Isolation of Neutral Mononuclear Copper Complexes Stabilized by Two Cyclic (Alkyl)(amino)carbenes

David S. Weinberger,[#] Nurul Amin SK,[†] Kartik Chandra Mondal,[†] Mohand Melaimi,[#] Guy Bertrand,*[,#] A. Claudia Stückl,[†] Herbert W. Roesky,*[,†] Birger Dittrich,[§,†] Serhiy Demeshko,[†] Brigitte Schwederski,[‡] Wolfgang Kaim,*[,‡] Paul Jerabek,[⊥] and Gernot Frenking*[,⊥]

[#]UCSD-CNRS Joint Research Chemistry Laboratory (UMI 3555), Department of Chemistry and Biochemistry, University of California–San Diego, La Jolla, California 92093-0343, United States

[†]Institut für Anorganische Chemie, Georg-August-Universität, Tammannstraße 4, 37077 Göttingen, Germany

[§]Institut für Anorganische und Angewandte Chemie, Universität Hamburg, Martin-Luther-King-Platz 6, Raum AC 15c (Erdgeschoss), 20146 Hamburg, Germany

[‡]Institut für Anorganische Chemie, Universität Stuttgart, Pfaffenwaldring 55, 70569 Stuttgart, Germany

[⊥]Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein-Straße, 35032 Marburg, Germany

ⓢ *Supporting Information*

ABSTRACT: Two $(cAAC)_2Cu$ complexes, featuring a two-coordinate copper atom in the formal oxidation state zero, were prepared by reducing $(Et_2-cAAC)_2Cu^+I^-$ with metallic sodium in THF, and by a one-pot synthesis using Me_2-cAAC, $Cu(II)Cl_2$, and KC_8 in toluene in a molar ratio of 2:1:2, respectively. Both complexes are highly air and moisture sensitive but can be stored in the solid state for a month at room temperature. DFT calculations showed that in these complexes the copper center has a d^{10} electronic configuration and the unpaired electron is delocalized over two carbene carbon atoms. This was further confirmed by the EPR spectra, which exhibit multiple hyperfine lines due to the coupling of the unpaired electron with $^{63,65}Cu$ isotopes, ^{14}N, and ^1H nuclei.

Copper has been shown to be prevalent in redox-active metalloproteins with its most common oxidation states being +I and +II.[1,2] While this has motivated research in the study of copper complexes that show reduction possibilities, to date, no stable complexes have been fully characterized in which the formal charge on the copper atom is zero. The closest copper complexes to be isolated in the zero oxidation state are thin layers and small clusters of copper deposited on a metal oxide surface. These have been shown to be active catalysts for the water–gas shift reaction and the hydrogenation of CO_2 to methanol;[3] however, it has been established, both experimentally and computationally, that the overall charge on the copper is between 0 and 1.[4]

Excluding elemental copper, mononuclear ligated copper(0) complexes have been reported as intermediates in copper-catalyzed arylation of nitrogen and oxygen and have only been detected by cyclic voltammetry (CV) at fast scan rates.[5] Addition of an aryl halide to the CV cell shows higher concentration of the proposed copper(0) species due to the suggested outer-sphere one-electron reduction of the aryl halide.[6] Furthermore, even with the addition of phenanthroline as a π-acceptor, copper(0) was still precipitated and absorbed at the electrode surface. On the other hand, the electrogenerated $[Cu(phen)_2]$ neutral species have been clearly identified by electron paramagnetic resonance (EPR) spectroscopy as Cu^I complexes with partially reduced non-innocent phenanthroline ligands.[6b]

There is some evidence presented by Bowmaker for the existence of $[Cu(PH_3)_n]^0$.[7] These complexes were claimed to be prepared by co-deposition of copper vapor with neat phosphine at 60 K. Subsequent calculations show the HOMO for $[Cu(PH_3)_2]^0$, $[Cu(PH_3)_3]^0$, and $[Cu(PH_3)_4]^0$ to be bonding orbitals with a combination of the Cu 4p and the ligand orbitals of π-symmetry.[8] While the calculations show the opportunity to isolate such complexes, they have only been characterized at low temperatures by infrared (IR) spectroscopy.

