

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/262941192>

Dynamic Complexation of Copper(I) Chloride by Carbene-Stabilized Disilicon

ARTICLE *in* CHEMISTRY · JULY 2014

Impact Factor: 5.73 · DOI: 10.1002/chem.201403095 · Source: PubMed

CITATIONS

8

READS

60

9 AUTHORS, INCLUDING:



Mingwei Chen

19 PUBLICATIONS 120 CITATIONS

SEE PROFILE



Yuzhong Wang

University of Georgia

51 PUBLICATIONS 2,122 CITATIONS

SEE PROFILE



Robert J. Gilliard

Case Western Reserve University

15 PUBLICATIONS 276 CITATIONS

SEE PROFILE

■ Computational Chemistry

Dynamic Complexation of Copper(I) Chloride by Carbene-Stabilized Disilicon

Mingwei Chen, Yuzhong Wang, Yaoming Xie, Pingrong Wei, Robert J. Gilliard, Jr., Nichole A. Schwartz, Henry F. Schaefer, III, Paul von R. Schleyer, and Gregory H. Robinson^{*[a]}



Abstract: Reaction of N-heterocyclic-carbene (NHC)-stabilized disilicon (**1**) with CuCl gave a carbene-stabilized disilicon–copper(I) chloride complex (**2**). The nature of the structure and bonding in **2** has been investigated by crystallographic, spectroscopic, and computational methods. The dynamic complexation behavior of **2** was experimentally explored by variable-temperature NMR analysis.

The twenty-three year span between the seminal synthetic reports of the first disilene^[1] and the first disilyne,^[2] arguably, suggests both a measure of frustration and fascination associated with the chemistry of low-oxidation-state organosilicon compounds. These unsaturated molecules are intriguing not only because of the distinctive nature of the bonding but also due to the new reactivity of the disilicon cores.^[3] In addition, the silylenes (i.e., siliconocenes^[4] and diamidosilylenes^[5]) have developed into potent tools in areas, such as small-molecule activation, organic synthesis, catalysis, and transition-metal coordination chemistry.^[6]

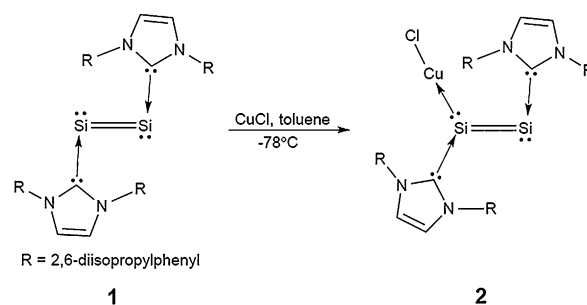
In contrast to the large number of disilenes (Si=Si double bonds) and silylenes (electron-pair donors), only a small group of organosilicon compounds possess both silicon–silicon double bonds and silicon-based electron pair donor capabilities: disilenides (**I**),^[7] carbene–disilyne complex (**II**),^[8] carbene-coordinated disilyl silylene (**III**),^[9] and carbene-stabilized disilicon (**IV**; Figure 1; L = carbene).^[10]

Because anionic derivatives of disilenes, disilenides (**I**)^[11] have proven to be unique organosilicon reagents.^[7] Notably, ion-separated disilenide also may be obtained by solvent coordination.^[12] Considering the π -donating capability of the Si=Si double bond, coupled with the σ -donor character of the electron lone pair(s) of silicon(s), compounds **I–IV** may exhibit versatile coordination modes toward various metal salts.

The only known **IV**-type example, **1**, was synthesized by potassium graphite reduction of L:SiCl₄ [L = :C(N(2,6-*i*Pr₂C₆H₃)CH₂)₂].^[10] Carbene-stabilized disilicon has shown unusual reactivity toward BH₃, forming a “push-pull” stabilized parent silylene (H₂Si:).^[13] Inspired by the utilization of N-heterocyclic carbene (NHC)–copper(I) complexes in catalysis and in C–H bond activation,^[14] we investigated the behavior of **1** as a coor-

minating ligand with copper(I) chloride and now report the synthesis,^[15] structure,^[15] and related computations^[16] of carbene-stabilized disilicon–copper chloride complex (**2**).

