

Egg-shaped Fullerene-Type and Dragon-Type Cages Unsuitable for Forming Donor-Acceptor Complexes with Noble Gases

Leonie Anna Mück¹

Johannes-Gutenberg Universität Mainz, Germany

Received 10.12.2010, accepted 27.12. 2010, published 28.12.2010

The discovery of the first neutral compound with chemically bound argon HArF in 2000 was a sensation in noble gas chemistry. If HArF is interpreted as a donor-acceptor complex with H^+ as a strong acceptor and F^- as a donor fragment the question arises if light noble gases helium, neon and argon could also form donor-acceptor complexes with common Lewis acids and bases like AlF_3 and NH_3 . A covalent interaction between a Lewis acid, a Lewis base and a noble gas could be achieved by spatially dividing the donor and acceptor fragment thus incorporating the donor-acceptor complex into a cage-like structure. Due to the small polarizability of the light noble gases the Lewis acidity and basicity of the employed donor and acceptor must be extremely high for the noble gas to react with the cage. Novel kinds of organic donors and acceptors were designed to fulfill these criteria. These novel donors and acceptors were included in organic cages that fix geometrical conditions to be most favourable for the formation of complexes with noble gases. Among the many considered cage-types were the particularly aesthetic egg-shaped fullerene-type cages and dragon-shaped cages. Despite their beauty and their conceptual originality, they did not meet the requirements of yielding a negative reaction energy with light noble gases but they may be useful for other purposes, e. g. as hosts for hydrogen molecules.

1 Introduction

Since the first discovery of a xenon compound by Bartlett and Hoppe[1, 2] noble gas chemistry has fascinated chemists from all over the world. A broad range of reactions and compounds with xenon and krypton has been discovered since then.[3] But due to their smaller polarizability, the chemistry of the lighter noble gases is more limited. Forcing the light noble gases to be involved in chemical bonding requires extremely reactive reagents and low temperatures. Therefore the discovery of the first neutral argon compound H-Ar-F in 2000[4, 5] was a sensation. Computational analyses confirmed that in H-Ar-F argon is indeed chemically bound.[6]

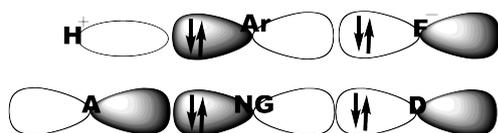


Figure 1: Bonding situation in H-Ar-F and in D-NG-A (D=Donor, A=Acceptor, NG=Noble Gas)

The bonding situation in H-Ar-F can be explained with the help of a 3-center-4-electron bond (see figure 1). The same bonding situation could be realized substituting the proton by a strong Lewis-acid and the fluorine-anion by a Lewis-

base, the argon can thus be viewed to be "trapped" between an electron donating and an accepting group. However, to realize such a compound an extremely strong acceptor and donor has to be used while especially the properties of the acceptor seem to be crucial.[7].

To increase acceptor strength in organic Lewis-acids, electron-withdrawing groups (e. g. fluorine atoms) can be placed close to the electron accepting atom. Electron density is then removed from the accepting atom by hyperconjugation. The acceptor strength of an ordinary Lewis-acid like AlF_3 can be enhanced by pyramidalization.[8, 9, 10, 11] Restricting F-Al-F and H-N-H angles to 109° in AlF_3 and NH_3 increases the reaction energy of AlF_3 with NH_3 enormously compared to the reaction energy of planar AlF_3 with planar NH_3 (F-Al-F/H-N-H angles in planar molecules: 120°). In table 1 the reaction energies of pyramidalized and planar AlF_3 and NH_3 computed on different levels of theory are listed. Depending on the level of theory pyramidalization of the donor and acceptor increases the reaction energy by up to 100 kJ mol^{-1} . Recent investigations showed that there exists a minimum on the potential energy surface (PES) of $F_3Al-Ar-NH_3$ between Al and Ar at covalent distances, if the F-Al-F and H-N-H angles were restricted to 109.47° . No minimum between N and Ar could be detected.