Additionally, Atkins and Timms reported that when P≡N was condensed with copper at low temperatures in a krypton matrix, the IR spectrum produced was different from that of the starting material.[9] It was postulated that the resulting complex, which decomposed upon warming, was N≡P→Cu←P≡N.

We reasoned, that in order to stabilize an electron-rich copper(0) and prevent it from precipitating as metal, a ligand that forms very strong bonds to copper and is capable of accepting electron density would be required. We recently demonstrated that cyclic (alkyl)(amino)carbenes (cAACs)[10,11] can stabilize transition metals such as gold(0),[12] manganese(0),[13] and zinc(0)[14] along with a wide variety of phosphorus-, boron-, silicon-, and even carbon-based radicals.[15] In this Communication we report the synthesis, single-crystal X-ray diffraction and EPR studies, and density functional theory (DFT) calculations of two-coordinate copper complexes featuring the metal in the formal oxidation state zero.
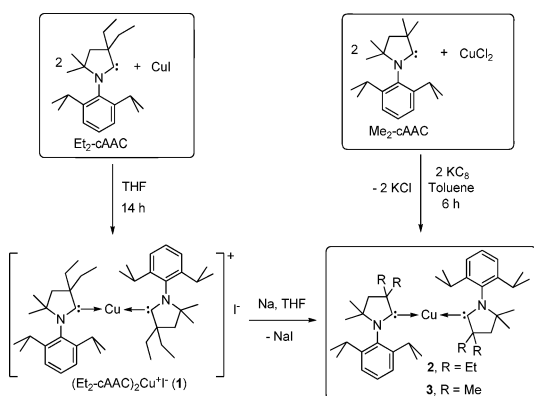
Complex $(Et_2-cAAC)_2Cu^+I^-$ (**1**) was synthesized by reacting 2 equivalents of free carbene and copper(I) iodide (Scheme 1).

Scheme 1. Synthetic Strategy for Carbene–Copper Complexes

The cyclic voltammogram of **1** in THF, containing 0.1 M nBu_4NPF_6 as electrolyte (see Supporting Information (SI)), showed a quasi-reversible one-electron reduction at $E_{1/2} = -1.36$ V versus $Cp*_2Fe^+/Cp*_2Fe$ ($Cp*_2Fe$ = decamethylferrocene). Therefore, we attempted the reduction of complex **1** with sodium metal (Scheme 1). In a glovebox a THF solution of **1** was stirred with a fresh piece of sodium metal for 2 h in a scintillation vial. The solution was filtered and evaporated. The solid was then extracted with *n*-hexane and the solvent removed to yield **2** (35% yield) as a highly water- and air-sensitive reddish-brown solid. Crystals of **2** were obtained from a concentrated solution of hexanes at −30 °C.

Similarly, a one-pot reaction of Me_2-cAAC, $CuCl_2$, and KC_8 in a molar ratio of 2:1:2 in toluene produced a green solution from which dark plates of the desired complex $(Me_2$-cAAC$)_2Cu$ (**3**) were isolated in 7% yield (Scheme 1). Single crystals were obtained from a toluene solution at −32 °C. **3** is stable under an inert atmosphere and decomposes above 142 °C. **3** is not stable in benzene and *n*-hexane, in which it decomposes to produce a light yellow solution. It has been observed that the toluene solution of **3** is stable and retains its color under an inert atmosphere. The crystals of **3** can be stored in a glovebox for a month at room temperature, whereas on exposure to air they slowly lose their color to produce a light yellow solid after 6 h. The UV–vis–near-IR spectrum of the toluene solution of **3** showed absorption bands at 330, 435, 482, 595, 655, 755, and 1214 nm (see SI).