Dark purple red crystals of **2** were isolated (51 % yield) from reaction of **1** with CuCl in toluene at –78 °C (Scheme 1). Due



Scheme 1. Synthesis of carbene-stabilized disilicon:CuCl complex (**2**).

to its high water sensitivity, **2** was decomposed by trace amounts of moisture to form L:CuCl [L = :C(N(2,6-*i*Pr₂C₆H₃)CH₂)₂] as the major by-product. However, compound **2** is thermally stable and persists in boiling C₆D₆. The stoichiometric ratio of the reactants affects the yield of **2**. Although **2** is a 1:1 adduct (L:Si=Si:L/CuCl), a better yield of **2** was achieved by combining **1** with CuCl in a 1:2 molar ratio. The possible 1:2 adduct was not formed, evidently due to the steric congestion of the two bulky carbene ligands. The copper chloride binding only shifted the ²⁹Si NMR resonance downfield marginally, from δ = 224.5 ppm for **1** to 226.7 ppm for **2**, indicating a certain amount of electron donation from the Si₂ core to the copper center in **2**.

X-ray structural analysis of **2** (Figure 2) showed that CuCl is bound to only one of the two silicon atoms in the solid state^[15] (akin to the coordination of [Fe(CO)₄] to a carbene-heavier vinylidene adduct).^[17] The Si–Cu bond length [2.2081(9) Å] in **2** compares well with the Si_{sp2}–Cu distances (2.2412(8) and 2.2458(8) Å) in a lithium bis(disilyl)cuprate,^[18] but is less than the 2.43 Å sum of the silicon and copper covalent radii.^[19] The bent Si–Cu–Cl angle (167.35(5)°) in **2** contrasts with the perfectly linear fragment in [CuCl{ μ - κ^1 Si: κ^3 N-Si(3,5-Me₂pz)₃Mo(CO)₃}][–].^[20] Coordination of CuCl to the L:Si=Si:L fragment in **1** affects the structure and bonding of the resulting complex, **2**. Although both the imidazole rings of the two NHC ligands are perpendicular to the Si₂ core in **1**,^[10] only one imidazole ring has this arrangement in **2**. The other imidazole ring in **2** (adjacent to the Si(1) atom) is almost coplanar with the Si₂ core (the N(2)–C(1)–Si(1)–Si(2) torsion angle is –0.72°), which favors the delocalization of the p π -electrons of the Si₂ core to the empty p orbital of the carbene carbon [i.e., C(1)]. Indeed, in **2** the Si(1)–C(1) bond (1.917(3) Å) is slightly shorter than the Si(2)–C(28) bond (1.939(3) Å) in **2** and that (1.9271(15) Å) in **1**. The Si=Si double bond (2.2061(12) Å) in **2** is only slightly shorter than that (2.2294(11) Å) in **1**. Moreover, in **2** the three-coordinate Si(1) atom adopts a trigonal-planar geometry, whereas the two-coordinate Si(2) atom, as those in **1** containing lone pairs of electrons, has a bent geometry.^[10]

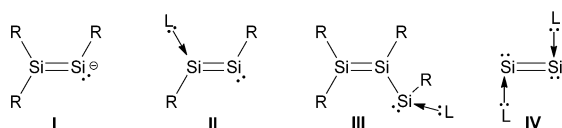


Figure 1. Donor compounds containing Si=Si double bonds.

[a] Dr. M. Chen, Dr. Y. Wang, Dr. Y. Xie, Dr. P. Wei, R. J. Gilliard, Jr., N. A. Schwartz, Prof. Dr. H. F. Schaefer, III, Prof. Dr. P. v. R. Schleyer, Prof. Dr. G. H. Robinson
Department of Chemistry and the Center for Computational Chemistry
The University of Georgia, Athens, Georgia 30602-2556 (USA)
E-mail: robinson@uga.edu

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/chem.201403095>.