¹Johannes Gutenberg-Universität, Jakob-Welder Weg 11, 55128 Mainz, MueckL@uni-mainz.de

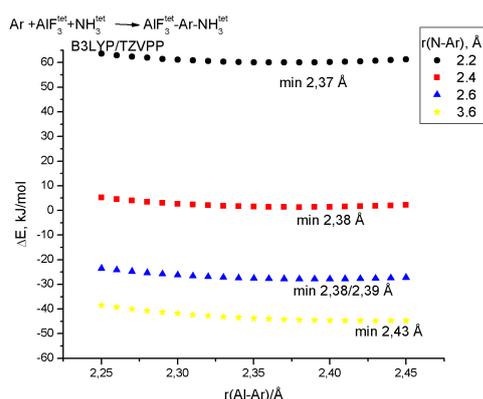


Figure 2: Scan of $r(\text{Ar-Al})$ at fixed Ar-N distances in pyramidalized $\text{AlF}_3\text{-Ar-NH}_3$

In figure 2 the scan of the Al-Ar bond at several fixed N-Ar bond lengths is plotted (B3LYP/def2-TZVPP level of theory)². If the Ar-N bond is sufficiently long the reaction energy is negative, which conveys favourable interaction of the donor-acceptor frame with the noble gas.[7] It should be noted, though, that optimizing the Ar-Al and Ar-N distance in $\text{AlF}_3\text{-Ar-NH}_3$ the complex decomposes into $\text{Ar}+\text{AlF}_3+\text{NH}_3$. Keeping the complex from decomposition requires connecting the donor and acceptor fragment thus keeping them at a fixed distance.

The aim of the presented project is to design donor-acceptor compounds that would entertain in chemical bonding with the light noble gases helium, neon, and argon. This is to be achieved by spatially dividing the donor and acceptor groups including them in a cage-like structure and thus fixing the geometrical conditions optimally for the noble gas to entertain in chemical bonding with the cage at covalent distances. This means that firstly the distance between donating and accepting group needs to be rigidly kept at the covalent minimum on the PES of D-NG-A (D=donor, A=acceptor, NG=noble gas). Secondly the donor/acceptor fragment should be chosen so that pyramidal geometry around the donating/accepting atom is secured. The requirements for a cage to be the host of a noble gas are therefore: 1. rigidity, 2. pyramidal geometry of donor/acceptor fragment, 3. little repulsive interaction of the noble gas with all parts of the cage, except the donor/acceptor fragment.

Table 1: Complex formation energy of $\text{AlF}_3\text{-NH}_3$, ΔE (1) with pyramidalized AlF_3 and NH_3 , ΔE (2) with planar AlF_3 and NH_3 , values in kJ mol^{-1}

Method/Basis Set	ΔE (1)	ΔE (2)
RHF/6-31G**	-286.6	-182.1
RHF/def2-TZVPP	-268.6	-167.7
B3LYP/6-31G**	-274.1	-180.4
B3LYP/def2-TZVPP	-254.5	-163.9
MP2(full)/def2-TZVPP	-279.8	-175.5

²This figure is also available in the supporting information of ref. [7]

³throughout the paper the following colour code of elements will be used for the figures: Carbon (grey), hydrogen (white), fluorine (yellow), aluminium (magenta), nitrogen (blue)

A plethora of cages were designed and considered, but only a fraction was successful in yielding a negative reaction energy with argon (refer to reference [7] for more details). Most did not show favourable reaction energies with the light noble gases. But although they did not meet these requirements, some of them are conceptually a lot more interesting than the cages presented in reference [7] and furthermore very aesthetic. These will be presented in this paper.

2 Computational Methods

Preliminary calculations were carried out with the Gaussian 03 program package on various levels of theory as noted.[12] Geometry optimization of the cages was carried out at the RHF/6-31G* level of theory using the Gaussian 03 program package. For xenon a stuttgart/RCP effective core potential was used to account for relativistic effects. In the calculations donor-acceptor complexes, the basis set superposition error (BSSE) can play an important role. The energies presented here are uncorrected for BSSE, however this error was estimated to be around 6 kJ mol^{-1} for similar argon containing cages at the RHF/6-31G* level of theory using the counterpoise correction method as implemented in Gaussian 03.[7]

