

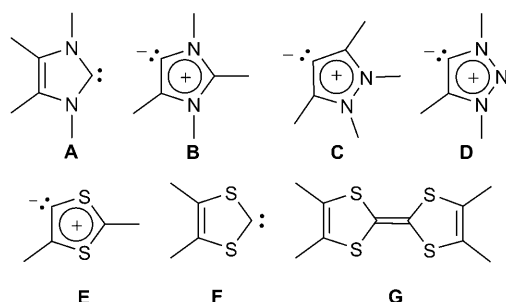
Mesoionic Carbenes

A Stable Acyclic Ligand Equivalent of an Unstable 1,3-Dithiol-5-ylidene**

Gaël Ung, Daniel Mendoza-Espinosa, Jean Bouffard, and Guy Bertrand*

Dedicated to Professor Didier Astruc on the occasion of his 65th birthday

During the last two decades, N-heterocyclic carbenes (NHCs), such as **A** (Scheme 1), have played a prominent role as ligands for transition-metal catalysts.^[1] Their popularity is mainly due to their strong σ -donor properties and the

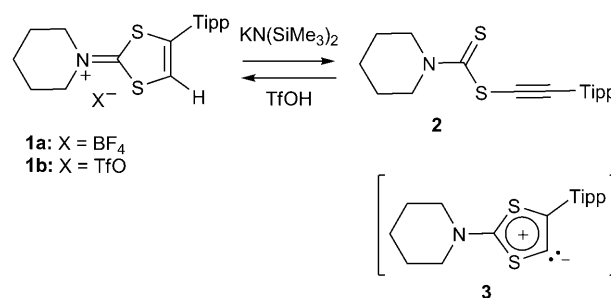


Scheme 1. Structural framework of classical NHCs (**A**), types of MIC that have been isolated previously (**B–D**), the targeted 1,3-dithiol-5-ylidenes (**E**), and their unknown 1,3-dithiol-2-ylidene isomers (**F**), which dimerize to tetrathiafulvalenes of type **G**.

robustness of the corresponding complexes. These two features result from the presence of the electropositive carbon center and the strength of the carbon–metal bond. Therefore, other types of carbon-based L ligands are highly desirable. The simplest method for the preparation of metal complexes featuring a given L ligand is by ligand substitution at the metal center; however, the availability of stable compounds with a lone pair of electrons at a carbon center is very limited.^[2] It has recently been shown that mesoionic carbenes (MICs)^[3–5] **B–D** can be isolated as free species.^[6] In contrast to “normal carbenes”, no obvious dimerization pathway can be foreseen for MICs. Consequently, a variety of these unusual carbenes should in principle be available

without the need for kinetic protection. No derivatives of the 1,3-dithiol-2-ylidene **F** are known owing to their dimerization into derivatives of tetrathiafulvalene **G**.^[7] Herein, we report our attempts to prepare a free MIC isomer by carbenes of type **F**, namely, a 1,3-dithiol-5-ylidene **E**. We show that this compound is unstable owing to spontaneous ring opening to form the corresponding ethynylcarbamodithioate. Importantly, the latter reacts with a variety of metals to give 1,3-dithiol-5-ylidene–metal complexes and therefore is a ligand equivalent of **E**.

In analogy with the classical synthetic route used to prepare NHCs and MICs, we chose the readily available dithiolium tetrafluoroborate salt **1a** as a precursor (Scheme 2).^[8] Deprotonation with potassium bis(trimethylsilyl)amide proceeded cleanly, as shown by the disappearance of the signal for the dithiolium-ring proton in the ¹H NMR



Scheme 2. Deprotonation of the dithiolium salt **1a** did not enable the isolation of MIC **3**, but led to ethynylcarbamodithioate **2**. The addition of trifluoromethanesulfonic acid to **2** induced ring closure to afford the dithiolium salt **1b**. Tipp = 2,4,6-triisopropylphenyl, Tf = trifluoromethanesulfonyl.