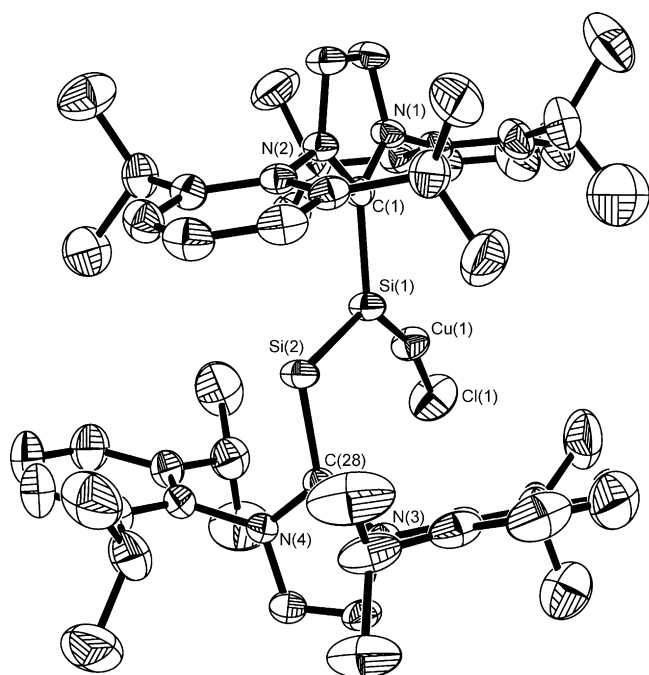


Figure 2. Molecular structure of **2**. Thermal ellipsoids represent 30% probability; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] are as follows: Si(1)–Si(2) 2.2061(12), Si(1)–Cu(1) 2.2081(9), Si(1)–C(1) 1.917(3), Si(2)–C(28) 1.939(3), Cu(1)–Cl(1) 2.1452(11); Si(1)–Cu(1)–Cl(1) 167.35(5), C(1)–Si(1)–Si(2) 106.53(9), C(1)–Si(1)–Cu(1) 119.83(9), Si(2)–Si(1)–Cu(1) 132.41(5), C(28)–Si(2)–Si(1) 95.60(9).

DFT computations at the B3LYP/6-311+G** level were performed on the simplified models, **2-H** ($L := :C[N(H)CH]_2$) and **2-Me** ($L := :C[N(Me)CH]_2$).^[16] The computed structural parameters of **2-Me** (d_{Si-Si} 2.247, d_{Si-Cu} 2.248, d_{Si-C} 1.922 Å; Cu–Si–Si bond angle 130.5°) are similar to the experimental data for **2** (d_{Si-Si} 2.2061(12), d_{Si-Cu} 2.2081(9), d_{Si-C} 1.917(3) Å; Cu–Si–Si bond angle 132.41(5)°). However, the conformation of model **2-H** exhibited obvious differences compared with **2**.^[16] For example, **2** has C_1 symmetry, whereas **2-H** resides in C_s symmetry. Notably, the Si–Cu–Cl bond angle in **2-H** (146.8°) is considerably less than that observed for **2** (167.4°) or computed for **2-Me** (176.0°). The intramolecular N–H...Cl hydrogen bond may be a contributing factor (N–H...Cl bond lengths: Cl...H 2.51 Å, N–H...Cl 3.49 Å; N–H...Cl bond angle 159°).^[21]

The localized molecular orbitals (LMOs) of **2-Me** (optimized in C_1 symmetry) are shown in Figure 3. According to natural-bond-orbital (NBO)^[22] analysis, the Si–Si σ -bonding orbital is formed by an overlap of the approximately sp^2 -hybridized Si(1) atomic orbital (37.7% s, 62.0% p, 0.3% d) with the predominantly p character Si(2) atomic orbital (17.4% s, 82.1% p, 0.5% d), whereas the Si–Si π orbital has essentially pure p character (99.7%). Both the Si–Si σ and π bonds are somewhat polarized (about 55%) toward the Si(1) atom. The 1.63 Wiberg bond index (WBI) of the central silicon–silicon bond in **2-Me**, which is only slightly less than the 1.73 WBI of the **1-Ph** model,^[10] supports the Si=Si double bond character. In contrast, the Si–Cu bond is polarized more highly (78%) towards silicon. The copper hybridization (NBO) is 82.3% s, 14.5% p, and 3.2% d in

