Titanocene Carbene

DOI: 10.1002/anie.201004145

$[Cp_2Ti^{III}(NCy)_2C{-}Ti^{III}Cp_2]$: A Transient Titanocene Carbene Complex?**

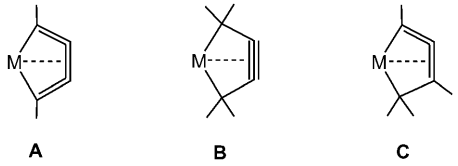
Oliver Theilmann, Martin Ruhmann, Alexander Villinger, Axel Schulz, Wolfram W. Seidel, Katharina Kaleta, Torsten Beweries, Perdita Arndt, and Uwe Rosenthal**

In memory of Herbert Schumann

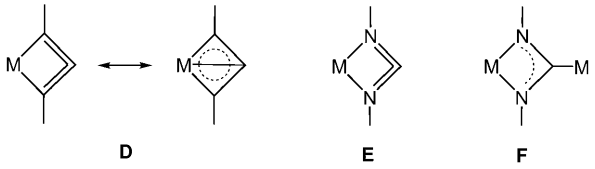
Metallacycles of transition metals are important for many synthetic and catalytic applications.[1] In recent years, our interest has focused on the synthesis, formation, and reactions of three-, four-, and five-membered titana-, zircona-, and hafnacycles,[1,2] which could be obtained by utilizing the reactive metallocene fragment {Cp_2M} (M = Ti,Zr,Hf) "hidden" in a η^2-bounded bis(trimethylsilyl)acetylene complex. The scope for using such metallocene complexes in catalytic or stoichiometric reactions resulting, for example, in unusual all-carbon-metallacycles has been shown on numerous occasions.[1,2]

Steric strain needs to be addressed, especially when cumulated double or triple bonds are part of small all-carbon metallacycles.[3] For example, Johnson et al. calculated ring-tension energies of 55 kcal mol^{-1} for 1,2-cyclopentadiene and 90 kcal mol^{-1} for 1,2-cyclobutadiene.[3f] Stabilization of small strained metallacycles is achieved by means of complexation and incorporation of external substituents.[1,2,4] As a result of rehybridization effects, the external complexation of a metal center to C=C=C=C, C=C=C, or C≡C moieties significantly reduces ring tension. But also internal complexation (that is, complexation of a metal center inside the ring) is observed, which is responsible for the stabilization of unusual sterically strained five-membered metallacycles of the early transition metals Ti, Zr, and Hf, such as metallacyclocumulenes (1-metallacyclopenta-2,3,4-trienes; **A**), metallacyclopentynes (1-metallacyclopent-3-ynes; **B**), and metallacycloallenes (1-metallacyclopenta-2,3-dienes; **C**, Scheme 1). Also isolobal substitution of carbon atoms by heteroatoms decreases ring tension owing to longer heteroatom–carbon bonds.[1,2]

Decreasing the ring size leads to increased steric strain which was expected when dealing with four-membered all-carbon-metallacycles, such as metallacycloallenes (1-metallacyclobuta-2,3-dienes; **D**) or diverse metallaheterocycloallenes (Scheme 2). To date we have not succeeded in isolating metallacycloallenes but following our interest in Group 4 metallacycle chemistry with strained rings,[1–3] we describe herein, for the first time, the synthesis, isolation, and full characterization of a formal titanaheterocycloallene of type **E**, however, it is not stabilized by an internal coordination mode as displayed in Scheme 2 but by external complexation resulting in the formation of a four-membered carbene-like complex (Scheme 2, **F**; Figure 1). Schrock and co-workers have prepared complexes featuring such allene moieties, for example, $[Mo\{C_3(t\mathrm{Bu})_2\}\{OCH(CF_3)_2\}_2(py)_2]$ (py = pyridine) and $[CpW\{C_3(t\mathrm{Bu})_2\}]Cl$.[5] Our attempts to obtain complexes of type **D** by elimination of LiCl employing lithiated allenes, such as LiRC=C=CRLi and metallocene dichlorides $[Cp'_2MCl_2]$ (Cp′ = Cp, C_5Me_5; M = Ti, Zr, Hf), failed.



