Chemical Bonding in the Inclusion Complex of He in Adamantane, He@adam: Antithesis and Complement

Moritz von Hopffgarten and Gernot Frenking*[a]

In the preceding paper in this issue[1] Strenalyuk and Haaland discuss the bonding situation in the inclusion complex of He in adamantane, He@adam. Based on common chemical reasoning, the authors use immaculately valid arguments which let them conclude that the interatomic interactions between the helium atom and the carbon atoms of the adamantane cage are repulsive. This is in apparent contradiction to the statements which were made by Bader and Fang,[2] who suggested that there are He−C chemical bonds between the helium atom and the four tertiary CH carbon atoms of adamantane. In the following we want to show that the conflicting views arise from different perspectives which are valid within their own scope of definition.[3]

In order to make our arguments easy to follow we will use the notation and numbers which are introduced in the paper by Strenalyuk and Haaland.[1] In the following we will thus assume that the reader is familiar with their work. For a discussion of the nature of the interatomic interactions and particularly for addressing the question if such interactions are attractive or repulsive, it is crucial to define an atom in a molecule. In the first part of their paper, Strenalyuk and Haaland do not explicitly give a definition of an atom. They rather discuss calculated energy values which show that the inclusion complex He@adam is 645 kJ mol^{-1} higher in energy than He + adam. They also show that the distortion of the adam cage from the equilibrium structure to the geometry in the complex is only 64 kJ mol^{-1} while the insertion of the He atom into the distorted adam requires 581 kJ mol^{-1}. It follows that the higher energy of He@adam relative to He + adam comes mainly from the interactions between He and the adamantane cage. The same conclusion is reached when the helium atom is first inserted into the adam cage which then relaxes to He@adam. The authors divide the total destabilization energy of He@adam by four

which gives a positive value of 161 kJ mol^{-1}. This value is identified as the mean interaction energy He$\cdots^t$C between helium and the tertiary carbon atoms which is, according to the work of Bader and Fang,[2] however, attractive. The interaction of He$\cdots$H$_3$CH calculated with the same He$\cdots$C distance as in He@adam gives a similar positive value of 178 kJ mol^{-1}. Since the former species, which is not a minimum on the potential energy surface, spontaneously dissociates if the He–H$_3$CH distance relaxes during the geometry optimization, the authors conclude that it is solely the presence of the C−C bonds in He@adam which prevents spontaneous dissociation.

In the following we will argue that the existence of He−C bonds in He@adam does not contradict the statement that the spontaneous dissociation of He is prevented by the C−C bonds of the adamantane cage, and that the instantaneous dissociation of He from He$\cdots$H$_3$CH also does not conflict with an attractive He–C interaction. In order to illustrate our case we first show in Figure 1a the contour line diagram of the Laplacian $\nabla^2\rho(r)$ of He@adam in the plane containing two tertiary CH carbon atoms, two secondary CH$_2$ carbon atoms and helium. Figure 1b shows the Laplacian $\nabla^2\rho(r)$ of free adamantane in the same plane.

Figure 1a nicely shows the zero-flux surface around He in the molecular plane which completely encapsulates the caged helium atom. The atomic basin within the boundaries of the zero-flux surface defines the atom in the molecule. Bader has shown that an atom in a molecule defined by the AIM obeys physical principles such as the virial theorem.[4] Figure 1a shows also the He−^{t}C bond paths which according to the AIM theory suggest that there are four helium−carbon bonds in He@adam, two of them being displayed in Figure 1a. A visual comparison of the Laplacian of He@adam with that of free adamantane shown in Figure 1b does not indicate major changes which is misleading, however. In the preceding paper by Strenalyuk and Haaland it is shown (Table 1 in that paper) that the total energy of the helium atom calculated by the AIM is significantly lowered while the energy of the carbon atoms and to a lesser extent also the energy of the hydrogen atoms increase. The sum of