3 Egg-Shaped Fullerene-type cages

Choice of donor and acceptor For the egg-shaped cages acceptors and donors with an adamantane framework inserting Al in case of the acceptor and N in case of the donor were chosen (see figure 3)³. The advantage of these compounds is their rigidity. The adamantane cage does not allow geometrical rearrangement during a donor-acceptor reaction, therefore pyramidal geometry is secured. To further increase acceptor-strength of aluoadamantane nine hydrogen atoms were substituted by fluorines. Aluminium was chosen over other group 13 elements to be the accepting center in the adamantane-type lewis acid after computing the acceptor strength of all group 13 adamantane derivatives towards NH_3 on B3LYP/def2-TZVPP level of theory. The reaction energy of the fluorinated aluoadamantane with ammonia amounts to $-195.6 \text{ kJ mol}^{-1}$ (B3LYP/def2-TZVPP level of theory). Aluoadamantane is experimentally unknown but boroadamantane has been synthesized by Mikhailov *et al.*[13] and is stable in air and water. Boroadamantane can be utilized to synthesize N-adamantane.[14]

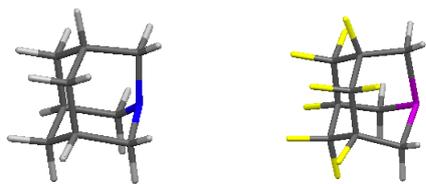


Figure 3: N-adamantane and fluorinated Al-adamantane

Cages If a suitable donor and acceptor are chosen the design of a cage comes down to building the connection between these fragments. The connection should be kept as rigid as possible to force the noble gas to a covalent distance with respect to the donor/acceptor fragment, thus in egg-shaped cages the connection between Al-adamantane and N-adamantane was chosen to contain only aromatic C_6 -units resembling an egg-shaped fullerene. It is crucial to keep the diameter of the cage as large as possible in order not to bring forth repulsive interactions between the noble gas and the cage. The distance between Al and N determines which noble gas is a suitable candidate for reaction with this particular cage. All cages built in this manner are presented in figure 5 and figure 6.

Egg 1 – although perfect in form – is too large in order to obtain a covalent bond length between the noble gas and the donor/acceptor, the noble gases inserted into the other cages were chosen in correspondence to their covalent radius. Interaction energies and geometrical data are displayed in table 2. Additionally the reorganization energy E_{RO} , which corresponds to the energy needed for the geometrical changes upon insertion of the noble gas, is listed. The sum of the reaction energy and the reorganization energy should be negative for the reaction to be exothermic. Furthermore the reorganization energy can be taken as a measure for the rigidity of the cage.

The only exothermic reaction energy obtained is that of krypton being inserted into Egg 2, but looking at $r(\text{Al-Kr})$ and $r(\text{N-Kr})$ the interaction is rather of Van-der-Waals nature and not a covalent interaction. The least endothermic interaction with covalent bond lengths exhibits krypton being inserted in Egg 3 (60.1 kJ mol^{-1}), but this can hardly be called a favourable interaction between the donor-acceptor complex and the krypton. As a positive aspect should be noted that the angles NG-Al-C and NG-N-C are in all cases close to 100° , which shows that pyramidality could be ensured. The reorganization energy is mostly smaller than 10 kJ mol^{-1} which underlines the rigidity of the cage. Exceptions are Egg 2 Xe and Egg 4 Ne. The large reorganization energies can be explained by a possible repulsive interaction between the noble gas and the fullerene-type connection between the donating and accepting group. In other words, the diameter of the cages seems to be too small in order to avoid repulsive interaction with the noble gas. Due to the high number of atoms in the cages the geometry and relative energies were only calculated on RHF/6-31G* level of theory. According to table 1 relative energies on RHF/6-31G* level of theory can differ by up

to 30 kJ mol^{-1} from more sophisticated levels of theory (B3LYP/def2-TZVPP in this case). In case of a possible covalent interaction of the noble gas with the donor-acceptor fragment in this error range of 30 kJ mol^{-1} it was planned to extend the computations to higher levels of theory, but none of the egg-shaped cages came close to this range.