Scheme 1. Unusual five-membered metallacycles of the early transition metals Ti, Zr, and Hf.



Scheme 2. Four-membered metallacycloallenes **D** and metallaheterocycloallenes **E** which is derived by formal substitution of C^- by N, and **F** which is derived from **E** stabilized by external complexation.

When one equivalent of 1,3-*N*,*N*′-dicyclohexylcarbodiimide dissolved in *n*-hexane was added to a solution of $[Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)]$, the light brown solution changed immediately to red. The color change indicated that Ti^{II} was oxidized to corresponding Ti^{III} (Scheme 3). Within 12 h at room temperature deep red crystals (black appearance) were formed. Astonishingly, these crystals disappeared after further seven days and the color changed from red to green (Scheme 3). Single-crystal X-ray studies revealed the formation of an intriguing carbene-like complex **1** in the first

[*] Dr. O. Theilmann, M. Ruhmann, Dr. A. Villinger, Prof. Dr. A. Schulz, Prof. Dr. W. W. Seidel
Universität Rostock, Institut für Chemie
Albert-Einstein-Strasse 3a, 18059 Rostock (Germany)
E-mail: axel.schulz@uni-rostock.de
uwe.rosenthal@catalysis.de
Dr. O. Theilmann, M. Ruhmann, Prof. Dr. A. Schulz, K. Kaleta, Dr. T. Beweries, Dr. P. Arndt, Prof. Dr. U. Rosenthal
Leibniz-Institut für Katalyse e.V. an der Universität Rostock
Albert-Einstein-Strasse 29a, 18059 Rostock (Germany)

[**] Cp = Cyclopentadienyl, Cy = Cyclohexyl.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201004145.

WILEY ONLINE LIBRARY
© 2010 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

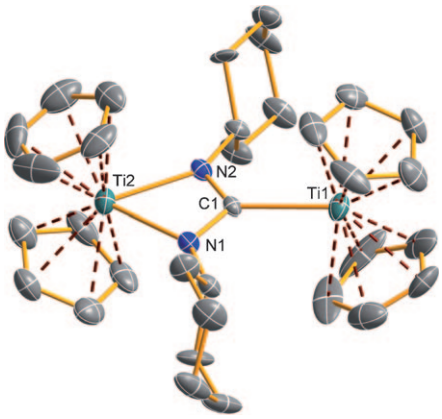
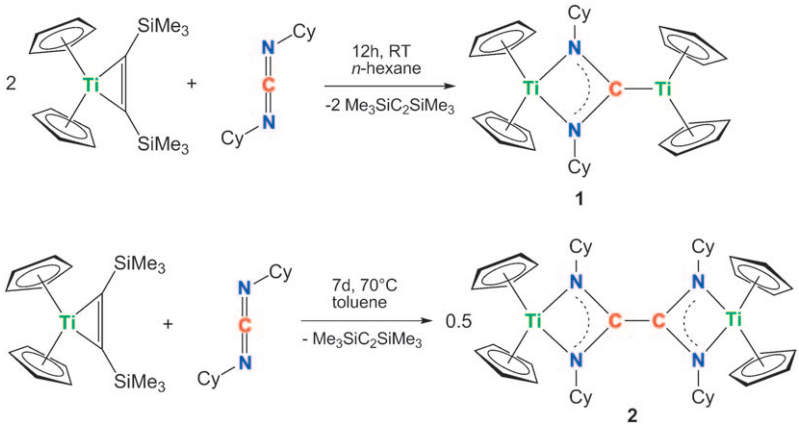


Figure 1. ORTEP drawing of the molecular structure of **1**.[17] Thermal ellipsoids set at 30% probability at 173 K. Selected bond lengths [Å] and angles [°]: Ti1–C1 2.199(4), Ti2–N1 2.154(3), Ti2–N2 2.144(3), N1–C1 1.325(4), N2–C1 1.340(4); C1-N1-Ti2 93.6(2), C1-N2-Ti2 93.6(2), N1-C1-N2 111.2(3), N1-C1-Ti1 128.1(3), N2-C1-Ti1 120.7(2), N1-C1-Ti2 55.8(2), N2-C1-Ti2 55.4(2), Ti1-C1-Ti2 175.8(2).