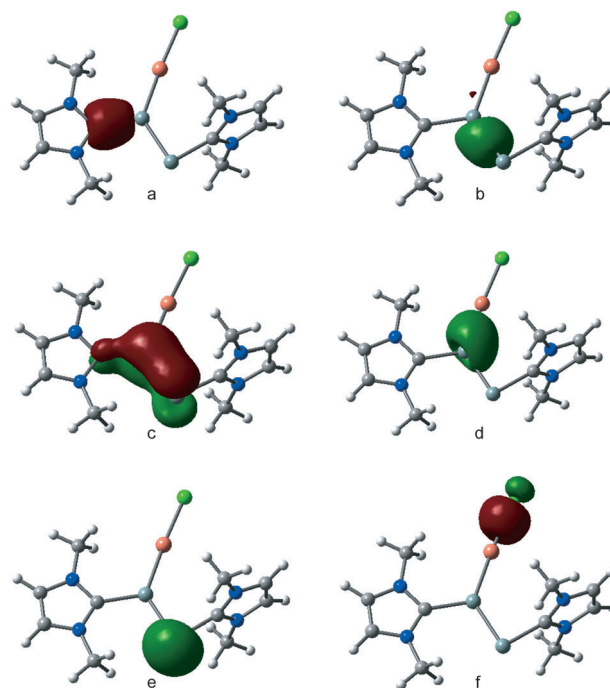


Figure 3. Localized molecular orbitals (LMOs) of model **2-Me**. a) Si–C σ -bonding orbital; b) Si–Si σ -bonding orbital; c) Si–Si π -bonding orbital; d) Si–Cu σ -bonding orbital; e) lone-pair orbital of Si; f) Cu–Cl σ -bonding orbital.

2-Me; the 0.66 WBI of its Si–Cu bond is consistent with single-bond character.

DFT computations of the simplified **2-Me** model also suggested that the carbene-stabilized disilicon–copper chloride complex may exist as either of two isomeric forms (Figure 4).^[16] Notably, the π complex **2'-Me** (a minimum with C_2 symmetry) is only 0.2 kcal mol^{−1} higher in energy than the σ -complex minimum, **2-Me**. The side-on coordination of the $L:Si=Si:L$ ($L := :C[N(Me)CH]_2$) fragment to CuCl in **2'-Me** only results in a slight elongation of the silicon–silicon distance (to 2.295 Å from 2.2294(11) Å in **1**).^[10] Indeed, the 2.295 Å silicon–silicon bond length in **2'-Me** is similar to those reported for disilene–transition-metal π complexes.^[23] Interestingly, **2** only gave a singlet ²⁹Si NMR resonance. This, coupled with the fact that two carbene ligands are chemically equivalent in both ¹H and ¹³C NMR spectra of **2**, suggests that in solution, **2** may exist in the C_2 symmetric π -complex isomer form or rapidly equilibrate at room temperature, very likely via a π -complex intermediate (Figure 5). Indeed, σ – π rearrangements of organotransition

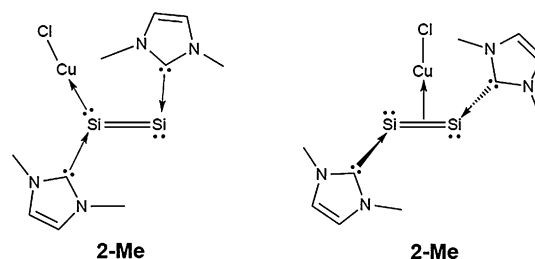


Figure 4. Isomers of the carbene-stabilized disilicon–CuCl complex.