spectrum. The ¹³C NMR spectrum displayed a signal at $\delta = 81.5$ ppm: significantly further upfield than those observed for other MICs (**B**: $\delta = 200$ ppm, **C**: $\delta = 115$ ppm, **D**: $\delta = 200$ ppm).^[6] However, the ¹³C NMR chemical shift for carbenes is unpredictable^[2b] (ranging from $\delta = 77$ ppm^[9] to $\delta = 326$ ppm^[10]). Therefore, in the hope of confirming quickly the MIC structure of the product, we added trifluoromethanesulfonic acid. We were pleased to observe the quantitative formation of the dithiolium triflate salt **1b** (Figure 1).^[11] However, when single crystals of the deprotonation product of dithiolium salt **1a** were obtained, an X-ray diffraction study revealed that it was not the expected cyclic 1,3-dithiol-5-ylidene **3**, but the acyclic ethynylcarbamodithioate **2** (see the Supporting Information). The true identity of **2** rationalizes

[*] G. Ung, Dr. D. Mendoza-Espinosa, Dr. J. Bouffard, Prof. G. Bertrand
UCR-CNRS Joint Research Chemistry Laboratory (UMI 2957)
Department of Chemistry, University of California, Riverside
Riverside, CA 92521-0403 (USA)
Fax: (+1) 951-827-2725
E-mail: guy.bertrand@ucr.edu
Homepage: <http://research.chem.ucr.edu/groups/bertrand/guybertrandwebpage/>

[**] We are grateful to the NSF (CHE-0808825) and the NIH (R01 GM 68825) for financial support of this research. We thank B. Donnadieu for his assistance with X-ray diffraction studies.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/ange.201100420>.

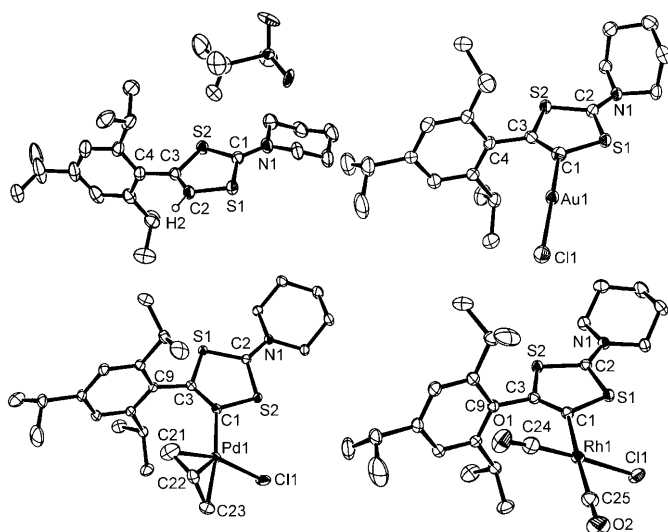
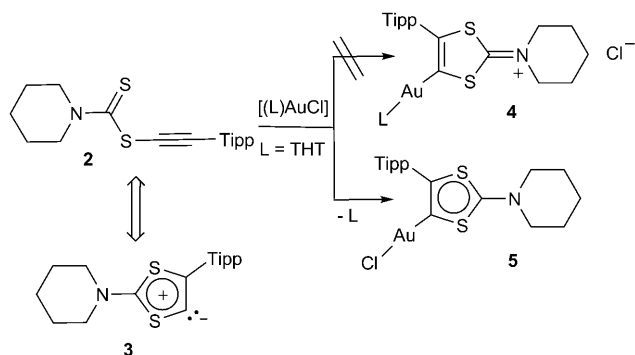


Figure 1. Molecular structures of **1b** (top left), **5** (top right), **6** (bottom left), and **9** (bottom right) in the solid state (hydrogen atoms are omitted for clarity).

the ^{13}C NMR spectroscopic data; furthermore, the infrared spectrum shows a band at 2160 cm^{-1} characteristic of a $\text{C}\equiv\text{C}$ triple bond. The formation of **2** is reminiscent of the ring-opening reaction observed in the deprotonation of isoxazolium^[12] and isothiazolium salts.^[13] Monitoring of the addition of potassium bis(trimethylsilyl)amide to **1a** by NMR spectroscopy showed, even at -60°C , the instantaneous formation of **2**. Note that the deprotonation/ring-opening process might be concerted and therefore does not necessarily imply the transient formation of MIC **3**.

