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Mesoionic Carbenes

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

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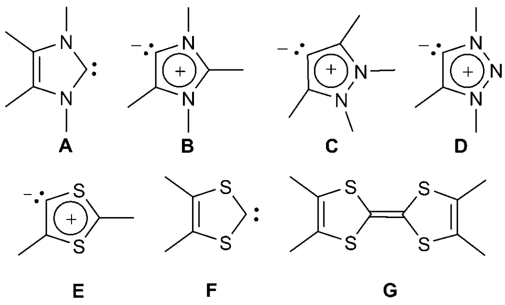
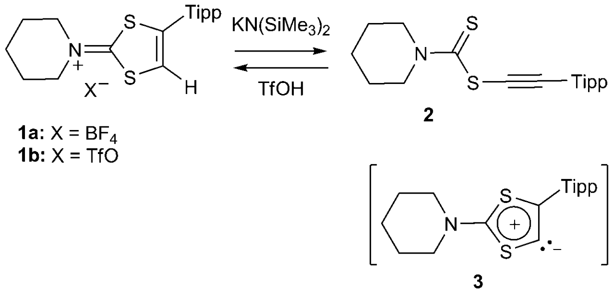
Dedicated to Professor Didier Astruc on the occasion of his 65th birthday

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 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**.



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**.

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 ^{1}H NMR spectrum. The ^{13}C 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 ^{13}C 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



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.

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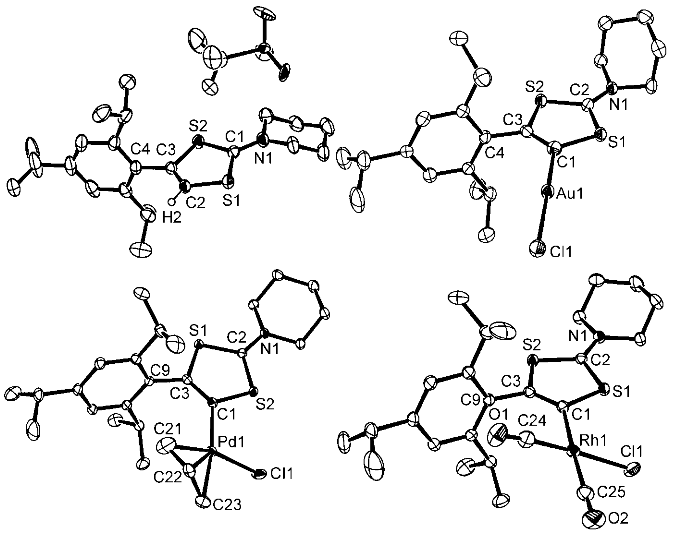
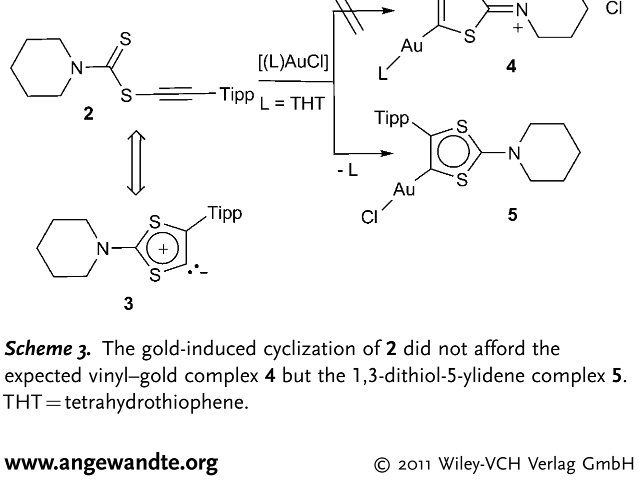


Figure 1. Molecular structures of **1b** (top left), **5** (top right), **6** (bottom left), and **9** (bottom right) in the solid state (hydrogen atoms are omitted for clarity).

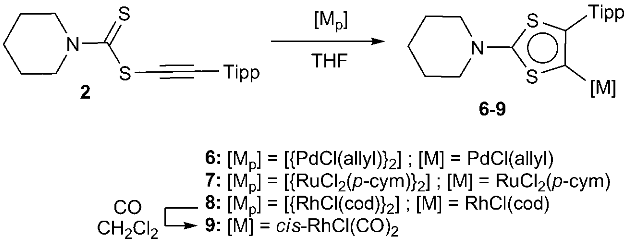
the ^{13}C NMR spectroscopic data; furthermore, the infrared spectrum shows a band at 2160 cm^{-1} characteristic of a C≡C triple bond. The formation of **2** is reminiscent of the ring-opening reaction observed in the deprotonation of isoxazolium[12] and isothiazolium salts.[13] Monitoring of the addition 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 [($R^1R^2C{=}CR^3$)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 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 $\delta = 146.9$ ppm: a chemical shift comparable to that observed for the [(MIC **B**)AuCl] complex ($\delta = 153.7$ ppm)[6a] and at significantly higher field than those of vinyl–gold complexes ($\delta = 178$–199 ppm).[14] Similarly, an X-ray diffraction study of **5** (Figure 1) revealed that the gold–carbon bond distance (1.978(4) Å) is similar to that found in [(MIC **B**)AuCl] (1.98 Å)[6a] and [(NHC)AuCl] (1.94–2.00 Å),[17] and slightly shorter than that in vinyl–gold complexes (2.04–2.06 Å).[15]



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.

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 [{PdCl(allyl)}$_2$] and [{RuCl$_2$(p-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 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 [{RhCl(cod)}$_2$] to **2**, followed by treatment with excess carbon monoxide. The CO vibration frequencies for **9** ($\nu_{av} = 2030.8\ cm^{-1}$) indicate that **3** is a stronger electron donor than classical NHCs ($\nu_{av} = 2039$–$2041\ cm^{-1}$)[18] and cyclic (alkyl)(amino)carbenes (CAACs; $\nu_{av} = 2036\ cm^{-1}$),[19] but is weaker than other MICs ($\nu_{av} = 2016$–$2025\ cm^{-1}$).[2a]



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–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** (R-C≡C-X-C(Y)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. ^{1}H 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; ^{1}H (500 MHz, C_6D_6): $\delta = 0.76$–0.84 (m, 2 H), 0.84–1.00 (m, 4 H), 1.05 (d, $J = 7.0$ Hz, 6 H), 1.23 (d, $J = 7.0$ Hz, 12 H), 2.61 (sept, $J = 7.0$ Hz, 1 H), 2.96 (br s, 2 H), 3.73 (br s, 2 H), 3.93 (sept, $J = 7.0$ Hz, 2 H), 6.95 ppm (s, 2 H); ^{13}C (125 MHz, C_6D_6): $\delta = 24.1$ ($CH(\mathit{C}H_3)_2$), 24.2 (CH_2), 24.4 ($CH(\mathit{C}H_3)_2$), 25.8 (br, CH_2), 32.8 ($\mathit{C}H(CH_3)_2$), 35.4 ($\mathit{C}H(CH_3)_2$), 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): $\tilde{\nu} = 2160.4\ cm^{-1}$ ($C\equiv C$); HRMS: m/z calculated for $C_{23}H_{34}NS_2$: 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.

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[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. Donnadieu, G. Bertrand, *Angew. Chem.* **2005**, *117*, 7402 – 7405; *Angew. Chem. Int. Ed.* **2005**, *44*, 7236 – 7239.