[a] Dipl.-Chem. M. von Hopffgarten, Prof. Dr. G. Frenking
Fachbereich Chemie, Philipps-Universität Marburg
Hans-Meerwein-Strasse, 35032 Marburg (Germany)
Fax: (+49) 6421 2825566
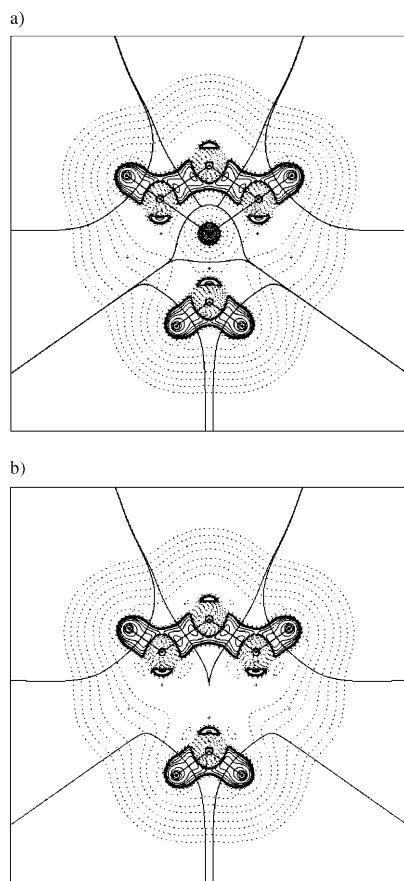E-mail: frenking@chemie.uni-marburg.de

a)

b)

Figure 1. Contour line diagrams $\nabla^2\rho(r)$ of a) He@adam and b) adamantane. Solid lines indicate areas of charge concentration ($\nabla^2\rho(r)0$) while dashed lines show areas of charge depletion ($\nabla^2\rho(r) > 0$). The thick solid lines connecting the atomic nuclei are the bond paths. The thick solid lines separating the atomic basins indicate the zero-flux surfaces crossing the molecular plane.

the energy changes of the atoms equals the increase in the total energy of the caged compound. Bader and Fang[2] calculated the Ehrenfest forces, which are the electrostatic forces acting on an entire atom in a molecule (unlike the Hellman–Feynman forces which act only on the nucleus), in He@adam. They calculated a value of −0.149 a.u. for the He−^{1}C bond which means that the Ehrenfest force on helium is attractive. Our calculations[5] at the same level of theory (MP2/6-311++G(2d,2p)) gave a value of −0.151 a.u. which is in essential agreement with their results.

The above results of the AIM calculations suggest that the repulsive forces which originate from the insertion of the helium atom into the adamantane cage are completely distributed over the carbon atoms and, to a much lesser extent, to hydrogen. This leads to a weakening of the C−C bonds in He@adam relative to free adamantane which becomes evident by the calculated values for the bond critical point data that are given in the paper by Bader and Fang[2] (see Table 2 in that work). Since chemists like to compare the behaviour of atoms and molecules with models which are accessible to human experience, we make a daring comparison of the response of the interatomic forces in adaman-

tane on the insertion of helium yielding He@adam with an everyday event. It goes like this: There is an elevator which is filled to maximally allowed capacity by young men. Before the door closes an attractive young lady wants to enter the elevator. The young men in the front row are pushing the other men behind them against the wall in order to make space for the lady who shall feel comfortable in spite of the pressure in the overcrowded elevator. When the door opens she is leaving the elevator and the young men take up their old positions in order to release the pressure.

What is the origin of the attraction between the helium atom (the young lady) and the carbon atoms (the young men) in He@adam? Helium has a closed valence shell and chemical knowledge does not provide any clue about possible sources for interatomic attraction toward He except for very weak van der Waals forces.[6] The answer to this question was given in the paper by Bader and Fang[2] who showed that the stabilization of the helium atom in He@adam comes mainly from the Coulombic attraction between the electron density of He and the nuclei of the cage atoms which is larger than the repulsive Coulombic interactions between the atoms. This is in agreement with the negative sign for the Ehrenfest force for the He–C interactions because the potential energy of interatomic interactions parallels the Ehrenfest force. Another yet smaller stabilizing contribution comes from the intraatomic attraction between the electrons and the nucleus of He because the atomic radius of helium in He@adam is smaller than in free He. Then where do the repulsive forces come from?