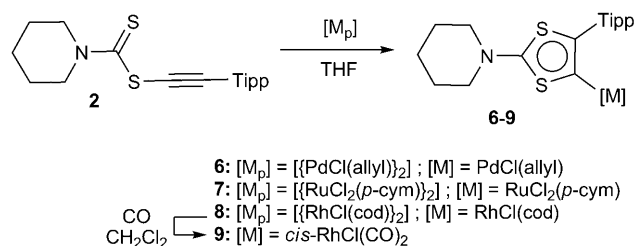
The proton-induced cyclization of **2** into **1** prompted us to study the reactivity of the ethynylcarbamodithioate **2** with gold(I) complexes, which are well-known alkynophilic π acids.^[14] We were particularly interested in the apparent suitability of compound **2** as a precursor for the formation of stable vinyl-gold complexes $[(\text{R}^1\text{R}^2\text{C}=\text{CR}^3)\text{AuL}]$ ^[15] (Scheme 3), which are still rare, although they are believed to be key intermediates in gold-catalyzed alkyne activation.^[16] The reaction of **2** with (tetrahydrothiophene)gold chloride in



Scheme 3. The gold-induced cyclization of **2** did not afford the expected vinyl-gold complex **4** but the 1,3-dithiol-5-ylidene complex **5**. THT = tetrahydrothiophene.

THF proceeded cleanly, but did not afford the expected complex **4**, in which the heterocycle acts as an X ligand as in vinyl-gold complexes. Instead, the MIC-gold(I) complex **5** was isolated in 68 % yield. The ^{13}C NMR spectrum of **5** showed a signal at $\delta = 146.9\text{ ppm}$: a chemical shift comparable to that observed for the $[(\text{MIC B})\text{AuCl}]$ complex ($\delta = 153.7\text{ ppm}$)^[6a] and at significantly higher field than those of vinyl-gold complexes ($\delta = 178\text{--}199\text{ ppm}$).^[14] Similarly, an X-ray diffraction study of **5** (Figure 1) revealed that the gold-carbon bond distance ($1.978(4)\text{ \AA}$) is similar to that found in $[(\text{MIC B})\text{AuCl}]$ ($1.98\text{ \AA}$)^[6a] and $[(\text{NHC})\text{AuCl}]$ ($1.94\text{--}2.00\text{ \AA}$),^[17] and slightly shorter than that in vinyl-gold complexes ($2.04\text{--}2.06\text{ \AA}$).^[15]

These results show that with a gold(I) complex, ethynylcarbamodithioate **2** acts as a ligand equivalent of 1,3-dithiol-5-ylidene **3**. To test the scope of this finding, we treated compound **2** with the less electrophilic complexes $[\text{PdCl}(\text{allyl})_2]$ and $[\text{RuCl}_2(p\text{-cym})_2]$ (Scheme 4). MIC complexes **6** (Figure 1) and **7** were isolated in 69 and 83 % yield, respectively. To evaluate the donor properties of



Scheme 4. The MIC-palladium, ruthenium, and rhodium complexes **6–9** were readily prepared. Thus, acyclic ethynylcarbamodithioate **2** is a ligand equivalent of MIC **3**. *p-cym* = *para*-cymene, *cod* = 1,5-cyclooctadiene.

the 1,3-dithiol-5-ylidene ligand **3**, we prepared the corresponding rhodium(I) dicarbonyl chloride complex **9** (Figure 1) by the addition of half an equivalent of $[\text{RhCl}(\text{cod})_2]$ to **2**, followed by treatment with excess carbon monoxide. The CO vibration frequencies for **9** ($\nu_{\text{av}} = 2030.8\text{ cm}^{-1}$) indicate that **3** is a stronger electron donor than classical NHCs ($\nu_{\text{av}} = 2039\text{--}2041\text{ cm}^{-1}$)^[18] and cyclic (alkyl)(amino)carbenes (CAACs; $\nu_{\text{av}} = 2036\text{ cm}^{-1}$),^[19] but is weaker than other MICs ($\nu_{\text{av}} = 2016\text{--}2025\text{ cm}^{-1}$).^[2a]

The 1,3-dithiol-5-ylidene-metal complexes reported herein are thermally robust (m.p. = 272 (**5**), 219 (**6**), 217 (**7**), 194 (**8**), 186°C (**9**)) and not air-sensitive. The precursor, namely, the acyclic ethynylcarbamodithioate **2**, can be prepared in gram-scale quantities within a day and is stable for several weeks in the solid state under an inert atmosphere and in solution for up to 1 h at 140°C .