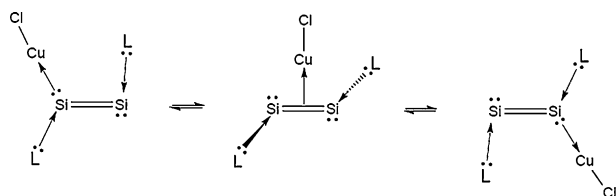


Figure 5. The proposed σ - π interconversion of **2** in solution [$L = :C(N(2,6\text{-}iPr_2C_6H_3)CH_2)_2$].

metal compounds are of great importance in catalytic processes.^[24]

Such dynamic complexation behavior of **2** in solution was further supported by variable-temperature (VT) 1H NMR experiments (Figures S1–S5 in the Supporting Information).^[15] The sharp singlet resonance of the imidazole protons of **2** at 25 °C broadens and then splits into two separate peaks when cooled to –66 °C. These VT spectral changes are reversible. These experimental observations may be ascribed either to the slowing of the carbene-ligand rotation around the C_{NHC} –Si axis in the symmetric π complex form of **2** or that the exchange shown in Figure 5 is frozen at low temperature.

Our investigation of the role of the carbene–disilicon complex (**1**) as a ligand coordinating to copper chloride showed that **1** may function as a σ donor to form the asymmetric isomer of **2** in the solid state, which in solution, however, either exists as a symmetric π -complex isomer or equilibrates rapidly at room temperature, highly likely via a π -complex intermediate.

Acknowledgements

We are grateful to the National Science Foundation for support: CHE-1265212 (G.H.R., Y.W.), CHE-1057466 (P.v.R.S.), and CHE-1054286 (H.F.S.). We are grateful to Professor Jeffrey Urbauer and Mr. Henry Niedermaier for the VT NMR measurements.