Scheme 3. Synthesis of **1** and **2** (Cy = cyclohexyl).

reaction step, and a diamidinate complex **2** as the final product in the reaction of dicyclohexylcarbodiimide with $[Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)]$. The major problem was when to isolate **1**, under which conditions (stoichiometry, solvent, temperatures, and concentration), from this reaction mixture. Optimization of the stoichiometry (utilization of a 2:1 ratio, Scheme 3) led to isolation of **1** in of 41% yield. For crystalline **2** the best yield was obtained with a 1:1 ratio and with toluene as the solvent.

Compounds **1** and **2** are thermally stable up to over 100 °C (decomposition of **1** at 190 °C and of **2** at 135 °C), they are moisture sensitive but stable as solids under argon atmosphere. Both compounds can be prepared in bulk and are stable when stored in a sealed tube. These properties, together with reasonable solubility in organic solvents, makes both compounds good precursors for further synthesis.

The solid-state structures of both compounds are shown in Figures 1 and 2. Complex **1** crystallizes in the monoclinic space group $P2_1$ with two formula units in the unit cell, while **2** crystallizes in the monoclinic space group $P2/c$ with four formula units (and two independent molecules) in the unit cell. Both nitrogen atoms and the carbon center of **1** are in a trigonal-planar coordination geometry indicating formal sp^2 hybridization. As depicted in Figure 1, the main structural motif of **1** is the planar four-membered N1-N2-C1-Ti2 ring, which is attached to Ti1 by the carbon atom with a Ti1–C1 distance of 2.199(4) Å.[6] Also Ti1 is part of the plane (∡Ti1-C1-N1-Ti2 = 179.0(6)°) and almost linearly linked to Ti2 through C1 (∡Ti1-C1-Ti2 = 175.8(5)°). The Ti1–C1 distance of 2.199(4) Å is in the range of a typical single bond (cf. 2.107(5) in $[CpTiMe_3]$[7] or 2.213(2) Å in the titanocene monomethyl complex $[(\eta^5\text{-}C_5Me_4SiMe_3)_2TiMe]$[8]). The N1-N2-C1-Ti2 ring is slightly distorted, with two short C–N bonds (N1–C1 1.325(4), N2–C1 1.340(4) Å); Σr_{cov}(C-N) = 1.47 and Σr_{cov}(C=N) = 1.27 Å; r_{cov} = covalent radius)[9] indicating partial C=N double-bond character, and two slightly elongated Ti–N single bonds (Ti2–N1 2.154(3), Ti2–N2 2.144(3) Å; cf. Σr_{cov}(Ti–N) = 2.02).[9]

The bridging ligand in **2**, which is formed from the dimerization of two *N*,*N*′-dicyclohexylcarbodimides, acts as a tetradentate ligand chelating the two Ti centers through four nitrogen atoms. The X-ray study of **2** revealed very similar structural features to those found for **1** (Figure 2): Both four-membered rings in **2** are planar but orthogonal to each other (∡(N1-C1-C24-N4) = 90.3(3), ∡(N2-C1-C24-N3) = 90.5(3)°), and as expected, all the C–N distances (N1–C1 1.323(3)/N2–C1 1.323(3), and N3–C24 1.328(3)/N4-C24 1.328(3) Å), indicate a delocalized π bond along each NCN unit. However, owing to the orthogonality of both NCN units, no delocalization occurs along the connecting C1–C24 bond, which is in accord with its length of 1.527(3) Å indicating a single bond (cf. Σr_{cov}(C–C) = 1.54 Å[9]).

Interestingly, bridging ligands of the type $\mu\text{-}\kappa^2\text{-}\kappa^2\text{-}C_2(NR)_4$ can act as diamide (**G**, Scheme 4) or diamidinate (**H**) ligands leading either to five- or four-membered metallacycles.