These results suggest that the variety of isolable free mesoionic carbenes will be limited by their propensity to undergo ring-opening reactions. However, the reverse process, triggered by transition metals, should be of broad applicability. Since many different analogues of ethynylcarbamodithioate **2** ($\text{R}-\text{C}\equiv\text{C}-\text{X}-\text{C}(\text{Y})\text{R}'$, in which X and Y are heteroatoms with a lone pair of electrons) can readily be

prepared, numerous MIC complexes will be available. The catalytic study of metal complexes supported by MIC **3** is a subject of current investigations in our laboratory.

Experimental Section

All manipulations were performed under an atmosphere of dry argon through the use of standard Schlenk or dry-box techniques. Solvents were dried by standard methods and distilled under argon. ^1H and ^{13}C NMR spectra were recorded on a Varian Inova 500 spectrometer at 25°C. Mass spectra were performed at the UC Riverside Mass Spectrometry Laboratory. Melting points were measured with a Büchi melting point apparatus system.

Synthesis of 2: THF (35 mL) was added to a solid mixture at -78°C of potassium bis(trimethylsilyl)amide (336 mg, 1.68 mol, 1 equiv) and **1a** (800 mg, 1.68 mmol, 1 equiv). The resulting light-yellow solution was stirred for 5 min at -78°C and then allowed to warm to room temperature. The THF was then evaporated, and the residue was extracted with pentane (40 mL). Evaporation of the pentane under vacuum yielded **2** (627 mg, 1.62 mmol, 96%) as a pale-yellow powder. Single crystals were obtained by slow evaporation of a saturated solution of **2** in hexanes/diethyl ether (9:1). M.p.: 101°C ; ^1H (500 MHz, C_6D_6): δ = 0.76–0.84 (m, 2H), 0.84–1.00 (m, 4H), 1.05 (d, J = 7.0 Hz, 6H), 1.23 (d, J = 7.0 Hz, 12H), 2.61 (sept, J = 7.0 Hz, 1H), 2.96 (br s, 2H), 3.73 (br s, 2H), 3.93 (sept, J = 7.0 Hz, 2H), 6.95 ppm (s, 2H); ^{13}C (125 MHz, C_6D_6): δ = 24.1 ($\text{CH}(\text{CH}_3)_2$), 24.2 (CH_2), 24.4 ($\text{CH}(\text{CH}_3)_2$), 25.8 (br, CH_2), 32.8 ($\text{CH}(\text{CH}_3)_2$), 35.4 ($\text{CH}(\text{CH}_3)_2$), 52.5 (br, NCH_2), 53.4 (br, NCH_2), 81.5 (C_{quat}), 103.2 (C_{quat}), 119.4 (C_{quat}), 121.2 (CH_{Ar}), 150.8 (C_{quat}), 152.8 (C_{quat}), 190.3 ppm (C_{quat}); IR (THF): $\tilde{\nu}$ = 2160.4 cm^{-1} ($\text{C}\equiv\text{C}$); HRMS: m/z calculated for $\text{C}_{23}\text{H}_{34}\text{N}_2\text{S}_2$: 388.2127 [M^+]; found: 388.2135.

Preparation of metal complexes: THF (5 mL) was added to a solid mixture of **2** (0.5 mmol, 1 equiv) and a precursor metal complex (0.5 mmol, 1 equiv) at room temperature. The resulting solution was stirred for 14 h at room temperature. The solvent was then evaporated, and the residue was washed with diethyl ether (4×10 mL). The resulting powder was dried under vacuum. Complexes **5**, **6**, **7**, and **8** were obtained in 68, 83, 69, and 66% yield, respectively.