Most chemists identify repulsive interactions between closed shell atoms with Coulombic interactions because the electronic "clouds" are in closer contact with each other than the nuclei. This intuitive reasoning is wrong! It has been shown in theoretical studies which were already published long time ago[7] and more recently by us[8] that the net electrostatic interactions between neutral atoms is attractive over a wide range of interatomic distances except for very short atom-atom separations which are much shorter than the equilibrium bond length and that the magnitude of the attractive forces is in most cases very high.[9] For example, the net Coulombic interaction between two nitrogen atoms in N_2 which is calculated by superimposing two nitrogen atoms with the frozen electron density of the (^{1}S) electronic ground state is stabilizing by −330 kcal mol^{-1}.[6b,7a,b] The very weak Coulombic attraction which is calculated for H_2 is atypical. Since dihydrogen is usually employed for teaching covalent bonding, most chemists believe that Coulombic attraction for covalent bonds is negligible which is not true.[6,7]

So what is the source for the repulsion which yields a large destabilization of He@adam with respect to He + adam? Figure 1a shows the atomic basin of He in He@adam which is available in free adamantane for the electron density of the carbon atoms (Figure 1b). The insertion of the helium atom into the adamantane cage requires removal of electronic charge from the region of the atomic basin designated for He due to the quantum theoretical law which pos-

tulates that electrons having the same spin must be located in different space regions. This is known as exchange repulsion or Pauli repulsion which is often neglected in chemical bonding models. A notable exception is the valence shell electron repulsion (VSEPR) model which considers Pauli repulsion as the dominant force for the geometry of molecules.[10] The strength of the Pauli repulsion between two electrons at shorter distances is much higher than the Coulombic repulsion. Figure 2 shows the electron–electron re-
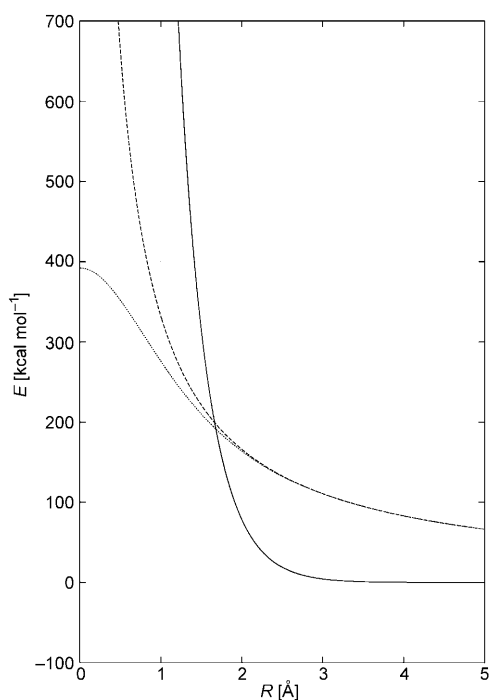

Figure 2. Calculated interaction energy between two electrons as a function of their distance r_{12}: Repulsive interactions calculated classically $\Delta E_{\text{elstat}}(\text{classical}) = q_1 \times q_2/r_{12}$ (-----); quasiclassical repulsion between two electrons in 1s orbitals $\Delta E_{\text{elstat}} = \int \rho_1 \times \rho_2/r_{12} \, d\tau_1 d\tau_2$ (•••••); exchange repulsion between two electrons with the same spin in 1s orbitals ΔE_{Pauli} (——). Reproduced from reference [7b].

pulsion between two electrons in 1s orbitals. It becomes obvious that the Pauli repulsion (solid line) clearly outstrips e–e Coulombic repulsion soon after the onset of the overlap between the 1s orbitals. The effect of the overlap becomes visible by the bifurcation of the two curves for the Coulombic repulsions which are calculated using the classical formular (dashed line) and the correct formular using the charge distribution of the 1s electrons (dotted line).[11] Since the overall Coulombic interactions in a molecule comprise also electron–nucleus attraction and nucleus–nucleus repulsion whose net effect is attractive in He@adam and most other neutral molecules,[6b, 7] it follows that the source for the repulsion between He and adamantane are the exchange (Pauli) forces.[12] The Pauli repulsion leads to a rearrangement of the electronic structure of the adamantane cage which weakens particularly the C−C bonds. It is the acting

of the Pauli repulsion which is responsible for the large energy increase of He@adam relative to He and the frozen structure of adamantane which is calculated by Strenalyuk and Haaland as 581 kJ mol^{-1}.

