Isolation of Bridging and Terminal Coinage Metal–Nitrene Complexes

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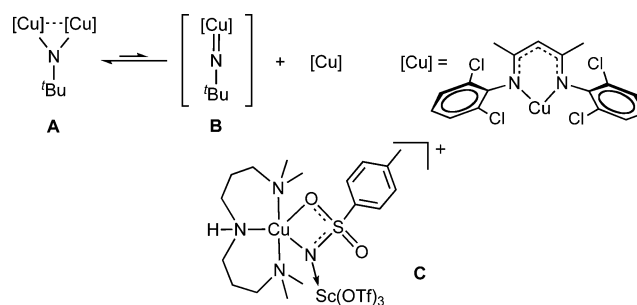
S *Supporting Information*

ABSTRACT: Transition metal complexes featuring a metal–nitrogen multiple bond have been widely studied due to their implication in dinitrogen fixation and catalytic nitrogen–carbon bond formation. Terminal copper– and silver–nitrene complexes have long been proposed to be the key intermediates in aziridination and amination reactions using azides as the nitrogen source. However, due to their high reactivity, these species have eluded isolation and spectroscopic characterization even at low temperatures. In this paper we report that a stable phosphinonitrene reacts with coinage metal trifluoromethanesulfonates, affording bridging and terminal copper– and silver–nitrene complexes, which are characterized by NMR spectroscopy and single crystal X-ray diffraction analysis.

Figure 1. Previously isolated copper–nitrene complexes **A** and **C**.

Numerous stable early transition metal complexes featuring a metal–ligand multiple bond have been prepared.[1] Although examples of isolated imido-complexes of Fe,[2] Ru,[3] Os,[4] Co,[5] Ir,[6] and Ni[7] are known, such compounds are not common with late transition metals.[8] Since the discovery that copper promotes the decomposition of the benzenesulfonyl azide,[9] numerous coinage metal-based catalysts have been developed for catalytic alkane amination and alkene aziridination reactions, whereby copper has been the most extensively studied.[10] Terminal Cu and Ag nitrene complexes have been proposed to be the key reactive intermediates,[11] but no terminal coinage metal–nitrene complexes have been structurally characterized so far. Warren and co-workers isolated a series of nitrene bridged dicopper compounds **A** that are active in nitrene transfer reactions (Figure 1).[12]

These authors provided strong evidence for a dissociation equilibrium of these compounds in solution into terminal metal–nitrene complexes **B**. Recently, Ray and co-workers trapped a copper–nitrene intermediate with scandium(III) triflate, and the resulting adduct **C** was sufficiently stable at −90 °C to allow for its spectroscopic characterization.[13]

We have recently reported the synthesis of a singlet phosphinonitrene (**1**), which is stable at room temperature.[14] Preliminary studies have shown the strong nucleophilic character of this compound, which prompted us to investigate its ligand behavior toward coinage metals. Here we report the synthesis, single crystal X-ray diffraction, and computational

studies of bridging and terminal copper and silver metal–nitrene complexes.

We first studied the reaction of phosphinonitrene **1** with 2 equiv of copper(I) and silver(I) triflate, in order to prepare a dinuclear complex similar to **A**.[12c] The reaction proceeded cleanly, and complexes **2a,b** were isolated as colorless crystals in 66 and 63% yield, respectively (Scheme 1).