Received: January 18, 2011

Published online: April 6, 2011

Keywords: cyclization · gold · mesoionic carbenes · transition metals

- [1] For reviews, see, for example: a) T. Dröge, F. Glorius, *Angew. Chem.* **2010**, *122*, 7094–7107; *Angew. Chem. Int. Ed.* **2010**, *49*, 6940–6952; b) G. C. Vougioukalakis, R. H. Grubbs, *Chem. Rev.* **2010**, *110*, 1746–1787; c) J. C. Y. Lin, R. T. W. Huang, C. S. Lee, A. Bhattacharyya, W. S. Hwang, I. J. B. Lin, *Chem. Rev.* **2009**, *109*, 3561–3598; d) P. L. Arnold, I. J. Casely, *Chem. Rev.* **2009**, *109*, 3599–3611; e) S. Díez-González, N. Marion, S. P. Nolan, *Chem. Rev.* **2009**, *109*, 3612–3676; f) M. Poyatos, J. A. Mata, E. Peris, *Chem. Rev.* **2009**, *109*, 3677–3707; g) C. Samojłowicz, M. Bieniek, K. Grela, *Chem. Rev.* **2009**, *109*, 3708–3742; h) W. A. L. van Otterlo, C. B. de Koning, *Chem. Rev.* **2009**, *109*, 3743–3782; i) S. Monfette, D. E. Fogg, *Chem. Rev.* **2009**, *109*, 3783–3816; j) B. Alcaide, P. Almendros, A. Luna, *Chem. Rev.* **2009**, *109*, 3817–3858; k) F. E. Hahn, M. C. Jahnke, *Angew. Chem.* **2008**, *120*, 3166–3216; *Angew. Chem. Int. Ed.* **2008**, *47*, 3122–3172.
- [2] For reviews on stable carbenes other than NHCs, see: a) M. Melaimi, M. Soleilhavoup, G. Bertrand, *Angew. Chem.* **2010**, *122*, 8992–9032; *Angew. Chem. Int. Ed.* **2010**, *49*, 8810–8849; b) D. Tapu, D. A. Dixon, C. Roe, *Chem. Rev.* **2009**, *109*, 3385–3407; c) J. Vignolle, X. Cattoën, D. Bourissou, *Chem. Rev.* **2009**, *109*, 3333–3384; d) Y. Canac, M. Soleilhavoup, S. Conejero, G. Bertrand, *J. Organomet. Chem.* **2004**, *689*, 3857–3865; e) D. Bourissou, O. Guerret, F. P. Gabbaï, G. Bertrand, *Chem. Rev.* **2000**, *100*, 39–91.
- [3] For the origin of the name MIC, see: S. Araki, Y. Wanibe, F. Uno, A. Morikawa, K. Yamamoto, K. Chiba, Y. Butsugan, *Chem. Ber.* **1993**, *126*, 1149–1155.
- [4] For the first example of abnormal NHC complexes, see: S. Gründemann, A. Kovacevic, M. Albrecht, J. W. Faller, R. H. Crabtree, *Chem. Commun.* **2001**, 2274–2275.
- [5] For reviews on abnormal and remote carbenes (MICs), see: a) P. L. Arnold, S. Pearson, *Coord. Chem. Rev.* **2007**, *251*, 596–609; b) M. Albrecht, *Chem. Commun.* **2008**, 3601–3610; c) O. Schuster, L. Yang, H. G. Raubenheimer, M. Albrecht, *Chem. Rev.* **2009**, *109*, 3445–3478; d) M. Albrecht, *Chimia* **2009**, *63*, 105–110.
- [6] a) E. Aldeco-Perez, A. J. Rosenthal, B. Donnadieu, P. Parameswaran, G. Frenking, G. Bertrand, *Science* **2009**, *326*, 556–559; b) V. Lavallo, C. A. Dyker, B. Donnadieu, G. Bertrand, *Angew. Chem.* **2008**, *120*, 5491–5494; *Angew. Chem. Int. Ed.* **2008**, *47*, 5411–5414; c) G. Guisado-Barrios, J. Bouffard, B. Donnadieu, G. Bertrand, *Angew. Chem.* **2010**, *122*, 4869–4872; *Angew. Chem. Int. Ed.* **2010**, *49*, 4759–4762.
- [7] D. Lorcy, N. Bellec, M. Fourmigue, N. Avarvari, *Coord. Chem. Rev.* **2009**, *253*, 1398–1438.
- [8] We prepared **1a** in three steps and 72% yield by a synthetic route adapted from: L. M. Birsa, L. V. Asaftei, *Monatsh. Chem.* **2008**, *139*, 1433–1438.