The driving force for the expulsion of the helium atom from He@adam after increasing the ^{t}C−^{s}C bond length from 160.0 pm in the equilibrium structure to 170.2 pm in the transition state according to the AIM analysis is the enhancement of the attractive carbon–carbon interactions which compensates for the loss of He⋯^{t}C attraction. The same reasoning holds true for the release of He from He⋯H$_3$CH. Our calculations of the latter species at MP2/6-311++G(2d,2p) showed that the energy of the helium atom is 70.2 kcal mol^{-1} lower than the energy of free He and that the value for the Ehrenfest force between He and C is −0.153 a.u. which means that the He–C interactions are attractive. The driving force for the expulsion of He comes again from the strengthening of the C−H bonds which are weakened by the helium–carbon attractive interactions in He⋯H$_3$CH. Note that, according to the AIM, there is no He–C chemical bond in the calculated He⋯H$_3$CH species because it is not a minimum on the potential energy surface.

Experimentally oriented chemists might wonder about the relevance of the arguments and conclusions which are reached here and in the previous studies[1,2] for chemistry. For practical purposes, it appears that there is no immediate gain in information for chemical research. Who cares whether the helium atom in He@adam—which has not and may never become synthesized—is bonded to carbon or not and whether the expulsion in the transition state is driven by the increase of the C−C bond energy or the release of the He–C repulsion? We think that there are two good reasons which justify to put efforts into the analysis of the interatomic interactions in He@adam which serves as a model for a molecule which has unconventional atomic connectivities. One reason is purely academic. Chemistry is the science of the understanding and alteration of the material world on a molecular scale.[13] A true scientific understanding of molecular species means that the forces which keep the atoms in a molecule together can be explained in terms of fundamental laws of physics. It is well known that the electrostatic force which are properly described by quantum chemical laws determines the physical and chemical properties of molecules.[14] It is thus a genuine goal of scientific chemistry unlike industrial chemistry to establish a connection between the appearance of a molecule and the underlying physical laws who describe the interatomic interactions. For practical purposes of synthetic chemistry it may be more useful to use heuristic bonding models which have been proven helpful for designing new molecules. But the patterns and schemes which are so powerful in chemistry[15] should not be confused with a correct description of the molecular electronic structure which can only be obtained from a quantum theoretical analysis. While the ad-hoc bonding models of chemistry are attractive for chemists whose research direction is frequently guided by intuitive reasoning which can be very fruitful, intuition is not a good guidepost

in the realm of quantum theory which is not accessible to human senses.

The second reason which makes it worthwhile for chemical research to analyze the interatomic forces and the electronic structure of molecules in more detail at the fine grained level of an atom lies in the possible improvement of the common bonding models which leads to a better understanding of chemical phenomena. A pertinent example is the electronic charge distribution in a molecule which in the present chemical literature is commonly described in terms of atomic partial charges. The atomic partial charges are then frequently used to estimate the nature of the ionic contribution to the interatomic interactions. This is misleading because atomic partial charges from whatever method they have been derived do not provide any information about the spatial distribution of the electronic charge within the atomic basin! Atomic partial charges are often used as indicator for ionic (electrostatic) bonding and two atoms which have partial charges with the same sign are supposed to be repel each other. But an atom which has an overall positive partial charge may have a local region of negative charge concentration which crutially determines the bond strength[16] and the chemical behaviour of the molecule. Figure 3 shows the Laplacian distribution of CO. The elec-
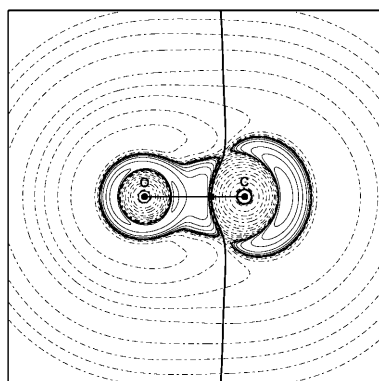

