DOI: 10.1002/anie.201200148

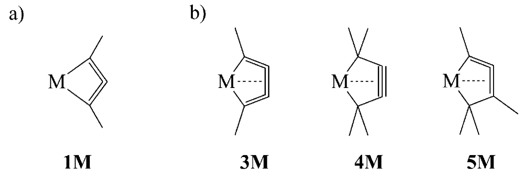
Metallacycloallenes

Theoretical Evidence of the Stabilization of an Unusual Four-Membered Metallacycloallene by a Transition-Metal Fragment**

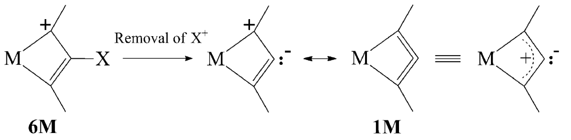
Subhendu Roy, Eluvathingal D. Jemmis, Axel Schulz,* Torsten Beweries, and Uwe Rosenthal**

Dedicated to Professor Roald Hoffmann on the occasion of his 75th birthday

Metallacycles, such as cycloallenes, dienes, alkynes, and cumulenes, with their significant role in multiple synthetic and catalytic processes, also attract much attention owing to their unusual geometrical parameters and bonding features.[1] There have been many reports on the metallacyclobutadiene,[2] but more exotic and challenging are the still unexplored 1-metallacyclobuta-2,3-dienes **1M** (four-membered metallacycloallenes MC_3R_2 with no substituent at the central carbon atom of the MC_3 ring; M = Ti, Zr, Hf; Scheme 1 a). The carbocyclic analogue, 1,2-cyclobutadiene, has a high calculated strain energy of 74.9 $kcal\,mol^{-1}$, thus reflecting the difficulty in isolating a molecule of this type.[3] Schrock et al. obtained two complexes described as "deprotiometallacyclobutadienes", $[Mo\{C_3(tBu)_2\}\{OCH(CF_3)_2\}_2(py)_2]$[4a] (**2Mo**) and $[CpW\{C_3(tBu)_2\}Cl]$,[4b] which were unexpectedly formed during the metathesis of terminal alkynes and have the structural skeleton of complex **1M**. Another related structure is a η^3-phenylallenyl zirconocene complex, $[Cp_2Zr(CH_3)(\eta^3\text{-}C(Ph){=}C{=}CH_2)]$,[5] but this compound has three substituents at the terminal carbon atoms of C_3 fragment rather than two substituents in complex **1M**. Generally, Group 4 metals have a fascinating reputation of stabilizing reactive C_4 fragments in the form of five-membered metallacyclocumulenes (**3M**),[6a,c] metallacyclopentynes (**4M**),[6b,c] and metallacycloallenes (**5M**)[5c,6d] (Scheme 1 b). These complexes are well-documented and show interaction of the metal with the internal carbon atoms along with the terminal carbon atoms. Incidentally, the secret for successful isolation of **1M** may also lie in stabilizing the central carbon atom of the four-membered ring by internal complexation, as is seen from the well-known metallcycloallyloid[7] **6M** (Scheme 2). Therefore, we attempted to isolate complex **1M** following previously successful strategies starting from lithiated allenes (LiRC=C=CRLi; R = Ph) and metallocene dichlorides $[Cp'_2MCl_2]$ ($Cp' = C_5H_5$ or C_5Me_5; M = Ti, Zr, Hf). The unexpected failure of this attempt to isolate complex **1M** prompted us to address the problem theoretically.



Scheme 1. Representations of a) a four-membered metallacycloallene (**1M**) and b) known unusual five-membered metallacycles (**3M–5M**).



Scheme 2. Generation of complex **1M** from a metallacycloallyloid complex **6M**.