Both complexes **2** and **3** crystallize in the triclinic space group $P\bar{1}$. The central copper atom resides on the center of symmetry and adopts a two-coordinate linear geometry (Figure 1). The C–Cu bond distances are experimentally found to be 1.8636(15) and 1.8674(10) Å for **2** and **3**, respectively. The C–N bond distances are 1.3492(19) Å in **2** and 1.3510(13) Å in **3**. The Cu–C and C–N bond distances of **1** range from 1.920(5) to 1.946(5) Å and from 1.299(6) to 1.310(6) Å, respectively (see SI), while the C–Cu–C bond angle in **1** is 180.0(2)/168.4(2)°, which is close to that of 180° in **2**/**3**.

Quantum chemical calculations using DFT at the M06/def2-SVP level give insight into the bonding situation. The calculated structure of **3**, which is shown in Figure S6, is in excellent agreement with the experiment. The theoretical C1–Cu bond length in the cation **3**$^+$ (1.935 Å, see Figure S9) is somewhat longer than in the neutral parent molecule, which concurs with the experimental data. The calculated spin density of the unpaired electron in **3** shows that it is delocalized over the $p(\pi)$ orbitals of the N1–C1–Cu–C1′–N1′ moiety, with
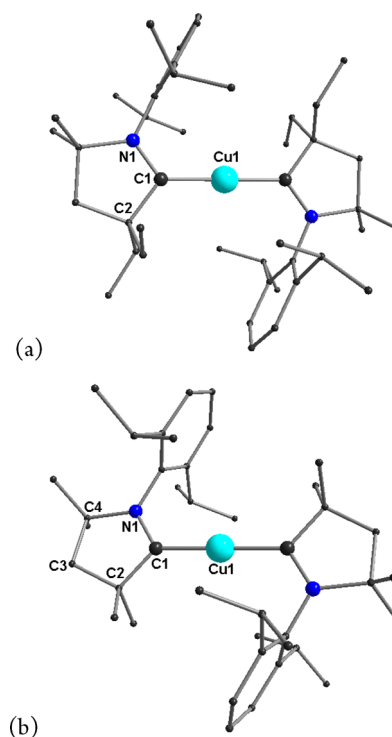

Figure 1. Molecular structures of compounds $(Et_2$-cAAC$)_2Cu$ (**2**) (a) and $(Me_2$-cAAC$)_2Cu$ (**3**) (b). H atoms are omitted for clarity. Selected experimental [calculated at M06/def2-SVP for **3**] bond lengths [Å] and angles [°] of **2**/**3**: Cu1–C1 1.8636(15)/1.8674(10) [1.887], N1–C1 1.3492(19)/1.3510(13) [1.353], N1–C9/1.4393(13) [1.430], C1–C2/1.5231(14) [1.518]; C1–Cu1–C1^i 180/180[180.0], N1–C1–C2/107.29(8) [107.5], N1–C1–Cu1/122.98(7) [122.3], C2–C1–Cu1/129.72(7) [130.2].

much larger coefficients at C1/C1′ (0.34) than at N1/N1′ (0.09) (Figure 2).
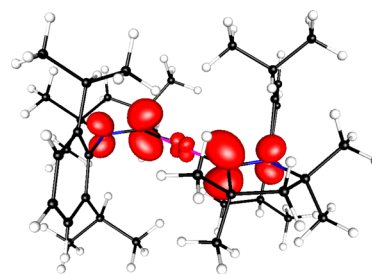
Figure 2. Spin density of $(Me_2$-cAAC$)_2Cu$ (**3**) (M06/def2-SVP). This singly occupied π orbital entails partial C1–Cu–C1′ π bonding, which explains why the bonds are shorter than in the cation **3**$^+$. The bonding situation in the copper compound **3** is very similar to that of the analogous gold species Au(cAAC)$_2$.[12]

Complexes **2** and **3** are EPR active (see SI). The room-temperature EPR spectrum of **2** shows a signal at $g = 1.997$, with partially resolved hyperfine coupling of about 7 G, involving the copper isotopes ^{63}Cu (69.2%, $I = 3/2$) and ^{65}Cu (30.8%, $I = 3/2$; ratio $a(^{65}Cu)/a(^{63}Cu) = 1.07$). A similar, well-resolved spectrum was obtained for **3** in toluene at room temperature ($g = 1.9996$; Figure 3). It could be simulated with $a(^{63}Cu) = 7.95$ G, $a(^{65}Cu) = 8.51$ G, $a(^{14}N) = 2.5$ G (2N), and $a(^1H) = 0.9$ G (12H). The latter coupling can be tentatively attributed to the four methyl groups (CMe$_2$) of the ligand in
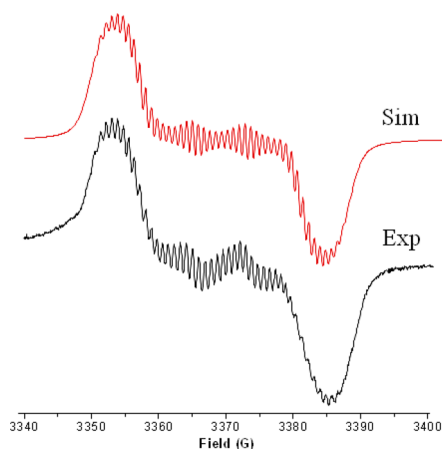
Figure 3. Experimental (black) and simulated (red) EPR spectra of $(Me_2\text{-}cAAC)_2Cu$ (**3**).

the position β to the carbene carbon, whose hyperfine coupling could not be determined due to the low natural abundance of ^{13}C. An alternative for the ^1H coupling would be the four inside-oriented methyl groups of the *N*-aryl substituents, as suggested by the spin density plot (Figure 2). In agreement with the calculated spin density distribution, the nitrogen hyperfine coupling is relatively small, as is the metal hyperfine coupling in comparison to that of paramagnetic compounds of Cu^I or Cu^{II},[16] signifying little copper participation at the singly occupied molecular orbital (SOMO). In the same vein, the isotropic *g* factors close to the free electron value of 2.0023 confirm marginal contributions from the transition element to the SOMO, suggesting a three-center carbene/copper/carbene description with predominantly carbene radical character.

The magnetic properties of **3** were further investigated by temperature-dependent susceptibility measurements (Figure 4).
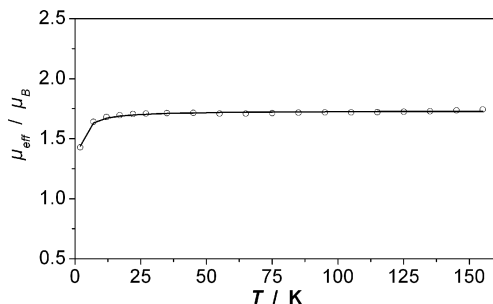
Figure 4. Magnetic moment vs temperature for **3**. The solid line represents the calculated curve.

The experimental magnetic moment of **3** is 1.74 μ_B at 155 K, which is very close to the spin-only value of 1.73 μ_B for one unpaired electron. Magnetic moment remains nearly constant down to 7 K. Some decrease below this temperature can be attributed to the weak intermolecular antiferromagnetic interaction. Analysis of the experimental data (see SI for more details) led to the values g = 2.00 and Weiss temperature Θ = -0.9 K (or zJ = -2.5 cm^{-1}, where J is the intermolecular interaction parameter between two nearest-neighbor magnetic species and z is the number of nearest neighbors; intermolecular C_{cAAC}–CH_3 distance is 5.25 Å).

The cyclic voltammogram of $(Me_2\text{-}cAAC)_2Cu$ (**3**) in DMF, containing 0.1 M nBu_4NPF_6 as electrolyte, exhibited a quasi-

reversible one-electron process at $E_{1/2}$ = -1.35 V versus $Cp*_2Fe^+$/ $Cp*_2Fe$ (see SI), suggesting the formation of **3$^-$**.

In conclusion, we have shown that by utilizing cAACs, which are both excellent σ-donor and π-acceptor ligands, the first neutral two-coordinate Cu complexes could be prepared, isolated, and fully characterized by X-ray crystallography and EPR. Accessing what previously had only been a hypothesized intermediate in copper catalysis will allow now for reactivity studies.

Synthesis of Complexes 1−3. *General.* All manipulations were performed under an inert atmosphere of dry nitrogen, using standard Schlenk techniques. Dry, oxygen-free solvents were employed. EPR spectra were recorded on a Bruker EMX instrument. ^1H and ^{13}C NMR spectra were recorded on Varian Inova 500 spectrometers (500.1 MHz for ^1H, 125.8 MHz for ^{13}C). All spectra were obtained in the solvent indicated at 25 °C. Chemical shifts are given in ppm and are referenced to $SiMe_4$ (^1H, ^{13}C). Melting points were measured with a Büchi melting point apparatus system.

$(Et_2\text{-}cAAC)_2Cu^+I^-$ (1). In a glovebox, a Schlenk flask was loaded with Et_2-cAAC (1.53 g, 4.88 mmol) and CuI (0.45 equiv, 0.418 g, 2.19 mmol). At -78 °C, 60 mL of THF was added, and the mixture was warmed to room temperature over 14 h. The THF solution was evaporated to dryness and subsequently washed with 20 mL of *n*-hexane three times. **1** was extracted with 3×10 mL of CH_2Cl_2, and after evaporation of the solvent under vacuum, **1** was obtained as a white powder (1.35 g; 75% yield): mp 203 °C (dec.); ^1H NMR (C_6D_6, 400 MHz) δ = 7.35 (t, J = 7.2 Hz, 1H), 7.14 (d, J = 7.2 Hz, 2H), 2.62 (br, 2H), 1.95 (s, 2H), 1.71 (br, 2H), 1.56 (br, 2H), 1.26 (br, 6H), 1.20 (br, 6H), 1.18 (d, J = 6 Hz, 6H), 0.94 (br, 6H), 0.7 (br, 6H); ^{13}C NMR (C_6D_6, 75 MHz) δ = 249.33 (C), 144.3 (C), 134.1 (C), 129.9 (CH), 124.1 (CH), 83.0 (C), 64.0 (C), 39.9 (CH_2), 31.5 (CH_2), 29.1 (CH_3), 28.8 (CH_3), 27.2 (CH), 21.8 (CH_3), 9.6 (CH_3) ppm; HRMS (ESI-TOFMS) m/z calculated for $[C_{44}H_{70}CuN_2]^+$ 689.4835, found 689.4843.

$(Et_2\text{-}cAAC)_2Cu$ (2). To a solution of **1** (125 mg, 0.153 mmol) in 20 mL of THF was added a clean piece of Na metal (200 mg). After 15 min at room temperature, the solution turned to a red/brown color. The solution was allowed to stir for an additional hour and subsequently filtered. The filtrate was evaporated under vacuum. The solid was then extracted with 4 $\times$ 20 mL of *n*-hexanes, and the solvent was evaporated under vacuum to yield **2** as a reddish-brown solid. Crystals suitable for X-ray analysis were grown at -30 °C from a concentrated solution of *n*-hexanes (37 mg; 35% yield); **2** decomposes above 131 °C.

$(Me_2\text{-}cAAC)_2Cu$ (3). A 1:2:2 molar mixture of $CuCl_2$ (76 mg, 0.562 mmol), Me_2-cAAC (322 mg, 1.13 mmol), and KC_8 (152 mg, 1.12 mmol) and toluene (70 mL) were separately cooled to -78 °C, and then the toluene was added to the mixture through a cannula. The reaction solution was then slowly warmed to room temperature and stirred for 12 h. During this period the color of the solution changed to dark green, and it was subsequently filtered. The filtrate was stored at room temperature for 6 h. Then the solution was filtered again to remove colorless byproducts and stored at -32 °C in a freezer overnight. Dark plates of **3** were formed (23 mg, 7% yield) which were separated by filtration. C, H, and N analysis (%) found (calcd) for $C_{40}H_{62}N_2Cu$; C, 75.70 (75.72); H, 9.65 (9.84); N, 4.45 (4.41). **3** decomposes above 142 °C and turns to a black liquid. UV−visible bands are observed at 330, 435, 482, 595, 655, 755, and 1214 nm.