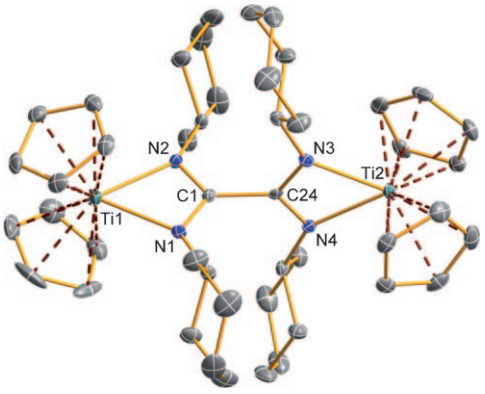
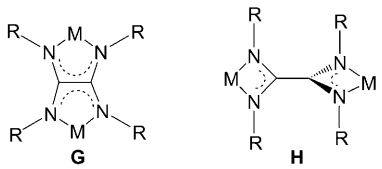


Figure 2. ORTEP drawing of the molecular structure of **2**.[17] Thermal ellipsoids set at 30% probability at 173 K. Selected bond lengths [Å] and angles [°]: Ti1–N1 2.177(2), Ti1–N2 2.189(2), Ti2–N3 2.163(2), Ti2–N4 2.199(2), N1–C1 1.323(3), N2–C1 1.323(3), N3–C24 1.328(3), N4–C24 1.328(3), C1–C24 1.527(3); C1-N1-Ti1 93.0(2), C1-N2-Ti1 92.4(2), N2-C1-N1 113.6(2), N2-C1-C24 124.1(2), N1-C1-C24 122.3(2), N2-C1-Ti1 57.1(1), N1-C1-Ti1 56.6(1), N1-Ti1-N2 60.95(7), N3-Ti2-N4 61.33(7).

 © 2010 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



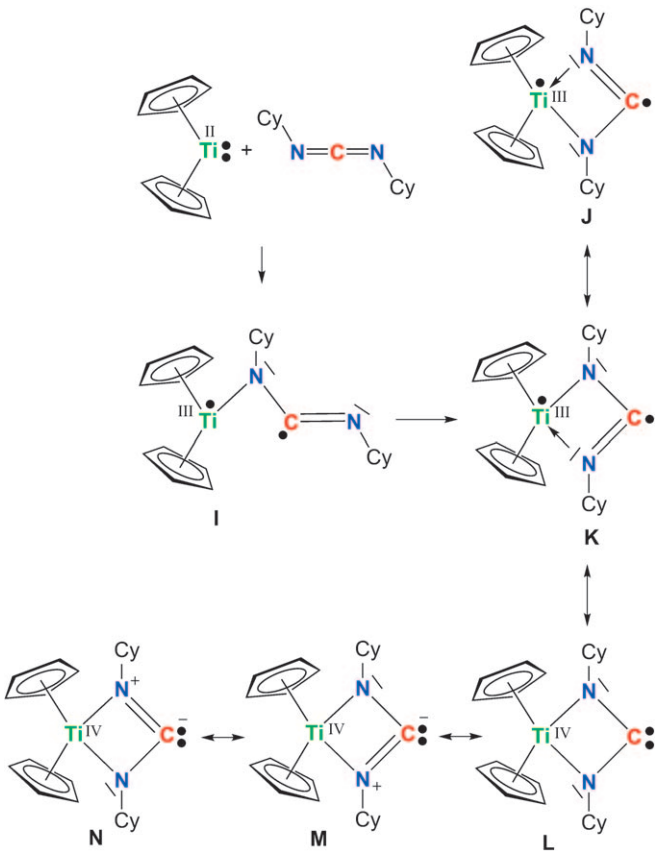
Scheme 4. Coordination modes for the μ-κ²-κ²-$C_2(NR)_4$ ligand.

Two examples[10] are known which have been obtained by reductive coupling: $[(MeC_5H_4)_2Sm(HMPA)]_2[\mu\text{-}\kappa^2\text{-}\kappa^2\text{-}C_2(NR)_4](thf)_2$ (R = *i*Pr and cyclohexyl, HMPA = hexamethylphosphoric triamide),[11] which adopts (like **2**) coordination mode **H** (Scheme 4) and is the only other example of such a complex, but with a considerably larger metal, and the $[Cp_2Ti]_2[\mu\text{-}\kappa^2\text{-}\kappa^2\text{-}C_2(NR)_4]$ (R = *para*-tolyl)[12] with two condensed planar five-membered titanacycles (**G**, Scheme 4) in contrast to the situation found for **2**. Presumably, the nature and size of the group R is important in favoring one of the two coordination modes. Although in contrast to **2** the $[\mu\text{-}\kappa^2\text{-}\kappa^2\text{-}C_2(NR)_4]$ ligand is planar in $[Cp_2Ti]_2[\mu\text{-}\kappa^2\text{-}\kappa^2\text{-}C_2(NR)_4]$ (R = *para*-tolyl)[12], the C–C distance is also in the range of a single bond, 1.504(6) Å (cf. 1.527(3) Å in **2**), hence only delocalization of the π bond over the two CN_2 units was assumed, in accord with the existence of two paramagnetic Ti^{III} centers.