Herein, we present a way of stabilizing an unusual structure **1M** using suitable substituents in conjunction with a transition-metal fragment in an experimentally viable way, whereby an unprecedented M···C interaction is observed. This challenging complex also presents insights into an all-pervasive but occasionally controversial topic, namely the chemical bond. The study gives a critical account of the various traditional analysis of bonding using molecular orbital (MO) and natural bond orbital (NBO)[8] approaches, especially for a chemical bond that appears to be very crucial for a molecule on the basis of chemical intuition. We have studied complexes **1M_R** (M = Ti, Zr, Hf in $\{Cp_2M\}$)[9] with substituents R = H, Ph, CH_3[*] as well as with several special substituents R = NH_2, NMe_2, piperidino, NHC, and CO at

---

[*] S. Roy, Prof. Dr. E. D. Jemmis
Department of Inorganic and Physical Chemistry
Indian Institute of Science
Bangalore-560012 (India)
Prof. Dr. E. D. Jemmis
Indian Institute of Science Education and Research
Thiruvananthapuram
CET Campus, TVM-695016 (India)
E-mail: jemmis@iisertvm.ac.in
Prof. Dr. A. Schulz
Abteilung Anorganische Chemie, Institut für Chemie, Universität Rostock
Albert-Einstein-Strasse 3a, 18059 Rostock (Germany)
E-mail: axel.schulz@uni-rostock.de
Dr. T. Beweries, Prof. Dr. U. Rosenthal
Leibniz-Institut für Katalyse e.V. an der Universität Rostock
Albert-Einstein-Strasse 29a, 18059 Rostock (Germany)
E-mail: uwe.rosenthal@catalysis.de

[**] S.R. and E.D.J. acknowledge the SERC of IISc for computational resources and the DST, New Delhi, India for financial support (J.C. Bose Fellowship).

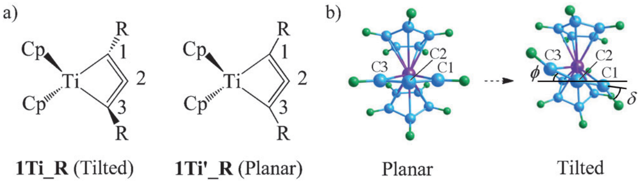
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201200148.

[*] Notations for the structures **1Ti_R**: The substituents on C1 and C3 are represented by **R**, for example **1Ti_CH₃** denotes $[Cp_2TiC_3(CH_3)_2]$ ($Cp = C_5H_5$); R = H, Ph, CH_3, NH_2, NMe_2, piperidino, NHC, CO (NHC = N-heterocyclic carbene, here imidazol-2-ylidene).

the BP86[10,11]/def2-SVP[12] level of theory[13] using the Gaussian suite of program packages.[14]

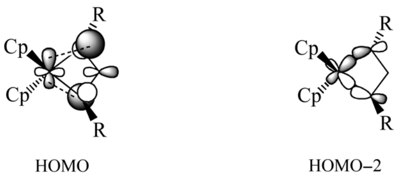
Stability of the wavefunction of complex **1Ti_R** was checked for each case regarding the possible complex electronic structure for this molecule. The singlet state is found to be the most preferred one over the triplet state and the open-shell singlet state for these complexes unless otherwise specified.

The optimized structure of complexes **1Ti_R** with R = H, Ph, CH_3 takes up a tilted geometry with the MC_3 ring deviating from the plane (equatorial plane) that bisects the Cp_2M angle; the substituents R deviate out of the M-C1-C2-C3 plane to a significant extent (Scheme 3a,b; Supporting Information, Table S1).



Scheme 3. a) Representations of the optimized structures of complex **1Ti_R** (R = H, Ph, CH_3) and the planar complex **1Ti'_R**. b) Planar versus tilted: ϕ represents the deviation of the MC_3 ring from the Cp-M-Cp bisecting plane and δ represents the deviation of the substituents R from the M-C1-C2-C3 plane in complex **1Ti_R**. C blue, M crimson, R green.