Keywords: carbenes • computational chemistry • copper • Lewis bases • silicon

- [1] R. West, M. J. Fink, J. Michl, *Science* **1981**, 214, 1343–1344.
- [2] A. Sekiguchi, R. Kinjo, M. Ichinohe, *Science* **2004**, 305, 1755–1757.
- [3] a) G. Raabe, J. Michl, *Chem. Rev.* **1985**, 85, 419–509; b) R. Okazaki, R. West, *Adv. Organomet. Chem.* **1996**, 39, 231–273; c) M. Kira, T. Iwamoto, *Adv. Organomet. Chem.* **2006**, 54, 73–148; d) A. Sekiguchi, M. Ichinohe, R. Kinjo, *Bull. Chem. Soc. Jpn.* **2006**, 79, 825–832; e) A. Sekiguchi, *Pure Appl. Chem.* **2008**, 80, 447–457; f) M. Asay, A. Sekiguchi, *Bull. Chem. Soc. Jpn.* **2012**, 85, 1245–1261; g) Y. Wang, G. H. Robinson, *Chem. Commun.* **2009**, 5201–5213; h) K. Abersfelder, D. Scheschkewitz, *Pure Appl. Chem.* **2010**, 82, 595–602.
- [4] P. Jutzi, D. Kanne, C. Kruger, *Angew. Chem.* **1986**, 98, 163; *Angew. Chem. Int. Ed. Engl.* **1986**, 25, 164.
- [5] M. Denk, R. Lennon, R. Hayashi, R. West, A. V. Belyakov, H. P. Verne, A. Haaland, M. Wagner, N. Metzler, *J. Am. Chem. Soc.* **1994**, 116, 2691–2692.
- [6] a) M. Haaf, T. A. Schmedake, R. West, *Acc. Chem. Res.* **2000**, 33, 704–714; b) M. Asay, C. Jones, M. Driess, *Chem. Rev.* **2011**, 111, 354–396; c) S.-L. Yao, Y. Xiong, M. Driess, *Organometallics* **2011**, 30, 1748–1767; d) Y. Xiong, S. Yao, M. Driess, *Angew. Chem.* **2013**, 125, 4398–4407; *Angew. Chem. Int. Ed.* **2013**, 52, 4302–4311; e) B. Blom, D. Gallego, M. Driess, *Inorg. Chem. Front.* **2014**, 1, 134–148; f) S. S. Sen, S. Khan, S. Nagendran, H. W. Roesky, *Acc. Chem. Res.* **2012**, 45, 578–587; g) R. S. Ghadwal, R. Azhakar, H. W. Roesky, *Acc. Chem. Res.* **2013**, 46, 444–456; h) H. W. Roesky, *J. Organomet. Chem.* **2013**, 730, 57–62.
- [7] a) D. Scheschkewitz, *Chem. Eur. J.* **2009**, 15, 2476–2485; b) D. Scheschkewitz, *Chem. Lett.* **2011**, 40, 2–11.
- [8] T. Yamaguchi, A. Sekiguchi, M. Driess, *J. Am. Chem. Soc.* **2010**, 132, 14061–14063.
- [9] M. J. Cowley, V. Huch, H. S. Rzepa, D. Scheschkewitz, *Nat. Chem.* **2013**, 5, 876–879.
- [10] Y. Wang, Y. Xie, P. Wei, R. B. King, H. F. Schaefer, III, P. v. R. Schleyer, G. H. Robinson, *Science* **2008**, 321, 1069–1071.
- [11] a) D. Scheschkewitz, *Angew. Chem.* **2004**, 116, 3025–3028; *Angew. Chem. Int. Ed.* **2004**, 43, 2965–2967; b) M. Ichinohe, K. Sanuki, S. Inoue, A. Sekiguchi, *Organometallics* **2004**, 23, 3088–3090.
- [12] R. Kinjo, M. Ichinohe, A. Sekiguchi, *J. Am. Chem. Soc.* **2007**, 129, 26–27.
- [13] M. Y. Abraham, Y. Wang, Y. Xie, P. Wei, H. F. Schaefer, P. v. R. Schleyer, G. H. Robinson, *J. Am. Chem. Soc.* **2011**, 133, 8874–8876.
- [14] a) J. D. Egbert, C. S. J. Cazin, S. P. Nolan, *Catal. Sci. Technol.* **2013**, 3, 912–926; b) S. Gaillard, C. S. J. Cazin, S. P. Nolan, *Acc. Chem. Res.* **2012**, 45, 778–787.
- [15] See the Supporting Information for synthetic and crystallographic details.
- [16] Computations: the structures of the simplified model compounds **2-Me**, **2-H**, and **2** were optimized at the B3LYP/6-311+G** DFT level with the: a) Gaussian 94 (Revision B.2), M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, A. Nanavakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **1995**; and b) 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. 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. Nanavakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Wallingford CT, **2004**.
- [17] A. Jana, M. Majumdar, V. Huch, M. Zimmer, D. Scheschkewitz, *Dalton Trans.* **2014**, 43, 5175–5181.
- [18] M. J. Cowley, K. Abersfelder, A. J. P. White, M. Majumdar, D. Scheschkewitz, *Chem. Commun.* **2012**, 48, 6595–6597.
- [19] B. Cordero, V. Gomez, A. E. Platero-Prats, M. Reves, J. Echeverria, E. Cremades, F. Barragan, S. Alvarez, *Dalton Trans.* **2008**, 2832–2838.
- [20] S. Styra, S. Gonzalez-Gallardo, F. Armbruster, P. Ona-Burgos, E. Moos, M. Vonderach, P. Weis, O. Hampe, A. Gruen, Y. Schmitt, M. Gerhards, F. Menges, M. Gaffga, G. Niedner-Schatteburg, F. Breher, *Chem. Eur. J.* **2013**, 19, 8436–8446.
- [21] D.-W. Zhang and Z.-T. Li in *Current Trends in X-Ray Crystallography* (Ed. A. Chandrasekaran), InTech, **2011**, pp. 95–112.
- [22] F. Weinhold, C. Landis, *Valency and Bonding: A Natural Bond Orbital Donor-Acceptor Perspective*, Cambridge University Press, Cambridge, **2005**, p. 749.
- [23] M. Kira, *Proc. Jpn. Acad. Ser. B* **2012**, 88, 167–191.
- [24] M. Tsutsui, A. Courtney in *σ - π Rearrangements of Organotransition Metal Compounds*, Vol. 16 (Eds.: F. G. A. Stone, R. West), **1977**, pp. 241–282.

Received: April 15, 2014

Published online on June 6, 2014