Figure 3. Contour line diagrams $\nabla^2\rho(r)$ of CO. Solid lines indicate areas of charge concentration ($\nabla^2\rho(r) < 0$) while dashed lines show areas of charge depletion ($\nabla^2\rho(r) > 0$). The thick solid lines connecting the atomic nuclei are the bond paths. The thick solid lines separating the atomic basins indicate the zero-flux surfaces crossing the molecular plane.

tronic charge in the C−O bonding region is clearly polarized toward the oxygen end which becomes obvious by the area of charge concentration at the oxygen end which is in agreement with the electronegativites of the atoms. Every charge partitioning method which we know gives a positive partial charge for carbon and a negative charge for oxygen in CO. But there is a K_{area} of charge concentration at the carbon atom whose maximum is located away from the nucleus. This local maximum is responsible for the unusual dipole moment of CO (0.11 D[17]) which has its negative end at the carbon side. It is also responsible for the stronger nucleophilicity and proton affinity of the carbon end because the local

charge concentration at carbon comes from the energetically highest lying molecular orbital (HOMO) of CO.[18]

In summary, we have shown that the statement about the existence of He−C bonds in of He@adam is not only supported by the AIM analysis of the electronic structure. The statement also does not contradict the conclusion that the expulsion of the helium atom is solely prevented be the C−C bond of the adamantane cage. The scientific activity with the seemingly exotic compound and topic is important and worthwhile for chemistry because it leads to a deeper understanding of the behaviour of atoms in a molecule and the nature of the interatomic forces which are grounded in elementary laws of physics.

We think that the arguments against the presence of He−C chemical bonds in He@adam given by Strenalyuk and Haaland[1] are valid within the realm of classical bonding models. However, we also think that the AIM analysis provides compelling evidence for the opposite view. In our view, the physical view of chemical bonding advocated by Bader and Fang is more sound and goes deeper when it comes to fundamental laws of physics than the chemical view of Strenalyuk and Haaland which is based on the pragmatic approach that is typical for chemistry. This may or may not be shared by chemists who rightfully point out that the classical bonding models have been proven as a powerful basis for experimental chemistry in the past century. This has not been achieved (yet) by the AIM based methods.

Acknowledgements

[1] T. Strenalyuk, A. Haaland, *Chem. Eur. J.* **2008**, *14*, DOI: 10.1002/chem.200800715, preceding paper in this issue.

[2] R. F. W. Bader, D.-C. Fang, *J. Chem. Theory Comput.* **2005**, *1*, 403.

[3] The topic was for the first time discussed in an earlier paper by A. Haaland, D. J. Shorokhov, N. V. Tverdova, *Chem. Eur. J.* **2004**, *10*, 4416. The arguments in this paper were supported by J. Poater, M. Solà, F. M. Bickelhaupt, *Chem. Eur. J.* **2006**, *12*, 2902. Opposing views have been published in reference [2] and by A. Krapp, G. Frenking, *Chem. Eur. J.* **2007**, *13*, 8256.

[4] R. F. W. Bader, *Atoms in Molecules: A Quantum Theory*, Oxford University Press, Oxford, **1990**.

[5] The MP2/6++311G(2d,2p) calculations were performed using Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W.

COMMUNICATION

Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Wallingford CT, **2004**. AIM analyses of the electron densities were performed using AIMAll (Version 08.05.04), Todd A. Keith, **2008** (aim.tkgristmill.com). The contour line diagrams were generated using AIMPAC: R. F. W. Bader: http://www.chemistry.mcmaster.ca/aimpac/imagemap/imagemap.htm.

[6] W. Koch, G Frenking, J. Gauss, D. Cremer, J. B. Collins, *J. Am. Chem. Soc.* **1987**, *109*, 5917.