The assignment of oxidation state III to Ti is corroborated by temperature-dependent magnetic measurements for **1** and **2** (Figure S1, in the Supporting Information). Complex **2** shows at 290 K a μ_{eff} value of 2.35 μ_B, which is close to the expected value of 2.38 μ_B for two $S = {}^1/_2$ centers with $g = 1.94$.[13] Whereas a very weak antiferromagnetic coupling is observed for **2** with $J = -8\ cm^{-1}$, the $S = 0$ ground state is much more stable in complex **1** with $J = -90\ cm^{-1}$. Consistent with this data, the shortening of the bridging moiety between the Ti centers from five bonds in **2** to three bonds in **1** leads to a considerable strengthening of the antiferromagnetic coupling, in accord with the observed structural features.

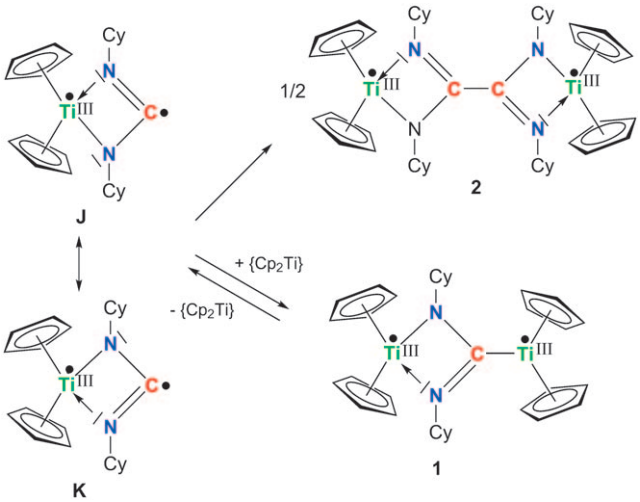
The generation of the carbene-like complex **1** (with the topology of a four-membered N-heterocyclic "Arduengo carbene", NHC)[14] and its disappearance with the formation of complex **2** deserves some comments. The key species for the formation of **1** and **2** and hence for the reductive metal-promoted C–C bond formation seems to be the biradical cyclic titanium(III) carbene-like species **3** (**J** and **K** in Scheme 5). Carbenes are neutral compounds featuring a divalent carbon atom. Singlet carbenes have an in-plane lone pair and an out-of-plane formally vacant orbital.[15] NHCs are stabilized by the presence of two heteroatoms interacting with the carbene center. All these characteristics of a NHC are also found in **3** except that only one electron is localized at the carbon atom. As for NHCs, the "true" carbene nature of "metalla-N-heterocyclic carbene" (M-NHC) **3** could be controversially discussed.

The Lewis picture of **3** also includes NHC-type Lewis representations (**L**–**N**) but their contribution should be negligible. Computations at the UHF, B3LYP, and CAS-(2,2)/6-31G(d) level of theory support the existence of a titanium(III) species **3** as a Ti- and C-centered biradical in accord with representations **J** and **K** in Scheme 5 (see Supporting Information Tables S6–S7). The calculated spin



Scheme 5. Lewis representations of the intermediate biradical species **3** (as structures **J**–**N**).

density (−1.08 at Ti, 0.82 at C, 0.07 at both N atoms for the ^1A singlet species; Figure S2 in the Supporting Information) indicates that nearly one electron is localized at the Ti atom and along the NCN unit (but with the largest probability at the C center). Either dimerization occurs (similar to the Wanzlick equilibrium[16] but in this case with only one electron at the C atom) yielding paramagnetic compound **2** with two Ti^{III} centers (Scheme 6) or this carbene-like species is



Scheme 6. Mechanism of the formation of **1** and **2**.