Figure 4: N-adamantane and perfluoroalumoaryl derivative

4 Dragon-type Cages

Choice of donor and acceptor For the *dragon* type cages an aluminium perfluoroaryl derivative was chosen as an acceptor. Group 13 perfluoroaryl acceptors of type $\text{E}(\text{C}_6\text{F}_5)_3$ ($\text{E}=\text{B}, \text{Al}, \text{Ga}$) are known to be extremely strong Lewis acids although the aryl groups are assembled in a planar geometry around the element E. There is still a dispute about which element – boron or aluminium – should be inserted to yield a stronger acceptor. According to Timoshkin *et al.*[15] the acceptor strength of $\text{Al}(\text{C}_6\text{F}_5)_3$ is larger than $\text{B}(\text{C}_6\text{F}_5)_3$ towards all lewis-bases except for H^- , therefore aluminium was used here. To enhance lewis acidity additionally the aryl groups were pyramidalized by binding them to a CH group yielding $\text{Al}(\text{C}_6\text{F}_4)_3\text{CH}$ as a sum formula (see figure 4). The reaction energy of $\text{Al}(\text{C}_6\text{F}_4)_3\text{CH}$ with ammonia is considerably lower than of aluoadamantane ($244.5 \text{ kJ mol}^{-1}$, B3LYP/def2-TZVPP level of theory), $\text{Al}(\text{C}_6\text{F}_4)_3\text{CH}$ seems to be the stronger acceptor. Just like in the egg-shaped cages N-adamantane was used as a donor-fragment (see figure 4).

Cages To make the cage as rigid as possible, aromatic units C_6H_4 were chosen as a connection between the donor and the acceptor fragment. Differing in the number of aromatic rings within the connection, two cages with different donor-acceptor distances – dragon 1 and dragon 2 – were designed as displayed in figure 7. To further increase the acceptor strength of the $\text{Al}(\text{C}_6\text{F}_4)_3\text{CH}$ fragment, fluorine atoms were added to all positions close to the aluminium atom. It should be noted that in dragon 1 there are fluorines pointing into the cage, while in dragon 2 fluorines were only added to positions on the outside of the cage. Due to the small Al-N distance only the light noble gases were suitable candidates for reacting with both cages. In dragon 1 neon and argon were inserted while for dragon 2 only argon was tested.

The reaction energies ΔE upon inserting the different noble gases into the cages as well as the reorganization energy E_{RO} and some important geometrical data are displayed in table 3. None of the reaction energies are neg-

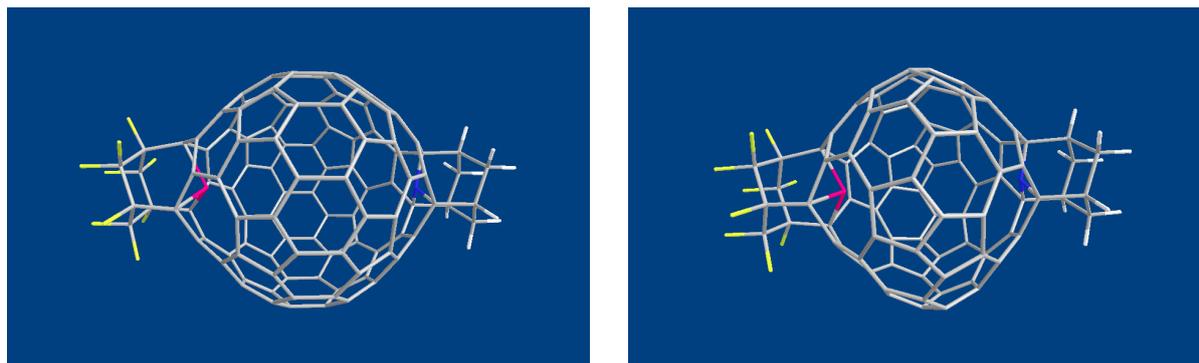


Figure 5: Left: Egg 1, $r(\text{Al-N})=8.37 \text{ \AA}$, diameter $\approx 9 \text{ \AA}$, right: Egg 2, $r(\text{Al-N})=6.38 \text{ \AA}$, diameter $\approx 9 \text{ \AA}$.