[7] a) F. L. Hirshfeld, S. Rzotkiewicz, *Mol. Phys.* **1974**, *27*, 1319; b) M. A. Spackman, E. N. Maslen, *J. Phys. Chem.* **1986**, *90*, 2020.

[8] a) A. Kovács, C. Esterhuysen, G. Frenking, *Chem. Eur. J.* **2005**, *11*, 1813; b) A. Krapp, F. M. Bickelhaupt, G. Frenking, *Chem. Eur. J.* **2006**, *12*, 9196.

[9] A mathematical explanation for this finding is given in: a) W. Kutzelnigg in: *The Concept of the Chemical Bond, Vol. 1* (Ed.: Z. B. Maksic), Springer, Berlin/Heidelberg, **1990**, p. 1; b) F. M. Bickelhaupt, E. J. Baerends, *Rev. Comput. Chem.* **2000**, *15*, 1.

[10] R. J. Gillespie, P. L. A. Popelier, *Chemical Bonding and Molecular Geometry*, Oxford University Press, New York, **2001**.

[11] For a more detailed discussion see reference [7b].

[12] The same statement holds true for steric repulsion between bulky substituents which are often wrongly explained in terms of Coulombic repulsion between the electrons.

[13] G. Frenking in *The Autonomy of Chemistry in Relationship to the other Natural Sciences; 3rd Erlenmeyer-Colloquy for the Philosophy of Chemistry at the University of Marburg* (Eds.: P. Janich, N. Psarros), Könighausen & Neumann, Würzburg, **1998**.

[14] Recent research which is presently a hot topic in physical chemistry has shown that for a truly comprehensive understanding of chiral molecules the electroweak interactions must be considered which comprise the weak force as well as the electrostatic force: M. Quack, J. Stohner, M. Willeke, *Ann. Rev. Phys. Chem.* **2008**, *59*, 741.

[15] It is important to realize that many fundamental concepts such as the Lewis electron-pair model for covalent bonding have been introduced before modern quantum theory was developed and applied to chemistry. For a discussion of the history and the application of the Lewis electron-pair model see the special issue devoted to the topic *90 Years of Chemical Bonding*: *J. Comput. Chem.* **2007**, *28*, issue 1.

[16] We give two striking examples which underline the relevance of the topography of the charge distribution for the strength of the interatomic interactions; a) The calculation of the atomic partial charges in $(CO)_4Fe–BCp$ give a negative value of -0.56 e for Fe and a positive value of 0.32 e at B. Intuitively this could be interpreted as indication for strong ionic (electrostatic)Fe–B binding interactions. A more detailed bonding analysis suggests that there is indeed strong electrostatic attraction between Fe and B which arises, however, from the local negative charge concentration of the electron-lone pair at boron of the BCp donor ligand and the Fe nucleus. The $(CO)_4Fe$ metal fragment has an area of local charged depletion at Fe in the direction toward the BCp ligand: J. Uddin, G. Frenking, *J. Am. Chem. Soc.* **2001**, *123*, 1683; b) The bond dissociation energy and the intrinsic interaction energy between the frozen fragments of $(CO)_5M–PX_3$ shows that the M−P bonds of the halogen substituted systems with X=F, Cl are clearly weaker yet shorter than the M−P bonds when X=H, Me. A bonding analysis shows that the attractive orbital interactions in the former species are stronger than in the latter. The weaker bonding and shorter distances for the PF_3 and PCl_3 complexes come from the significantly smaller M-P electrostatic attraction which is caused by the much more compact electron lone-pair at phosphorous which overlaps much less with the metal nucleus than the electron lone-pair of the PH_3 and PMe_3 ligands: K. Wichmann, N. Fröhlich, J. Grobe, W. Golla, D. Le Van, B. Krebs, M. Läge, *Organometallics* **2002**, *21*, 2921.

[17] J. S. Muenter, *J. Mol. Spectrosc.* **1975**, *55*, 490.

[18] For a detailed discussion of the electronc structure and bonding situation in CO see: G. Frenking, C. Loschen, A. Krapp, S. Fau, S. H. Strauss, *J. Comput. Chem.* **2007**, *28*, 117.