6237

dx.doi.org/10.1021/ja502521b | *J. Am. Chem. Soc.* 2014, 136, 6235−6238

EPR. Simulation for the EPR spectrum was done using EasySpin.[17]

ASSOCIATED CONTENT

S Supporting Information

General syntheses; UV–vis–NIR, EPR, crystal structure determination, and magnetic measurements; and theoretical details. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Authors
guybertrand@ucsd.edu
hroesky@gwdg.de
kaim@iac.uni-stuttgart.de
frenking@chemie.uni-marburg.de

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

REFERENCES

(1) Barondeau, D. P.; Getzoff, E. D. *Curr. Opin. Struct. Biol.* **2004**, *14*, 765–774. (b) Lu, Y.; Berry, S. M.; Pfister, T. D. *Chem. Rev.* **2001**, *101*, 3047–3080. (c) Malkin, R.; Malmstro, B. G. *Adv. Enzymol. Relat. Areas Mol. Biol.* **1970**, *33*, 177–244. (d) Rorabacher, D. B. *Chem. Rev.* **2004**, *104*, 651–698. (e) Valentine, J. S.; Doucette, P. A.; Potter, S. Z. In *Annual Review of Biochemistry*; Annual Reviews: Palo Alto, CA, 2005; Vol. 74, pp 563–593.

(2) Jernigan, G. G.; Somorjai, G. A. *J. Catal.* **1994**, *147*, 567–577.

(3) (a) Ratnasamy, C.; Wagner, J. P. *Catal. Rev.* **2009**, *51*, 325–440. (b) Gokhale, A. A.; Dumesic, J. A.; Mavrikakis, M. *J. Am. Chem. Soc.* **2008**, *130*, 1402–1414.

(4) Zuo, Z.-J.; Han, P.-D.; Li, Z.; Hu, J.-S.; Huang, W. *Appl. Surf. Sci.* **2012**, *261*, 640–646.

(5) Lefèvre, G.; Franc, G.; Tlili, A.; Adamo, C.; Taillefer, M.; Ciofini, I.; Jutand, A. *Organometallics* **2012**, *31*, 7694–7707.

(6) (a) Mansour, M.; Giacovazzi, R.; Ouali, A.; Taillefer, M.; Jutand, A. *Chem. Commun.* **2008**, *45*, 6051–6053. (b) Stange, A. F.; Waldhör, E.; Moscherosch, M.; Kaim, W. *Z. Naturforsch.* **1995**, *50b*, 115–122.

(7) Bowmaker, G. A. *Aust. J. Chem.* **1978**, *31*, 2549–2553.

(8) Bowmaker, G. A.; Pabst, M.; Roesch, N.; Schmidbaur, H. *Inorg. Chem.* **1993**, *32*, 880–887.

(9) Atkins, R. M.; Timms, P. L. *Inorg. Nucl. Chem. Lett.* **1978**, *14*, 113–115.

(10) (a) Lavallo, V.; Canac, Y.; Präsang, C.; Donnadieu, B.; Bertrand, G. *Angew. Chem., Int. Ed.* **2005**, *44*, 5705–5709; *Angew. Chem.* **2005**, *117*, 5851–5855. (b) Jazzar, R.; Dewhurst, R. D.; Bourg, J.-B.; Donnadieu, B.; Canac, Y.; Bertrand, G. *Angew. Chem., Int. Ed.* **2007**, *46*, 2899–2902; *Angew. Chem.* **2007**, *119*, 2957–2960.