**Scheme 1. Reaction of the Phosphinonitrene 1 with Cu(I) and Ag(I) Triflates (Dipp = 2,6-Diisopropylphenyl)**
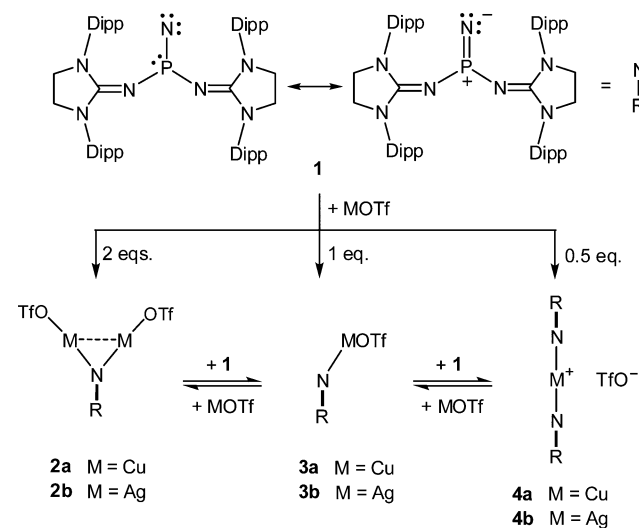
The bimetallic nature of **2b** was clearly indicated by the ^{31}P NMR spectrum, which shows a triplet (J_{AgP} = 42 Hz) at 65.6 ppm. A downfield shift, with respect to the nitrene precursor **1** (7.7 ppm),[14a] was also observed for **2a** (64.9 ppm), in agreement with the enhanced electron deficiency of the phosphorus center. This was confirmed by X-ray diffraction studies (Figure 2), which show that the electron donation from
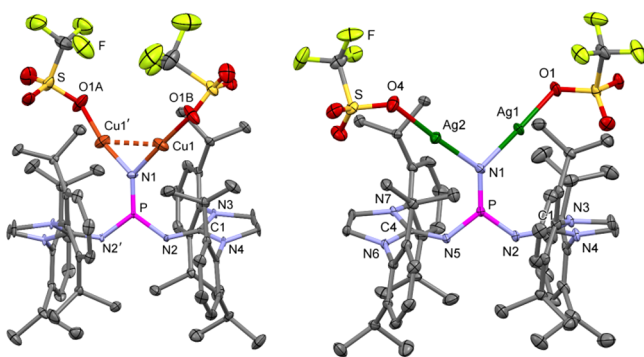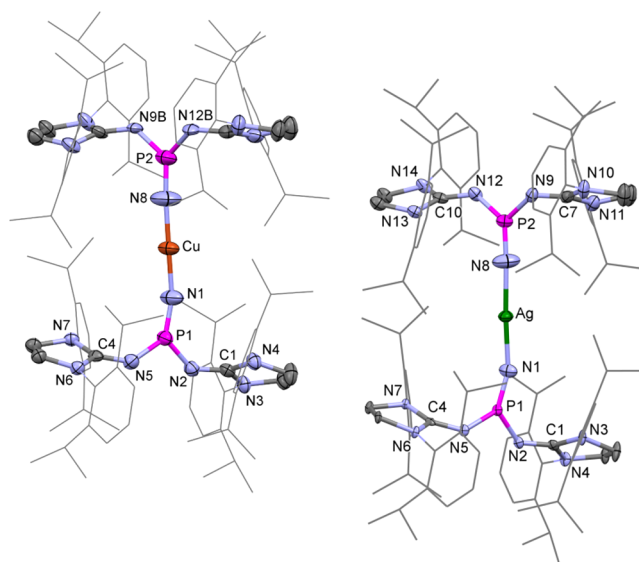

Figure 2. Solid-state structure of **2a** (left) and **2b** (right) with thermal ellipsoid plots at the 50% levels of probability. Hydrogen atoms are omitted for clarity.

the imidazolidin-2-iminato substituents is even stronger for **2a,b** than for **1**. Indeed, there is a shortening of the P−N2 and C1−N3 bonds and a lengthening of the C1−N2 bond compared to those of **1** [**2a**: 1.573(3), 1.359(4), 1.310(4); **2b**: 1.561(3), 1.351(4), 1.324(4); **1**: 1.629(8), 1.374(11), 1.282(11) Å]. The phosphorus atom in **2a,b** is in a planar environment (sum of the angles: 360°). The P−N1 bonds [**2a**: 1.510(5) Å; **2b**: 1.528(3) Å] are significantly lengthened compared to that of **1** [1.457(8) Å] and are in the range reported for PN double bonds (1.50 to 1.60 Å).[15] It is interesting to note that the Cu−N$_{nitrene}$ distances in **2a** [1.817(3) Å] are nearly identical to those of the dicopper−nitrene complex **A** [1.808(3) and 1.815(3) Å],[12c] although the Cu⋯Cu distance in **2a** [2.6697(9) Å] is significantly shorter [**A**: 2.9147(6) Å]. Complexes **2a,b** are stable at room temperature, both in the solid state and in CH$_2$Cl$_2$ solutions, but rapidly decompose upon exposure to air.

In the hope of preparing the terminal imido complexes **3a,b**, 1 equiv of copper(I) and silver(I) triflate was added to a THF solution of nitrene **1**. The ^{31}P NMR spectra of the reaction mixtures show a singlet for **3a** (42.0 ppm) and a doublet for **3b** (46.3 ppm, J_{AgP} = 53 Hz) as the major species, indicating the formation of mononuclear nitrene complexes. However, signals for **2a,b** and for an additional mononuclear species **4a,b** were also present (Figure 3), and all attempts to isolate the major species **3a,b** resulted in a dismutation and the concurrent crystallization of **2a,b** and **4a,b** as a result of the lower solubility of **2a,b**. We quickly realized that, in the presence of excess nitrene **1**, complexes **4a,b** became the major products. Adding 2 equiv of **1** to copper(I) and silver(I) triflate led after workup to **4a,b**, which were isolated as single crystals in 76 and 72% yield, respectively. As suggested by the stoichiometry of the reaction, single crystal X-ray diffraction studies revealed that in **4a,b** two nitrenes are terminally bound to one Cu and Ag center, respectively (Figure 4). The Cu−N−P [165.20(16)°, 175.7(2)°] and Ag−N−P angles [159.9(2)°, 176.1(3)°] deviate only slightly from linearity just like it was observed for Fe,[2c] Co,[5c] and Ni[7a] imido complexes. The Cu−N$_{nitrene}$ [1.801(2)
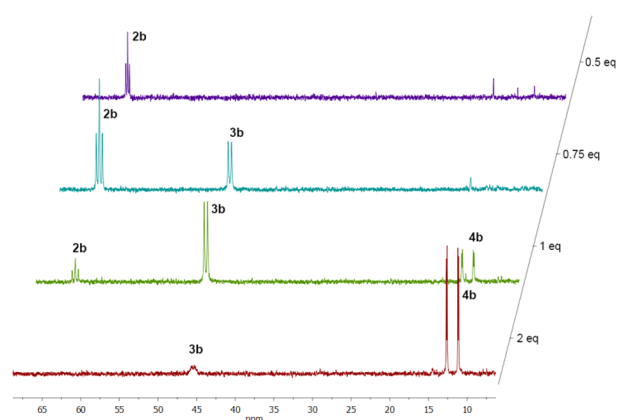
Figure 3. ^{31}P NMR spectra of mixtures of AgOTf with 0.5−2 equiv of **1** in THF.

Figure 4. Solid-state structure of **4a** (left) and **4b** (right) with thermal ellipsoid plots at the 50% levels of probability. Hydrogens and triflate anions are omitted for clarity.

and 1.807(3) Å] and Ag−N$_{nitrene}$ distances [2.017(3) and 2.029(4) Å] are even shorter than those in **2a** [1.817(3) Å] and **2b** [2.080(3) and 2.086(3) Å], respectively. The geometrical parameters for the phosphinonitrene ligand in **4a,b** indicate a less pronounced donation from the imidazolidin-2-iminato substituents to the phosphorus center than in **2a,b**, and a less pronounced elongation of the P1−N1 bonds [**4a**: 1.479(2) Å; **4b**: 1.491(3) Å] compared to free **1** (1.457(8) Å). This is in line with the upfield shift of the ^{31}P NMR signals [**4a**: 2.1 ppm; **4b**: 12.4 ppm (J_{107AgP} = 168 Hz, J_{109AgP} = 194 Hz)].

We also attempted to prepare **3a,b** by adding 1.0 equiv of nitrene **1** to the dinuclear complexes **2a,b** and 1.0 equiv of metal triflate to **4a,b**. In both cases, we obtained a mixture identical to that obtained using a stoichiometric amount of **1** and metal triflate. These results demonstrate that the metal−nitrene bond in all these complexes is labile and confirm that **3a,b** are mononuclear mononitrene triflate complexes.

Quantum chemical calculations were carried out for **2a**, **2b**, **4a**, **4b** and for the free phosphinonitrene ligand **1**.[16] The optimized geometries of the metal complexes (BP86/def2-SVP) are in satisfying agreement with the experimental data. The calculated bond orders suggest that upon coordination the

P1−N1 bond becomes significantly weaker while the P1−N2/N5 bonds become stronger (Tables S28 and S29). The complete geometries of the complexes and the free ligand **1** are given in the Supporting Information. NBO calculations indicate a charge donation **1**→(M-triflate)$_2$ of 0.34 e in **2a** and 0.32 e in **2b**. The partial charges at the formal M$^+$ are +0.62 for the copper complex **4a** and +0.55 e for the silver complex **4b**. This indicates a total charge donation **1**→M$^+$←**1** of 0.38 e in **4a** and 0.45 e in **4b**. The bigger charge donation does not imply that the silver complexes have stronger bonds. The energy decomposition analysis (EDA) suggests (Table S30) that the intrinsic interaction energies ΔE_{int} between the frozen fragments **1** and (M-triflate) are −156.1, −129.9, −212.5, and −170.3 kcal/mol for **2a**, **2b**, **4a**, and **4b**, respectively. The predicted (BP86/TZ2P*//BP86/def2-SVP) bond dissociation energy D_e for removing both M-triflate ligands amounts to 135.1 and 99.2 kcal/mol for **2a** and **2b**, respectively. Stronger metal−ligand bonds were calculated for the cations **4a** and **4b**. The calculated bond dissociation energies D_e for breaking both bonds **1**→M$^+$←**1** are 182.9 and 143.7 kcal/mol for **4a** and **4b**. Inspection of the orbital term of the EDA results (Tables S30 and S31) reveals that the phosphinonitrene ligand **1** is a four-electron donor in **2a** and **2b** where the occupied σ and $\pi_{\|}$ orbitals at nitrogen strongly contribute to the **1**→(M-triflate)$_2$ bonding, while the $\pi_{\perp}$ backdonation M→L(p) is only a minor component. In contrast, ligand **1** in compounds **4a,b** serves as a two-electron donor only. The EDA data suggest that the major contribution to the orbital interactions comes from the σ donation L(LP)→M(s).

In conclusion, we have demonstrated that bridging and terminal silver and copper metal−nitrene complexes can be prepared directly from a nitrene and coinage metal triflates and are stable enough to be isolated. The metal−nitrene bond is labile, and these complexes can be made reversibly depending on the stoichiometry. We are currently exploring the reactivity of these complexes.

■ ASSOCIATED CONTENT

ⓈSupporting Information

Full experimental and theoretical details, and X-ray crystallographic data for **2a**, **2b**, **4a**, and **4b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Munhá, R. F.; Zarkesh, R. A.; Heyduk, A. F. *Dalton Trans.* **2013**, *42*, 3751−3766. (b) Hinrichsen, S.; Broda, H.; Gradert, C.; Söncksen, L.; Tuczek, F. *Annu. Rep. Prog. Chem., Sect. A: Inorg. Chem.* **2012**, *108*, 17−47. (c) Heyduk, A. F.; Zarkesh, R. A.; Nguyen, A. I. *Inorg. Chem.* **2011**, *50*, 9849−9863. (d) Eikey, R. A.; Abu-Omar, M. M. *Coord. Chem. Rev.* **2003**, *243*, 83−124. (e) Gade, L. H.; Mountford, P. *Coord. Chem. Rev.* **2001**, *216−217*, 65−97.

(2) (a) Kuppuswamy, S.; Powers, T. M.; Johnson, B. M.; Bezpalko, M. W.; Brozek, C. K.; Foxman, B. M.; Berben, L. A.; Thomas, C. M. *Inorg. Chem.* **2013**, *52*, 4802−4811. (b) King, E. R.; Hennesy, E. T.; Betley, T. A. *J. Am. Chem. Soc.* **2011**, *133*, 4917−4923. (c) Bowman, A. C.; Milsmann, C.; Bill, E.; Turner, Z. R.; Lobkovsky, E.; DeBeer, S.; Wieghardt, K.; Chirik, P. J. *J. Am. Chem. Soc.* **2011**, *133*, 17353−17369.

(3) (a) Takaoka, A.; Moret, M.-E.; Peters, J. C. *J. Am. Chem. Soc.* **2012**, *134*, 6695−6706. (b) Takaoka, A.; Gerber, L. C. H.; Peters, J. C. *Angew. Chem.* **2010**, *122*, 4182−4185; *Angew. Chem., Int. Ed.* **2010**, *49*, 4088−4091. (c) Fantauzzi, S.; Gallo, E.; Caselli, A.; Ragaini, F.; Casati, N.; Macchic, P.; Cenini, S. *Chem. Commun.* **2009**, 3952−3954.

(4) (a) Lutz, C. M.; Wilson, S. R.; Shapley, P. A. *Organometallics* **2005**, *24*, 3350−3353. (b) Muniz, K.; Nieger, M.; Mansikkamäki, H. *Angew. Chem.* **2003**, *115*, 6140−6143; *Angew. Chem., Int. Ed.* **2003**, *42*, 5958−5961.