 © 2010 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

quenched by a second $\{Cp_2Ti^{II}\}$ equivalent resulting in the formation of **1** which slowly converts into **2**. Since **1** seems to be less soluble it was possible to isolate and characterize this transient species.

In conclusion, we have shown that the unusual carbene-like complex **1** is easily prepared in good yields and is stable as a solid but slowly dissociates in solution into **3**, a biradical carbene-like species with unpaired electron density at the ring carbon and the Ti^{III} center. Dimerization of this intermediate species **3** leads to the bimetallic complex **2**, the final product of the reduction-coupling reaction of a carbodiimide and $[Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)]$.

Received: July 7, 2010
Revised: August 20, 2010
Published online: October 21, 2010

Keywords: biradicals · carbenes · heterocycles · structure elucidation · titanocenes

[1] a) U. Rosenthal, V. V. Burlakov, M. A. Bach, T. Beweries, *Chem. Soc. Rev.* **2007**, *36*, 719–728; b) U. Rosenthal in *Acetylene Chemistry—Chemistry, Biology, and Material Science* (Eds.: F. Diederich, P. Stang, R. R. Tykwinski), Wiley-VCH, Weinheim, **2004**, pp. 139–171; c) N. Suzuki, D. Hashizume, *Coord. Chem. Rev.* **2010**, *254*, 1307–1326.

[2] a) U. Rosenthal, V. V. Burlakov, P. Arndt, W. Baumann, A. Spannenberg, *Organometallics* **2003**, *22*, 884–900; b) J. Ugolotti, G. Dierker, G. Kehr, R. Fröhlich, S. Grimme, G. Erker, *Angew. Chem.* **2008**, *120*, 2662–2665; *Angew. Chem. Int. Ed.* **2008**, *47*, 2622–2625; c) N. Suzuki, D. Hashizume, H. Koshino, T. Chihara *Angew. Chem.* **2008**, *120, 5276–5280; Angew. Chem. Int. Ed.* **2008**, 47, 5198–5202; *Angew. Chem. Int. Ed.* **2008**, *47*, 5198–5202; d) J. Ugolotti, G. Kehr, R. Fröhlich, S. Grimme, G. Erker, *J. Am. Chem. Soc.* **2009**, *131*, 1996–2007; e) U. Rosenthal, V. V. Burlakov, P. Arndt, A. Spannenberg, U. Jäger-Fiedler, M. Klahn, M. Hapke in *Activating Unreactive Substrates* (Eds.: C. Bolm, E. Hahn), Wiley-VCH, Weinheim, **2009**, pp. 165–182, and references therein.

[3] a) A. von Baeyer, *Ber. Dtsch. Chem. Ges.* **1885**, *18*, 2269–2281; b) A. Krebs, J. Wilke, *Top. Curr. Chem.* **1983**, *109*, 189–233; c) R. Gleiter, R. R. Merger in *Modern Acetylene Chemistry* (Eds.: P. J. Stang, F. Diederich), Wiley-VCH, Weinheim, **1995**, pp. 284–319; d) W. M. Jones, J. Klosin, *Adv. Organomet. Chem.* **1998**, *42*, 147–221; e) R. P. Johnson, *Chem. Rev.* **1989**, *89*, 1111–1124; f) K. J. Daoust, S. M. Hernandez, K. M. Konrad, I. D. Mackie, J. Winstanley, R. P. Johnson, *J. Org. Chem.* **2006**, *71*, 5708–5714.

[4] a) A. Krebs, H. Kimling, *Angew. Chem.* **1971**, *83*, 540–541; *Angew. Chem. Int. Ed. Engl.* **1971**, *10*, 509–510; b) W. Ando, F. Hojo, S. Sekigawa, N. Nakayama, T. Shimizu, *Organometallics* **1992**, *11*, 1009–1011.

[5] a) L. G. McCullough, R. R. Schrock, J. C. Dewan, J. C. Murdzek, *J. Am. Chem. Soc.* **1985**, *107*, 5987–5998; b) L. G. McCullough, M. L. Listemann, R. R. Schrock, M. R. Churchill, J. W. Ziller, *J. Am. Chem. Soc.* **1983**, *105*, 6729–6730.