The constrained structure with no distortion, denoted **1Ti'_H**, comes out as a first-order saddle point that is 20.0 kcal mol^{-1} higher in energy than the optimized complex **1Ti_H**. The triplet state of complex **1Ti_H**, which adopts a planar structure, is calculated to be less stable than the singlet state by 10.0 kcal mol^{-1} (for other complexes, see the Supporting Information, Table S3). Fragment molecular orbital (FMO) analysis[15] using the ADF2007.01 program package[16] was carried out for complex **1Ti_Ph** to obtain a better understanding of the interactions in the complex by dividing it into two fragments: the metal fragment (Cp_2Ti), where the Ti atom is in the formal oxidation state +2 with two valence (d^2) electrons, and the allenic ligand fragment C_3R_2. There are two MOs found in complex **1Ti_Ph**: HOMO and HOMO−2 (Scheme 4; Supporting Information, Figure S1) that are responsible for two Ti−C bonds, which can be assigned to the two terminal Ti−C bonds of 2.202 Å (compared to the calculated Ti−C σ bond length of 2.168 Å in $[Cp_2TiMe_2]$). Despite close interatomic distances of the Ti−C1/C3 bonds (2.202 Å) and Ti···C2 (2.211 Å), there is no MO corresponding to a distinct Ti···C2 interaction. We could not locate any lone pair on the central carbon atom C2 in complex **1Ti_Ph** as may have been anticipated from Scheme 2. Both C1−C2 and C2−C3 have two bonding orbitals, one σ and another π with high occupancies (Supporting Information, Table S4).



Scheme 4. Important molecular orbitals of complex **1Ti_Ph**.

The correlation diagram (Figure 1) between the planar and tilted structure of complex **1Ti_Ph** reveals that the planar complex **1Ti'_Ph** has a very small HOMO–LUMO energy gap and consequently it undergoes structural distortion, thus allowing mixing of these MOs to stabilize the tilted complex **1Ti_Ph** to a greater extent.[18] Importantly, the metal can effectively interact with the central carbon atom C2 in the planar structure (LUMO; Figure 1). However, this MO needs to be filled up by electrons to stabilize the planar structure **1Ti'_Ph**, where the MC_3 ring is coplanar with the equatorial plane of the Cp_2M moiety. Indeed, the dianionic complex **1Ti''_Ph**, which has two more electrons than **1Ti_Ph**, adopts a planar structure. There are specific ways of providing two electrons to complex **1Ti_R** in neutral state: a) by using Group 6 metals (complex **7M**); b) by incorporating two nitrogen atoms in the ring to form a heterometallcycloallene (**8Ti**); and c) by using appropriate substituents that are capable of donating two electrons to complex **1Ti_R** (R = NH_2, NMe_2, piperidino, NHC, CO; Scheme 5).

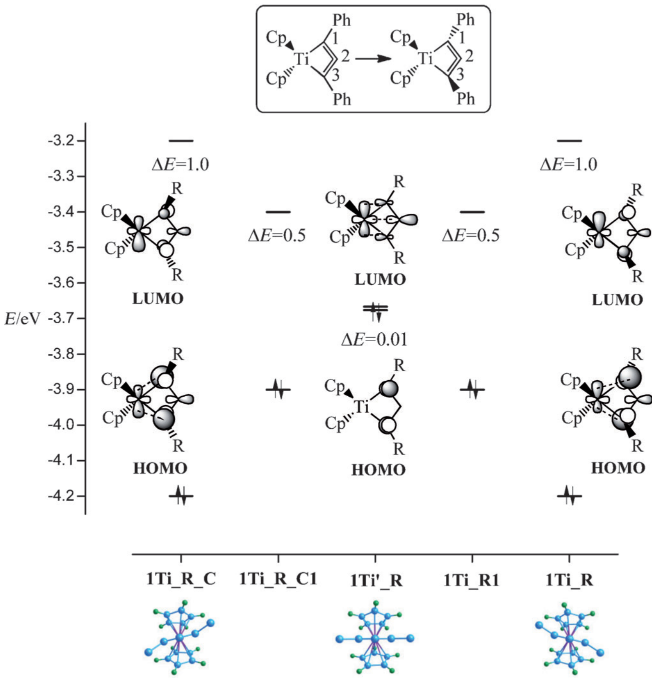
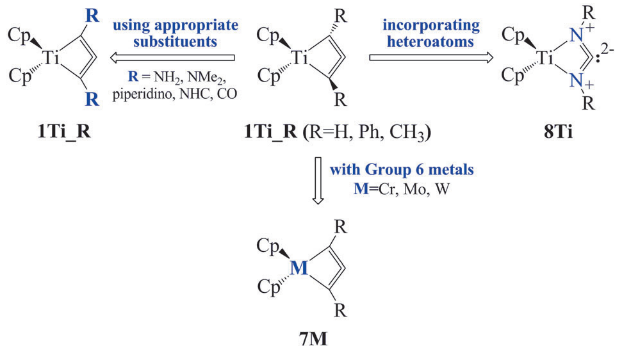


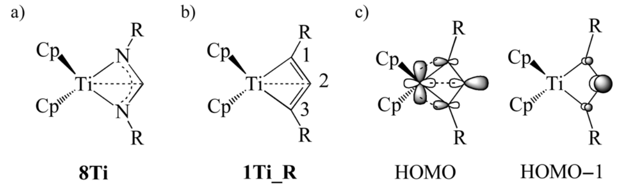
Figure 1. Correlation diagram between the untilted (or planar) structure **1Ti'_R** and the tilted structure **1Ti_R** (R = Ph). The variation of the energy of HOMO and LUMO is plotted as a function of distortion in complex **1Ti_R** (on both sides). **1Ti_R_C** refers to the other conformer of complex **1Ti_R. 1Ti_R1** and **1Ti_R_C1** are intermediate structures.[17]

In support of the first possibility, there are already the two above-mentioned Group 6 complexes, namely the molybdenum **2Mo** and tungsten complexes. Thus, our theoretical study also provides a justification for the ease of formation of the Mo and W complexes during the metathesis of alkynes. We



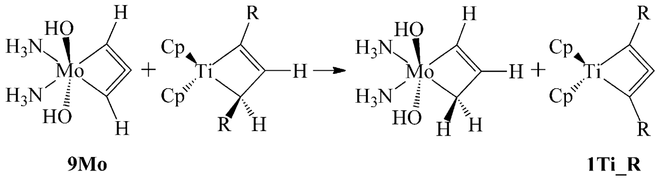
Scheme 5. Representation of the transformation of tilted complex **1Ti_R** to planar species.

have also reported Ti-NCN metallacycles (**8Ti**; Scheme 6a), which undergo coupling with another Cp$_2$Ti fragment or dimerize to form two dinuclear titanocene complexes.[19]



Scheme 6. Representations of a) complex **8Ti** (R = cyclohexyl) and b) complex **1Ti_R** (R = NH$_2$, NMe$_2$, piperidino, NHC, CO). c) Important molecular orbitals of complex **1Ti_Pip**.

The isodesmic equation devised to ascertain the thermodynamic feasibility of synthesizing complexes **1Ti_R** with substituents R = H, Ph, CH$_3$ with respect to the model known complex **9Mo**[20] shows the reactions to be endergonic, which is in agreement with our unsuccessful attempted synthesis (Scheme 7).



R	H	Ph	CH$_3$	NH$_2$	NMe$_2$	Piperidino	NHC	CO
Δ*G*	17.2	9.7	13.8	-0.6	-8.4	-8.6	-3.7	-6.6

Scheme 7. Isodesmic equation for complexes **1Ti_R** (R = H, Ph, CH$_3$, NH$_2$, NMe$_2$, piperidino, NHC, CO) and Δ*G* [kcal mol^{-1}] calculated at the BP86/def2-SVP level of theory.

Complexes **1Ti_R** with substituents R = NH$_2$, NMe$_2$, piperidino, NHC, and CO that are capable of providing two more electrons to the complex in comparison to complexes **1Ti_R** (R = H, Ph, CH$_3$), have a planar structure (Scheme 6b).

The significant change in Ti−C bond lengths, which range between 2.072 Å and 2.081 Å in these planar complexes compared to that of complexes **1Ti_R** (2.202 Å for R = H, Ph), is attributed to the occupation of HOMO (Scheme 6c) of the complexesalong with the presence of a HOMO−2 orbital (Scheme 4). These MOs involve in-phase interaction between the metal d orbital and the terminal carbon (C1 and C3) p orbitals.

Significantly, in the complex **1Ti_Pip** (Pip = piperidino) we can locate the filled MO (HOMO, Scheme 6c) that is responsible for interaction between the Ti atom and the central carbon atom C2 (Ti···C2 = 2.242 Å). NBO analysis also confirms the existence of a distinct Ti−C2 bond with an occupancy of 80.9% with 0.297 Ti(d) + 0.703 C2(p) composition. This is crucial for the stability of the unusual four-membered ring. The Wiberg bond index (WBI) of the Ti−C2 bond is 0.603 compared to WBI of 0.840 of the terminal Ti−C bonds. Furthermore, a considerable decrease in the NBO charge at the Ti center in complex **1Ti_Pip** compared to that of complex **1Ti_Ph** (from 0.98 e to 0.15 e) is indicative of electronic charge-sharing between the C2 and Ti atoms, thus providing support for the Ti−C2 bonding in the former complex.

The average allene C−C bond length in complex **1Ti_Pip** is 1.378 Å, which is longer than the standard allene C−C bond length of 1.307 Å.[21] This is ascribed to the π-donating effect of the piperidino group into the p orbitals at C1 and C3 of complex **1Ti_Pip**, which disturbs the π system of the allene moiety by causing polarization of the π bonds towards the central carbon atom. This effect has been observed in a four-membered carbocyclic allene molecule synthesized by Bertrand et al. with cyclic amine substituents.[22] The resulting bent C-C-C skeleton is consistent with the nonlinear structures of heavier Group 14 element analogues with weak π bonds (Si=Si=Si 136.58,[23a] Ge=Ge=Ge 122.68[23b]).[23c] The HOMO, which has significant interaction between the Ti atom and the central carbon atom C2 and the HOMO−1, which is non-bonding, have larger contributions from the central carbon atom C2 (Scheme 6c). The Ti···C2 interaction presented herein is unprecedented. The π MO, which has large coefficient at C2, can be treated as lone pair, as shown by NBO analysis. In the case of complex **1Ti_NHC**, involvement of π electrons of the NHC in conjugation with the p orbitals at C1 and C3 causes disturbance to the π system of the allene moiety, resulting in the increase of C−C bond lengths.

Importantly, these complexes do not have a typical reactivity like biradicals or carbenes at the central carbon atom C2, which increases the chances of isolating the complexes significantly. The calculated NICS (nucleus-independent chemical shift)[24] values at the ring center, NICS(0), and 1 Å above the ring, NICS(1), are −27.0 and −14.0, respectively, in complex **1Ti_Pip** (compared to NICS(0) and NICS(1) values of −8.5 and −10.7 of benzene at the same BP86/def2-SVP level of theory). These results suggest that the MC$_3$ ring is in-plane aromatic, as might have been envisaged from the HOMO of the complex. Moreover, the extraordinary electronic situation at C2 may render the complexes with interesting chemical properties.

Encouragingly, complexes **1Ti_R** with R = NH_2, NMe_2, piperidino, NHC, and CO are calculated to be energetically feasible from the isodesmic equation (Scheme 7). The reactions are significantly exergonic for complexes **1Ti_R** with substituents NMe_2, piperidino, NHC, and CO. The enhanced stability of these complexes is attributed to the filling-up of the in-plane molecular orbital (HOMO, Scheme 6c), which renders planar structures for the complexes endowed with the crucial Ti···C2 interaction. Formation of the Ti–C2 bond in the planar complex **1Ti_R** (Scheme 6b, compare with stable 18-electron [Cp_2ML_3] complexes;[25] M = d^0 transition metal, L = σ-donor ligand), engenders it with the familiar 18-electron configuration, justifying further its stability. In contrast, absence of this bond in the tilted complex **1Ti_Ph** makes it an unfeasible 16-electron complex. Recent characterization of the four-membered carbocyclic allene[22] molecule with cyclic amine substituents also strengthens the possibility of experimental realization of these complexes.

In conclusion, we have shown from a comprehensive theoretical study that a Group 4 metal can stabilize the exotic four-membered metallacycloallene by interacting with the central carbon atom of the MC_3 ring along with two strong terminal M–C bonds. Substituents, such as acyclic and cyclic alkylated amines like NMe_2, piperidino, and NHCs, which are capable of donating two electrons to the complex, stabilize it significantly to make it synthetically viable. The existence of the crucial M–C2 bond in the MC_3 ring is supported by MO and NBO analyses as well as by the enhanced stability of the complexes.

Received: January 7, 2012
Published online: April 23, 2012

Keywords: cycloallenes · density functional calculations · electronic structure · metallacycles · transition metals

---

[1] a) U. Rosenthal, V. V. Burlakov, M. A. Bach, T. Beweries, *Chem. Soc. Rev.* **2007**, *36*, 719; b) N. Suzuki, D. Hashizume, *Coord. Chem. Rev.* **2010**, *254*, 1307.

[2] C. H. Suresh, G. Frenking, *Organometallics* **2010**, *29*, 4766, and references therein.

[3] Calculated partial hydrogenation energy (at the BP86/def2-SVP level of theory) of the 1,2-cyclobutadiene molecule is taken as a measure of strain in the four-membered rings (see the Supporting Information, Scheme S1).

[4] a) L. G. McCullough, R. R. Schrock, J. C. Dewan, J. C. Murdzek, *J. Am. Chem. Soc.* **1985**, *107*, 5987; b) L. G. McCullough, M. L. Listemann, R. R. Schrock, M. R. Churchill, J. W. Ziller, *J. Am. Chem. Soc.* **1983**, *105*, 6729.

[5] a) P. W. Blosser, J. C. Gallucci, A. Wojcicki, *J. Am. Chem. Soc.* **1993**, *115*, 2994; b) A. Wojcicki, *Inorg. Chem. Commun.* **2002**, *5*, 82; c) S. Roy, E. D. Jemmis, M. Ruhmann, A. Schulz, K. Kaleta, T. Beweries, U. Rosenthal, *Organometallics* **2011**, *30*, 2670.

[6] a) U. Rosenthal, A. Ohff, W. Baumann, R. Kempe, A. Tillack, V. V. Burlakov, *Angew. Chem.* **1994**, *106*, 1678; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1605; b) N. Suzuki, M. Nishiura, Y. Wakatsuki, *Science* **2002**, *295*, 660; c) E. D. Jemmis, A. K. Phukan, H. Jiao, U. Rosenthal, *Organometallics* **2003**, *22*, 4958; d) J. Ugolotti, G. Kehr, R. Fröhlich, S. Grimme, G. Erker, *J. Am. Chem. Soc.* **2009**, *131*, 1996.

[7] a) D. B. Werz, G. Klatt, J. A. Raskatov, H. Köppel, R. Gleiter, *Organometallics* **2009**, *28*, 1675; b) E. D. Jemmis, R. Hoffmann, *J. Am. Chem. Soc.* **1980**, *102*, 2570.

[8] A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.* **1988**, *88*, 899.