(11) (a) Melaimi, M.; Soleilhavoup, M.; Bertrand, G. *Angew. Chem., Int. Ed.* **2010**, *49*, 8810–8849; *Angew. Chem.* **2010**, *122*, 8992–9032. (b) Martin, D.; Melaimi, M.; Soleilhavoup, M.; Bertrand, G. *Organometallics* **2011**, *30*, 5304–5313.

(12) Weinberger, D. S.; Melaimi, M.; Moore, C. E.; Rheingold, A. L.; Frenking, G.; Jerabek, P.; Bertrand, G. *Angew. Chem., Int. Ed.* **2013**, *52*, 8964–8967; *Angew. Chem.* **2013**, *125*, 9134–9137.

(13) Samuel, P. P.; Mondal, K. C.; Roesky, H. W.; Hermann, M.; Frenking, G.; Demeshko, S.; Meyer, F.; Stückl, A. C.; Christian, J. H.; Dalal, N. S.; Ungur, L.; Chibotaru, L. F.; Pröpper, K.; Meents, A.; Dittrich, B. *Angew. Chem., Int. Ed.* **2013**, *52*, 11817–11821; *Angew. Chem.* **2013**, *125*, 12033–12037.

(14) Singh, A. P.; Samuel, P. P.; Roesky, H. W.; Schwarzer, M. C.; Frenking, G.; Sidhu, N. S.; Dittrich, B. *J. Am. Chem. Soc.* **2013**, *135*, 7324–7329.

(15) (a) Back, O.; Kuchenbeiser, G.; Donnadieu, B.; Bertrand, G. *Angew. Chem., Int. Ed.* **2009**, *48*, 5530–5533; *Angew. Chem.* **2009**, *121*, 5632–5641. (b) Ruiz, D. A.; Ung, G.; Melaimi, M.; Bertrand, G. *Angew. Chem., Int. Ed.* **2013**, *52*, 7590–7592; *Angew. Chem.* **2013**, *125*, 7739–7742. (c) Martin, C. D.; Weinstein, C. M.; Moore, C. E.; Rheingold, A. L.; Bertrand, G. *Chem. Commun.* **2013**, *49*, 4486–4488. (d) Martin, C. D.; Soleilhavoup, M.; Bertrand, G. *Chem. Sci.* **2013**, *4*, 3020–3030. (e) Mahoney, J. K.; Martin, D.; Moore, C. E.; Rheingold, A. L.; Bertrand, G. *J. Am. Chem. Soc.* **2013**, *135*, 18766–18769. (f) Kinjo, R.; Donnadieu, B.; Celik, M. A.; Frenking, G.; Bertrand, G. *Science* **2011**, *333*, 610–613. (g) Back, O.; Donnadieu, B.; Parameswaran, P.; Frenking, G.; Bertrand, G. *Nat. Chem.* **2010**, *2*, 369–373. (h) Back, O.; Celik, M. A.; Frenking, G.; Melaimi, M.; Donnadieu, B.; Bertrand, G. *J. Am. Chem. Soc.* **2010**, *132*, 10262–10263. (i) Mondal, K. C.; Roesky, H. W.; Schwarzer, M. C.; Frenking, G.; Niepötter, B.; Wolf, H.; Herbst-Irmer, R.; Stalke, D. *Angew. Chem., Int. Ed.* **2013**, *52*, 2963–2967; *Angew. Chem.* **2013**, *125*, 3036–3040. (j) Mondal, K. C.; Samuel, P. P.; Tretiakov, M.; Singh, A. P.; Roesky, H. W.; Stückl, A. C.; Niepötter, B.; Carl, E.; Wolf, H.; Herbst-Irmer, R.; Stalke, D. *Inorg. Chem.* **2013**, *52*, 4736–4743.

(16) Rall, J.; Kaim, W. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 2905–2908.

(17) Stoll, S.; Schweiger, A. *J. Magn. Reson.* **2006**, *178*, 42–55.