- [9] T. Kato, H. Gornitzka, A. Baceiredo, A. Savin, G. Bertrand, *J. Am. Chem. Soc.* **2000**, *122*, 998–999.
- [10] V. Lavallo, J. Mafhouz, Y. Canac, B. Donnadieu, W. W. Schoeller, G. Bertrand, *J. Am. Chem. Soc.* **2004**, *126*, 8670–8671.
- [11] CCDC 798263 (**1b**), 798264 (**5**), 798265 (**6**), and 798266 (**9**) 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.
- [12] R. B. Woodward, D. J. Woodman, *J. Am. Chem. Soc.* **1966**, *88*, 3169–3170.
- [13] A. Dehope, V. Lavallo, B. Donnadieu, W. W. Schoeller, G. Bertrand, *Angew. Chem.* **2007**, *119*, 7047–7050; *Angew. Chem. Int. Ed.* **2007**, *46*, 6922–6925.
- [14] For reviews on gold chemistry, see, for example: a) D. J. Gorin, B. D. Sherry, F. D. Toste, *Chem. Rev.* **2008**, *108*, 3351–3378; b) A. S. K. Hashmi, *Chem. Rev.* **2007**, *107*, 3180–3211; c) A. Fürstner, P. W. Davies, *Angew. Chem.* **2007**, *119*, 3478–3519; *Angew. Chem. Int. Ed.* **2007**, *46*, 3410–3449; d) D. J. Gorin, F. D. Toste, *Nature* **2007**, *446*, 395–403; e) S. Díez-González, S. P. Nolan, *Acc. Chem. Res.* **2008**, *41*, 349–358; f) E. Jiménez-Núñez, A. M. Echavarren, *Chem. Commun.* **2007**, 333–346; g) A. S. K. Hashmi, *Catal. Today* **2007**, *122*, 211–214; h) A. S. K. Hashmi, *Gold Bull.* **2004**, *37*, 51–65; i) H. C. Shen, *Tetrahedron* **2008**, *64*, 3885–3903; j) R. A. Widenhoefer, *Chem. Eur. J.* **2008**, *14*, 5382–5391; k) A. S. K. Hashmi, *Angew. Chem.* **2010**, *122*, 5360–5369; *Angew. Chem. Int. Ed.* **2010**, *49*, 5232–5241.
- [15] See, for example: a) L.-P. Liu, B. Xu, M. S. Mashuta, G. B. Hammond, *J. Am. Chem. Soc.* **2008**, *130*, 17642–17643; b) Y. Shi, S. D. Ramgren, S. A. Blum, *Organometallics* **2009**, *28*, 1275–1277; c) A. S. K. Hashmi, A. M. Schuster, F. Rominger, *Angew. Chem.* **2009**, *121*, 8396–8398; *Angew. Chem. Int. Ed.* **2009**, *48*, 8247–8249; d) D. Weber, M. A. Tarselli, M. R. Gagné, *Angew. Chem.* **2009**, *121*, 5843–5846; *Angew. Chem. Int. Ed.* **2009**, *48*, 5733–5736; e) X. Zeng, R. Kinjo, B. Donnadieu, G. Bertrand, *Angew. Chem.* **2010**, *122*, 954–957; *Angew. Chem. Int. Ed.* **2010**, *49*, 942–945.
- [16] a) A. S. K. Hashmi, T. D. Ramamurthi, F. Rominger, *Adv. Synth. Catal.* **2010**, *352*, 971–975; b) Z. Li, C. Brouwer, C. He, *Chem.*

- Rev.* **2008**, *108*, 3239–3265; c) A. Arcadi, *Chem. Rev.* **2008**, *108*, 3266–3325; d) E. Jiménez-Núñez, A. M. Echavarren, *Chem. Rev.* **2008**, *108*, 3326–3350; e) N. T. Patil, Y. Yamamoto, *Chem. Rev.* **2008**, *108*, 3395–3442.
- [17] a) P. de Frémont, N. M. Scott, E. D. Stevens, S. P. Nolan, *Organometallics* **2005**, *24*, 2411–2418; b) M. C. Jahnke, J. Paley, F. Hupka, J. J. Weigand, F. E. Hahn, *Z. Naturforsch. B* **2009**, *64*, 1458–1462.
- [18] A. Fürstner, M. Alcarazo, H. Krause, C. W. Lehmann, *J. Am. Chem. Soc.* **2007**, *129*, 12676–12677.
- [19] V. Lavallo, Y. Canac, A. Dehope, B. Donnadiou, G. Bertrand, *Angew. Chem.* **2005**, *117*, 7402–7405; *Angew. Chem. Int. Ed.* **2005**, *44*, 7236–7239.
-