[6] A similar structural motif is found in a) $[CpMo(CO)_2(\eta^2\text{-}NR)_2C{-}MoCp(CO)_3]$, see H. Brunner, W. Meier, J. Wachter, I. Bernal, E. Raabe, *J. Organomet. Chem.* **1989**, *362*, 95–103; b) $[(nacnac)Mg(\eta^2\text{-}NR)_2C{-}Mg(nacnac)]$ (nacnac = $[(Ar)NC(Me)]_2$): S. P. Green, C. Jones, A. Stasch, *Science* **2007**, *318*, 1754–1757.

[7] R. Blom, K. Rypdal, M. Mena, P. Royo, R. Serrano, *J. Organomet. Chem.* **1990**, *391*, 47–51.

[8] J. Pinkas, L. Lukesova, R. Gyepes, I. Cisarova, P. Lönnecke, J. Kubista, M. Horacek, K. Mach, *Organometallics* **2007**, *26*, 3100–3110.

[9] A. F. Holleman, E. Wiberg, *Lehrbuch der Anorganischen Chemie*, 102. Aufl., Walter de Gruyter, Berlin, **2007**, Anhang IV.

[10] In addition to these two examples, a few diamide complexes are known, however they are always obtained from deprotonation of the oxalic amidines: for example a) T. Döhler, H. Görls, D. Walther, *Chem. Commun.* **2000**, 945–946; b) M. Ruben, D. Walther, R. Knake, H. Görls, R. Beckert, *Eur. J. Inorg. Chem.* **2000**, 1055–1060.

[11] M. Deng, Y. Yao, Y. Zhang, Q. Shen, *Chem. Commun.* **2004**, 2742–2743.

[12] M. Pasquali, C. Floriani, A. Chiesi-Villa, C. Guastini, *Inorg. Chem.* **1981**, *20*, 349–355.

[13] a) L. Lukeova, M. Horacek, P. Stepnicka, K. Fejfarova, R. Gyepes, I. Cisarová, J. Kubista, K. Mach, *J. Organomet. Chem.* **2002**, *663*, 134–144; b) E. Samuel, J. Hénique, *J. Organomet. Chem.* **1996**, *512*, 183–187.

[14] a) A. J. Arduengo, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1991**, *113*, 361–363; b) A. J. Arduengo, *Acc. Chem. Res.* **1999**, *32*, 913–921; c) O. Schuster, L. Yang, H. G. Raubenheimer, M. Albrecht, *Chem. Rev.* **2009**, *109*, 3445–3478; d) E. Teuma, C. Lyon-Saunier, H. Gornitzka, G. Mignani, A. Baceiredo, G. Bertrand, *J. Organomet. Chem.* **2005**, *690*, 5541–5545; e) R. H. Crabtree, *Coord. Chem. Rev.* **2007**, *251*, 595; f) F. Glorius, *Top. Organomet. Chem.* **2007**, *21*, 1–20; g) *N-Heterocyclic Carbenes in Synthesis*, 1st ed. (Ed.: S. P. Nolan), Wiley-VCH, Weinheim, **2006**; h) F. E. Hahn, M. C. Jahnke, *Angew. Chem.* **2008**, *120*, 3166–3216; *Angew. Chem. Int. Ed.* **2008**, *47*, 3122–3172.

[15] J. Vignolle, X. Cattoen, D. Bourissou, *Chem. Rev.* **2009**, *109*, 3333–3384.

[16] a) H.-W. Wanzlick, H. J. Schönherr, *Angew. Chem.* **1968**, *80*, 154; *Angew. Chem. Int. Ed. Engl.* **1968**, *7*, 141; b) K. Öfele, *J. Organomet. Chem.* **1968**, *12*, P42–P43; c) D. J. Cardin, B. Cetinkaya, M. F. Lappert, L. Manojlovic-Muir, K. W. Muir, *J. Chem. Soc. Chem. Commun.* **1971**, 400–401; d) F. E. Hahn, L. Wittenbecher, D. Le Van, R. Fröhlich, *Angew. Chem.* **2000**, *112*, 551–554; *Angew. Chem. Int. Ed.* **2000**, *39*, 541–544.

[17] CCDC 795585 (**1**) and 795584 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

 © 2010 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim