands? To answer this question, we investigated theoretically the complexes **6** and **7**, which have SiH_2 and CH_2 bridges between the acetylide ligands. Table 3 shows the calculated results. The $CuCH_3$−acetylide bond energies of **6** (D_e = 15.3 kcal/mol) and **7** (D_e = 11.5 kcal/mol) are clearly lower than in **1a**. The changes in the geometries of the ligands upon complex formation agree with the low bond energies of the copper complexes **6** and **7**. The C≡C and $Cu-CH_3$ distances are stretched in **6** and **7** to a lesser extent than in **1a**. The reasons for the large differences between the bond energies are discussed below.

Bonding Analysis

The nature of the metal−(η^2-alkyne) bonding is not trivial, because different bonding models appear plausible. There could be charge donation from the π orbitals of the alkyne ligands into the partially empty valence s orbital of M (M = Cu, Ag, Au), because the group 11 atoms in MCH_3 carry a positive partial charge. On the other hand, the $[Cl_2Ti(C_2H)_2]$ moiety might act as a Ti(IV) Lewis acid, although there is no direct $Ti-MCH_3$ contact in **1**−**3**.

Table 4 shows the results of the NBO analysis. Titanium carries a large positive charge (∼+0.9) in **1a**−**3a**, which is a little less than in the free ligand $[Cl_2Ti(C_2H)_2]$ (+1.07), while the acetylide ligand is negatively charged. The differences in the charge distribution show that there is a large charge transfer from the MCH_3 moiety to the $[Cl_2Ti(C_2H)_2]$ molecule, which acts like molecular tweezers. The charge transfer from MCH_3 to $[Cl_2Ti(C_2H)_2]$ is largest for M = Cu (0.56 e) and slightly less for M = Ag and Au (0.43 e). It is interesting to note that in spite of the electronic charge flow $MCH_3 \rightarrow [Cl_2Ti(C_2H)_2]$ the methyl group of MCH_3 becomes even slightly more negative in the complexes **1a**−**3a**, while the metal atoms become much more positively charged (Table 4). It follows that the bonding scenario between MCH_3 and $[Cl_2Ti(C_2H)_2]$ involves charge donation from the metal atoms to the bisalkynyl−titaniumdichloride. The charge flow is somewhat paradoxical, because negative charge is donated from the positively charged metal atom toward negatively charged carbon atoms (Table 4). The calculated charge distribution shows that the titanium atom and C_2 carry most of the additional electronic charge in **1a**−**3a**, while the partial charge at Cl and C_1 remains nearly constant. The direction of the

Table 3. Calculated Geometries[a] and Bond Energies[b] of 4, 5, 6, 7, and Their Fragments at the B3LYP/B Level

variable	**4**	**5**	**6**	**7**	$SiH_2(C_2H)_2$	$CH_2(C_2H)_2$	C_2H_2
X−H			1.485	1.092	1.488	1.094	
$X-C_1$			1.848	1.469	1.843	1.465	
C_1-C_2	1.228	1.215	1.233	1.217	1.204	1.197	1.196
C_2-H	1.066	1.065	1.067	1.064	1.062	1.061	1.062
$Cu-C_{Me}$	1.984	1.920	1.954	1.936			
$C_{Me}-H_1$	1.093	1.092	1.092	1.092			
$C_{Me}-H_{2/3}$	1.091	1.093	1.091	1.092			
X···Cu			2.975	2.991			
$Cu\cdots C_1$	2.115	2.097	2.288	2.396			
$Cu\cdots C_2$	2.023	2.097	2.103	2.207			
H−X−H			111.5	107.1	110.0	106.1	
$C_1-X-C_{1'}$			100.5	104.8	110.0	113.6	
$X-C_1-C_2$			156.9	164.8	180.0	180.0	
C_1-C_2-H	162.2	170.5	158.6	161.9	180.0	180.0	180.0
$Cu-C_{Me}-H_1$	109.0	111.7	109.3	109.9			
$Cu-C_{Me}-H_{2/3}$	112.1	110.8	111.2	111.0			
$C_1\cdots Cu\cdots C_{1'}$	91.9		76.8	58.1			
$C_2\cdots Cu\cdots C_{2'}$	160.8		141.3	118.7			
D_e	20.0	17.4	15.3	11.5			
D_0	22.4	18.3	15.9	12.1			

[a] X = Si in **6**, X = C in **7**. Bond lengths in angstroms, bond angles in degrees. [b] Alkyne−MCH_3 bond dissociation eneriges D_e (ZPE corrected values D_0) in kcal/mol.

Table 4. Results of NBO Analysis at the B3LYP/B Level[a]

	charge													
atom/group	**1a**	**1a′**	**2a**	**3a**	**4**	**5**	**6**	**7**	[Ti]	[Si]	[C]	CuMe	AgMe	AuMe
s	0.42	0.41	0.47	0.68	0.40	0.66	0.45	0.53				0.81	0.77	1.11
p				0.01		0.01								
d	9.60	9.60	9.68	9.54	9.64	9.73	9.70	9.76				9.84	9.90	9.76
$q(X)^b$	+0.90	+0.90	+0.94	+0.91			+1.26	−0.52	+1.07	+1.24	−0.53			
$q(Y)^b$	−0.25	−0.26	−0.25	−0.25			−0.18	+0.25	−0.23	−0.18	+0.25			
$q(C_1)$	−0.41	−0.43	−0.42	−0.39	−0.36	−0.27	−0.57	−0.02	−0.41	−0.50	+0.02			
$q(C_2)$	−0.31	−0.28	−0.27	−0.28	−0.31	−0.27	−0.29	−0.32	−0.12	−0.17	−0.23			
$q(M)$	+0.96	+0.97	+0.83	+0.76	+0.94	+0.60	+0.83	+0.70				+0.35	+0.33	+0.12
$q(C_{Me})$	−0.99	−0.99	−0.97	−0.91	−1.11	−1.16	−1.08	−1.09				−0.96	−0.92	−0.74
$q(CH_3)$	−0.40	−0.41	−0.40	−0.33	−0.56	−0.56	−0.52					−0.35	−0.33	−0.12
$q(C_2H_x)$	−0.47	−0.47	−0.44	−0.42	−0.19	−0.04	−0.61	−0.08	−0.30	−0.88	+0.04			
$\Delta q(MMe\rightarrow[L])$	0.56	0.56	0.43	0.43	0.38	0.04	0.31	0.18						

[a] s, p, d give the populations of the valence orbitals of M, q gives the partial charge, Δq gives the charge transfer from the MMe unit to the ligand. [Ti] means the optimized $[TiCl_2(C_2H)_2]$, [Si] the $[SiH_2(C_2H)_2]$, and [C] the $[CH_2(C_2H)_2]$ fragment. [b] X = Ti in **1a**, **2a**, **3a**; X = Si in **6** and [Si]; X = C in **7** and [C]; Y = Cl in **1a**, **2a**, **3a**; Y = H in **6**, **7**, [Si], and [C].

charge flow in the complexes $CH_3M \rightarrow [Cl_2Ti(C_2H)_2]$ is in agreement with previous EHT studies, which indicated that the alkyne ← metal back-bonding component is more important than the alkyne → metal donation.[4a]

The differences in the charge distribution and charge donation $H_3CCu \rightarrow$ acetylide between **1a** and **4**−**7** can be used to analyze the role of the $TiCl_2$ bridge. The breakdown of the charge donation $H_3CCu \rightarrow [Cl_2Ti(C_2H)_2]$ shows that 0.34 e is accepted by the acetylide ligands, while 0.22 e is accepted by $TiCl_2$. The acetylene ligands in **4** accept about the same amount of charge (0.38 e) as the acetylide groups in **1a**. This indicates that the $TiCl_2$ group enhances the Lewis acidity of the acetylide ligands. This is *not* the case for the SiH_2 and CH_2 groups in **6** and **7**, respectively. Table 4 shows that the partial charges at the bridging moieties of **6** and **7** remain nearly the same as in the isolated ligands $SiH_2(CCH)_2$ and $CH_2(CCH)_2$. However, the increase in the acceptor strength seems to be not the most important role played by the $TiCl_2$ group. Proper positioning of the acetylide ligands for optimal metal−ligand interactions is also very important. The CH_2 group in **7** is more electronegative than SiH_2 in **6**. Yet, charge donation from $CuCH_3$ to the acetylide ligands is much higher in **6** (0.31 e) than in **7** (0.18 e). The acetylide ligands in **6** are placed in a more favorable position for a trigonal planar coordination of Cu^+ than in **7**, because the Si−C bonds are longer than C−C.

Please note that the charge donation $H_3CCu \rightarrow (C_2H_2)$ in **5** is very small (0.04), and yet, the bond energies of **5** and **6** are comparable in magnitude. The change from dicoordination to tricoordination leads to significant electron repulsion between the metal and the ligand, which must be overcome by strong charge attraction between a positively charged metal and negatively charged ligand.[19] The large positive charge of Cu and negative charge of the C_2H ligands in **1a** are probably the main reason for the stabilization of the tricoordinate bis(η^2-alkyne) complex. The analysis of the charge distribution suggests that both optimal placement of the acetylide ligands in the coordination sphere of the metal and additional electron-withdrawing ability of the bridging moiety are necessary to make tweezer-type complexes like **1** become stable.

Figure 2a shows the Laplacian distribution of **1a** in the molecular plane. The Laplacian distributions of **1a′**, **2a**, and **3a** are very similar and therefore not shown. The copper atom in **1a** is surrounded by an area of charge depletion (dashed lines, $\nabla^2\rho(r) > 0$), while the carbon atoms have areas of charge concentration (solid

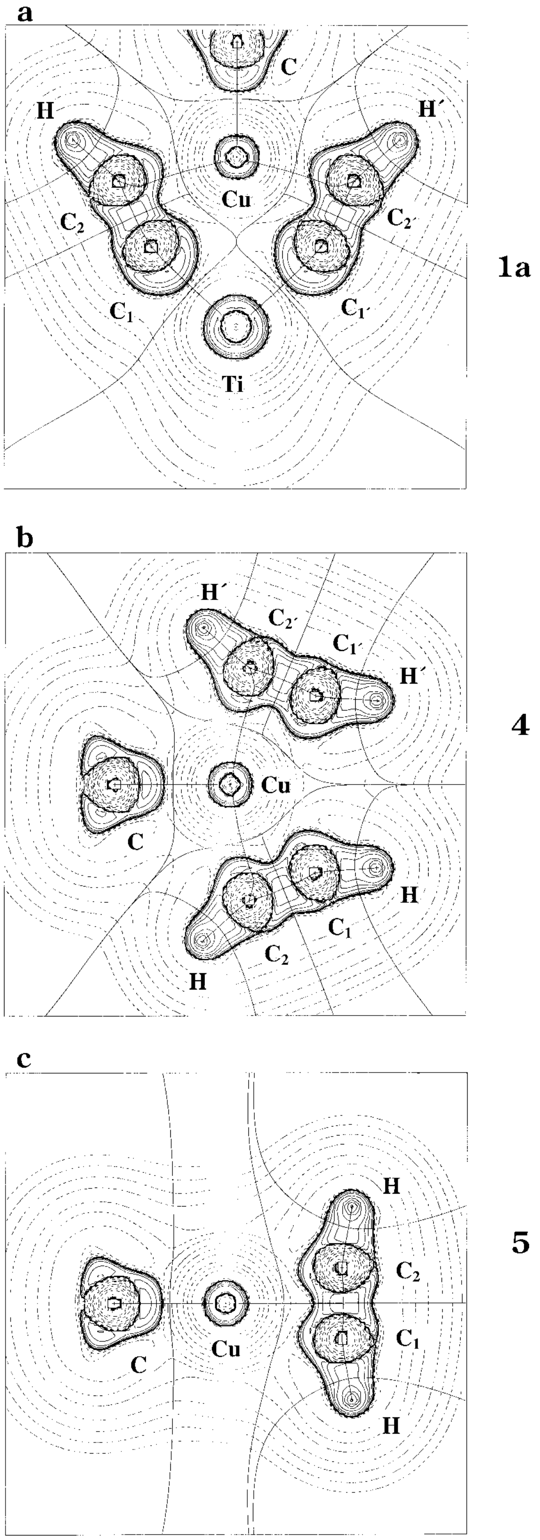


Figure 2. Contour line diagrams of the Laplacian distribution $\nabla^2\rho(r)$ at B3LYP/B for (a) **1a** in the molecular plane, (b) **4** in the molecular plane, (c) **5** in the molecular plane. Dashed lines indicate charge depletion ($\nabla^2\rho(r) > 0$); solid lines indicate charge concentration ($\nabla^2\rho(r) < 0$). The solid lines connecting the atomic nuclei are the bond paths. The solid lines separating the atoms show the zero-flux surfaces in the plane.

Table 5. Characteristics of the M$-$C$_2$ Bond Critical Points from the Topological Analysis of the Electron Density at B3LYP/B[a]

property	**1a**	**1a′**	**2a**	**3a**	**4**	**5**
$\rho(r_b)$	0.533	0.527	0.416	0.508	0.556	0.499
$-\nabla^2\rho(r_b)$	7.029	7.498	4.732	4.745	7.303	7.975
H_b	−0.073	−0.063	−0.069	−0.138	−0.082	−0.052

[a] Charge density at the bond critical point $\rho(r_b)$ (e Å^{-3}); Laplacian at the bond critical point $-\nabla^2\rho(r_b)$ (e Å^{-5}); energy density at the bond critical point H_b (hartree/Å^3).