[9] Only analysis of complex **1Ti_R** is discussed here in detail. Similar analyses of complexes **1M_R** (M = Zr, Hf) will be published in a separate full paper.

[10] a) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648; b) A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098; c) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785.

[11] P. Perdew, *Phys. Rev. B* **1986**, *33*, 8822.

[12] A. Schaefer, H. Horn, R. Ahlrichs, *J. Chem. Phys.* **1992**, *97*, 2571.

[13] The nature of the stationary points is characterized by vibrational frequency calculations at the same level of theory. All of the complexes are found to be minima on the potential energy surface unless otherwise stated.

[14] a) Gaussian 09, Revision A.02, M. J. Frisch, et al., Gaussian, Inc., Wallingford CT, **2009**; b) Gaussian 03: M. J. Frisch, Gaussian 03, Revision D.01; Gaussian, Inc. Wallingford, CT, **2004**. See the Supporting Information for full details.

[15] a) R. Hoffmann, *J. Chem. Phys.* **1963**, *39*, 1397; b) R. Hoffmann, W. N. Lipscomb, *J. Chem. Phys.* **1962**, *36*, 2179; c) H. Fujimoto, R. Hoffmann, *J. Phys. Chem.* **1974**, *78*, 1167.

[16] a) *ADF2007.01*, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, http://www.scm.com; b) G. te Velde, F. M. Bickelhaupt, S. J. A. v. Gisbergen, C. Fonseca-Guerra, E. J. Baerends, J. G. Snijders, T. Ziegler, *J. Comput. Chem.* **2001**, *22*, 931.

[17] Single-point calculations were carried out for complexes **1Ti′_R**, **1Ti_R1**, and **1Ti_R_C1**, as efforts to optimize these structures lead to the tilted complex.

[18] a) H. A. Jahn, E. Teller, *Proc. R. Soc.* **1937**, *A161*, 220; b) T. A. Albright, J. K. Burdett, M.-H. Whangbo, *Orbital Interactions In Chemistry*, Wiley, New York, **1985**, pp. 95–97.

[19] O. Theilmann, M. Ruhmann, A. Villinger, A. Schulz, W. W. Seidel, K. Kaleta, T. Beweries, P. Arndt, U. Rosenthal, *Angew. Chem.* **2010**, *122*, 9469; *Angew. Chem. Int. Ed.* **2010**, *49*, 9282.

[20] The model complex **9Mo** is formed by replacing the $OCH(CF_3)_2$ groups and the pyridine ligands by OH groups and NH_3 ligands, respectively, in complex **2Mo**, as well as having R = H (Scheme 7) to reduce the computational cost.

[21] F. H. Allen, O. Kennard, D. G. Watson, *J. Chem. Soc. Perkin Trans. 2* **1987**, S1.

[22] M. Melaimi, P. Parameswaran, B. Donnadieu, G. Frenking, G. Bertrand, *Angew. Chem.* **2009**, *121*, 4886; *Angew. Chem. Int. Ed.* **2009**, *48*, 4792.

[23] a) S. Ishida, T. Iwamoto, C. Kabuto, M. Kira, *Nature* **2003**, *421*, 725; b) T. Iwamoto, H. Masuda, C. Kabuto, M. Kira, *Organometallics* **2005**, *24*, 197; c) O. Kaufhold, F. E. Hahn, *Angew. Chem.* **2008**, *120*, 4122; *Angew. Chem. Int. Ed.* **2008**, *47*, 4057.

[24] a) P. von R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao, N. J. R. van Eikema Hommes, *J. Am. Chem. Soc.* **1996**, *118*, 6317; b) P. v. R. Schleyer, M. Manoharan, Z.-X. Wang, B. Kiran, H. Jiao, R. Puchta, N. J. R. van Eikema Hommes, *Org. Lett.* **2001**, *3*, 2465.

[25] J. W. Lauher, R. Hoffmann, *J. Am. Chem. Soc.* **1976**, *98*, 1729.