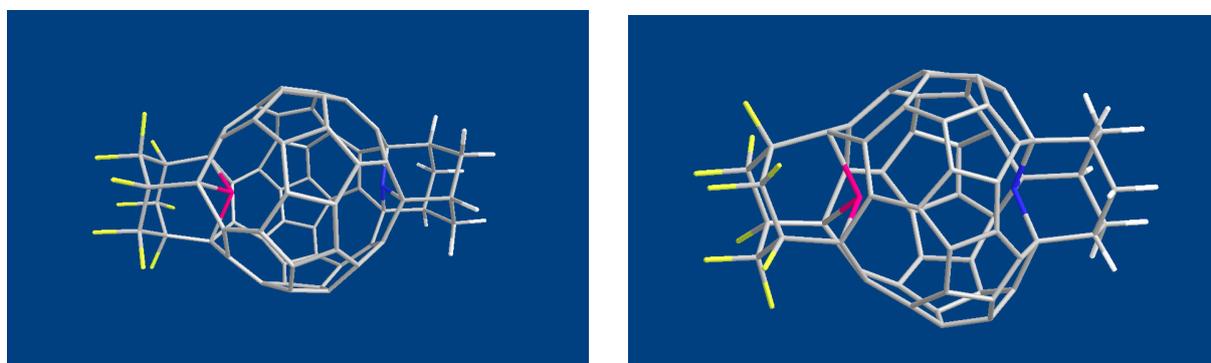


Figure 6: Left: Egg 3, $r(\text{Al-N})=5.25 \text{ \AA}$ diameter $\approx 7 \text{ \AA}$, right: Egg 4, $r(\text{Al-N})=3.88 \text{ \AA}$, diameter $\approx 6.5 \text{ \AA}$.

Table 2: Reaction energy ΔE for inserting a noble gas into an egg-shaped cage, reorganization energy E_{RO} of the cage, angles around aluminium and around nitrogen (averaged) and the distances $r(\text{NG-Al})$ as well as $r(\text{NG-N})$, RHF/6-31G* level of theory, *for Xe stutt/RCP basis set was used.

Cage with NG	ΔE , kJ mol^{-1}	E_{RO} , kJ mol^{-1}	$\angle \text{NG-Al-C}$	$\angle \text{NG-N-C}$	$r(\text{NG-Al})$, \AA	$r(\text{NG-N})$, \AA
Egg 2 Kr	-16.95	1.7	105.3 °	100.8 °	2.97	3.39
Egg 2 Xe*	71.9	39.9	105.6 °	100.9 °	2.95	3.41
Egg 3 Ar	82.8	3.3	102.0 °	102.1 °	2.49	2.85
Egg 3 Kr	60.1	7.2	102.4 °	101.9 °	2.49	2.85
Egg 4 Ne	100.0	21.5	100.0 °	106.2 °	1.92	2.27



Figure 7: Left: Dragon 1, $r(\text{Al-N})=3.76 \text{ \AA}$, right: Dragon 2, $r(\text{Al-N})=4.65 \text{ \AA}$.

Table 3: Reaction energy ΔE for inserting a noble gas into a Dragon type cage, reorganization energy E_{RO} of the cage, angles around aluminium and around nitrogen and $r(\text{NG-Al})$ as well as $r(\text{NG-N})$, RHF/6-31G* level of theory.

Cage with NG	ΔE , kJ mol ⁻¹	E_{RO} , kJ mol ⁻¹	\angle NG-Al-C	\angle NG-N-C	$r(\text{NG-Al})$, Å	$r(\text{NG-N})$, Å
Dragon 1 Ne	31.2	24.5	115.9°	107.5°	1.94	2.44
Dragon 1 Ar	118.6	54.7	115.9°	106.7°	2.21	2.55
Dragon 2 Ar	88.5	42.9	113.0°	107.1°	2.28	2.61

ative. The least repulsive interaction seems to take place between neon and dragon 1, but 31.2 kJ mol⁻¹ can hardly be called favourable. Furthermore the Ne-N and Ne-Al distances are relatively large, it is questionable if a covalent bond is obtained. Reorganization energies are comparably high, the dragon-type cages are a lot less rigid than the egg-type cages.

In Dragon No. 1 the high reorganization energies (54 kJ mol⁻¹ for argon and 24 kJ mol⁻¹ for neon) could be explained by the fluorines in the middle of the cage being repulsed by hydrogens that are connected with the aromatic system. The angles along the aromatic units in the connection change greatly during insertion of the noble gas thus this process is high in energy. In dragon 2 the reorganization energy upon insertion of argon is lower than in dragon 1 by around 12 kJ mol⁻¹, but the absolute value (42.9 kJ mol⁻¹) is still very high. This could be explained by the fact that in dragon 2 only hydrogens – and no fluorines – point into the cage, therefore the repulsive interaction between the atoms that are "cramped" inside the cage are less pronounced.