(5) (a) Lyaskovskyy, V.; Suarez, A. I. O.; Lu, H.; Jiang, H.; Zhang, X. P.; Bruin, B. d. *J. Am. Chem. Soc.* **2011**, *133*, 12264−12273. (b) King, E. R.; Sazama, G. T.; Betley, T. A. *J. Am. Chem. Soc.* **2012**, *134*, 17858−17861. (c) Jones, C.; Schulten, C.; Rose, R. P.; Stasch, A.; Aldridge, S.; Woodul, W. D.; Murray, K. S.; Moubaraki, B.; Brynda, M.; Macchia, G. L.; Gagliardi, L. *Angew. Chem.* **2009**, *121*, 7542−7546; *Angew. Chem., Int. Ed.* **2009**, *48*, 7406−7410.

(6) (a) Kimura, T.; Koiso, N.; Ishiwata, K.; Kuwata, S.; Ikariya, T. *J. Am. Chem. Soc.* **2011**, *133*, 8880−8883. (b) Schau-Magnussen, M.; Malcho, P.; Herbst, K.; Brorsona, M.; Bendix, J. *Dalton Trans.* **2011**, *40*, 4212−4216. (c) Glueck, D. S.; Wu, J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 2041−2054.

(7) (a) Waterman, R.; Hillhouse, G. L. *J. Am. Chem. Soc.* **2008**, *130*, 12628−12629. (b) Iluc, V. M.; Miller, A. J. M.; Anderson, J. S.; Monreal, M. J.; Mehn, M. P.; Hillhouse, G. L. *J. Am. Chem. Soc.* **2011**, *133*, 13055−13063. (c) Laskowski, C. A.; Miller, A. J. M.; Hillhouse, G. L.; Cundari, T. R. *J. Am. Chem. Soc.* **2011**, *133*, 771−773.

(8) (a) Berry, J. F. *Comment. Inorg. Chem.* **2009**, *30*, 28−66. (b) Ray, K.; Heims, F.; Pfaff, F. F. *Eur. J. Inorg. Chem.* **2013**, 3784−3807.

(9) (a) Kwart, H.; Khan, A. A. *J. Am. Chem. Soc.* **1967**, *89*, 1950−1951. (b) Kwart, H.; Khan, A. A. *J. Am. Chem. Soc.* **1967**, *89*, 1951−1953.

(10) (a) Diaz-Requejo, M. M.; Perez, P. J. *Chem. Rev.* **2008**, *108*, 3379−3394. (b) Müller, P.; Fruit, C. *Chem. Rev.* **2003**, *103*, 2905−2919. (c) Li, Z.; He, C. *Eur. J. Org. Chem.* **2006**, 4313−4322. (d) Gephart, R. T.; Warren, T. H. *Organometallics* **2012**, *31*, 7728−7752.

(11) (a) Li, Z.; Quan, R. W.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1995**, *117*, 5889−5890. (b) Maestre, L.; Sameera, W. M. C.; Díaz-Requejo, M. M.; Maseras, F.; Pérez, P. J. *J. Am. Chem. Soc.* **2013**, *135*, 1338−1348.

(12) (a) Badiei, Y. M.; Krishnaswamy, A.; Melzer, M. M.; Warren, T. H. *J. Am. Chem. Soc.* **2006**, *128*, 15056−15057. (b) Badiei, Y. M.; Dinescu, A.; Dai, X.; Palomino, R. M.; Heinemann, F. W.; Cundari, T. R.; Warren, T. H. *Angew. Chem.* **2008**, *120*, 10109−10112; *Angew. Chem., Int. Ed.* **2008**, *47*, 9961−9964. (c) Aguila, M. J. B.; Badiei, Y. M.; Warren, T. H. *J. Am. Chem. Soc.* **2013**, *135*, 9399−9406.

(13) Kundu, S.; Miceli, E.; Farquhar, E.; Pfaff, F. F.; Kuhlmann, U.; Hildebrandt, P.; Braun, B.; Greco, C.; Ray, K. *J. Am. Chem. Soc.* **2012**, *134*, 14710−14713.

(14) (a) Dielmann, F.; Back, O.; Henry-Ellinger, M.; Jerabek, P.; Frenking, G.; Bertrand, G. *Science* **2012**, *337*, 1526−1528. (b) Schulz, A.; Villinger, A. *Angew. Chem.* **2013**, *125*, 3146−3148; *Angew. Chem., Int. Ed.* **2013**, *52*, 3068−3070. (c) Dielmann, F.; Moore, C. E.; Rheingold, A. L.; Bertrand, G. *J. Am. Chem. Soc.* **2013**, *135*, 14071−14073.

(15) Niecke, E. *Multiple Bonds And Low Coordination In Phosphorus Chemistry*; Georg Thieme: Stuttgart, 1990.

(16) Details about the quantum chemical calculations are given in the Supporting Information.