lines, ($\nabla^2\rho(r) < 0$). The shape of the charge concentration at the carbon atoms reveals the dominant interactions. There is an area of charge concentration at the carbon atoms C$_1$ and C$_{1'}$ pointing toward titanium, but *not* toward copper. Carbon atoms C$_2$ and C$_{2'}$ have droplet-like areas of charge concentration pointing toward copper. There are bond paths for Cu$-$C$_2$ and Cu$-$C$_{2'}$, but not between copper and C$_1$ or C$_{1'}$. Thus, the topology of the charge distribution and its associated Laplacian suggest that the copper atom is primarily bonded to C$_2$ and C$_{2'}$. A closer examination of the Cu$-$C$_{2/2'}$ bond paths shows an inward bending at the carbon atoms toward C$_{1/1'}$ rather than a straight line. The best description for the copper$-$alkyne bonding in **1a** appears that the positively charged Cu is attracted by the negative π charge of the alkyne groups, which are polarized towards C$_{2/2'}$. This is in agreement with the charge distribution calculated by the NBO method, which suggests that C$_{2/2'}$ carries a higher negative charge than C$_{1/1'}$ (Table 4).

Table 5 shows the numerical results of the topological analysis of the electron density distribution. The most relevant information is given by the energy density at the bond critical point H_b. It has been suggested that covalent bonds ("shared interactions")[7] have negative values for H_b, while ionic bonds or van der Waals complexes (closed-shell interactions) have $H_b \geq 0$.[20] Numerous investigation have proven that this is a very useful criterion to distinguish between closed-shell and shared interactions.[5d,21] Table 5 shows that the H_b values for the metal$-$C2/2′ bonds of **1a**$-$**3a** have very small negative numbers. Strong covalent bonds have H_b values between -1 and -2 hartree/Å^3.[21] Recent studies of Fischer and Schrock-type carbene and carbyne complexes gave H_b values for W$-$C bonds between -0.1 and -0.5 hartree/Å^3.[21h,i] The H_b values shown in Table 5 indicate that the metal$-$alkyne bonds in **1a**$-$**3a** are largely ionic. The largest covalent contribution is calculated for the gold complex **3a**.

Figure 2b shows the Laplacian distribution of the bisacetylene complex **4**. Both carbon atoms exhibit areas of charge concentration pointing toward Cu. Again, there is only one bond path from copper to each alkyne ligand. It connects Cu with the C$_{2/2'}$ atoms of the alkyne ligands, which are slightly less negatively charged than C$_{1/1'}$ (Table 4). The Laplacian distribution of **5** is shown in Figure 2c. The topology of the charge distribution reveals a T-shaped structure, where the bond path from Cu ends at the CC midpoint, i.e., the bond critical point of the C$_1$$-C_2$ bond. The same result has previously been reported for the complex [Cu(HCCH)]$^+$.[5d] A topological analysis of the electron density distribution of **6** and **7** was not carried out, because we do not expect further insight into the electronic structure of the molecules.

In a previous EHT study of the binding interactions in [Cp$_2$Ti(C$_2$H)$_2$]CuCH$_3$ it was found that the overlap between Cu and C$_{1/1'}$ is larger than the Cu$-$C$_{2/2'}$ overlap.[4a] This appears to be in conflict with the results of the topological analysis of the charge distribution, which indicates that the primary metal−alkyne bonding is between the metal and $C_{2/2'}$. We want to point out that the overlap criterion does not say anything about the charge density in the region, which is given by the occupation of the respective orbitals.

Summary and Outlook

The most important results of this work can be summarized as follows. The bond strength between $CuCH_3$ and the bis(η^2-alkyne) $[Cl_2Ti(C_2H)_2]$ in the model compound **1a** is theoretically predicted as $D_e = 39.2$ kcal/mol ($D_0 = 40.8$ kcal/mol). The related silver and gold complexes have clearly lower bond strength $D_e = 21.2$ kcal/mol ($D_0 = 21.7$ kcal/mol) for **2a** and $D_e = 17.3$ kcal/mol ($D_0 = 18.2$ kcal/mol) for **3a**. The metal−ligand interactions yield significant charge donation from MCH_3 to the alkyne groups in $[Cl_2Ti(C_2H)_2]$, which leads to strong Coulomb attraction between the positively charged group 11 atoms and the acetylide ligands. The role of the bridging TiY_2 moiety in **1**−**3** is a twofold one. It serves to position the alkyne groups in a proper position for tricoordination around the group 11 metals, and it enhances the Lewis acidity of the ligands. This means that other tweezer complexes should be synthesized, which could be calculated prior to experimental work in order to focus synthetic efforts on promising candidates. For example, the present study suggests that substituted analogues of the gold complex **3a** should be quite stable, because the metal−alkyne bond energies are even higher than those of the copper and silver complexes **1a** and **2a**.

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