Compared to the egg-shaped cages, the angles around aluminium are larger than in the dragon-type cages. This conveys that Al(C₆F₄)₃CH is less rigid than aluoadamantane, which may weaken the acceptor strength of Al(C₆F₄)₃CH.

5 Conclusion

In this project the bonding model of the first neutral argon compound H-Ar-F (a 4-electron 3-center bond) was applied to donor-acceptor complexes with noble gases. Since these complexes are very sensitive to geometrical changes, cages were designed to spatially divide the donor and acceptor fragment forcing the noble gas to interact with the donor and acceptor fragment at covalent distances by the rigid cage structure. Especially pyramidalization of the donor and acceptor is important as it increases the acceptor strength enormously. Two types of acceptor fragments (aluoadamantane and Al(C₆F₄)₃CH) and one type of donor fragment (N-adamantane) were used to build two types of cages, namely egg-shaped and dragon-shaped ones. As a connection between the donor and acceptor fragment two types of units were utilized, fullerene-type and aromatic units. Non of the cages presented here have the desired properties of readily reacting with a light noble gas in contrast to the cage presented in Reference [7]. This is probably due to the repulsive interaction between the noble gas and the connection between the donor and the acceptor fragment that constitutes the cage-like structure. The "successful" cage of reference [7] employs a linear alkyne-

connection thus minimizing the repulsive energy between the noble gas and the cage. Another reason for the failure of the presented egg-type and dragon-type cages might be an unsuitable distance between the donor and the acceptor fragment. Further investigations would be necessary to thoroughly study the reasons for the unfavourable reaction energies of the egg-type and dragon-type cage

Although the cages turned out to be unsuitable for their original purpose, they are conceptually very interesting in terms of the design of the connection between donor/acceptor fragment and in terms of choice and construction of donor/acceptor fragment. Possibly they could be used for other purposes, e. g. trapping different atoms/molecules like hydrogen in the cages.

6 Acknowledgements

The author would like to thank Alexey Yu. Timoshkin for hospitality in St. Petersburg and for initiating this project, Prof. Gernot Frenking for advice and the Marburger Rechencluster MaRC for excellent service. Funding by the *Go East* program of the *Deutsche Akademische Austauschdienst* is gratefully acknowledged. Furthermore the author would like to express her gratitude to the MAINZ Graduate School of excellence for support.

Supplementary information available Cartesian coordinates of selected cages with and without noble gases are available as supplementary material.

References

- [1] N. Bartlett, *Proc. Chem. Soc.* **1962**, 218.
- [2] R. Hoppe, W. Dähne, H. Mattauch, K. M. Rödder, *Angew. Chem.* **1962**, 74, 903.
- [3] J. F. Lehmann, H. P. Mercier, S. G. J., *Coord. Chem.* **2002**, 1, 233–234.
- [4] L. Khriachtchev, M. Pettersson, N. Runeberg, J. Lundell, R. M., *Nature* **2000**, 406, 874–877.
- [5] N. Runeberg, P. M., L. Khriachtchev, L. J., M. Räsänen, *J. Chem. Phys.* **2001**, 114, 836–841.
- [6] J. Frunze, M. Lein, F. G., *Chem. in unserer Zeit* **2002**, 36, 128–130.

- [7] L. A. Mück, M. von Hopffgarten, A. Timoshkin, G. Frenking, *J. Am. Chem. Soc.* **2009**, *131*, 3942–3949.
- [8] V. Horvath, I. Hargittai, *J. Chem. Phys.* **2003**, *107*, 1197–1202.
- [9] V. Horvath, I. Hargittai, *Struct. Chem.* **2004**, *15*, 233–236.
- [10] S. Geier, A. Gille, T. Gilbert, D. W. Stephan, *Inorg. Chem.* **2009**, *48*, 10466–10474.
- [11] E. Otten, R. Neu, D. W. Stephan, *J. Am. Chem. Soc.* **2009**, *131*, 9918–9919.
- [12] 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. 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 03, Revision C.02*, Gaussian, Inc., Wallingford, CT, 2004.
- [13] B. M. Mikhailov, *Pure & Appl. Chem.* **1983**, *55*, 1439–1452.
- [14] Y. N. Bubnov, M. E. Gursky, D. G. Pershin, *J. Organometall. Chem.* **1991**, *412*, 1–8.
- [15] A. Timoshkin, G. Frenking, *Organometallics* **2008**, *27*, 371–380.