ORGANOMETALLICS

N-Phosphorylated Azolylidenes: Novel Ligands for Dinuclear Complexes of Coinage Metals

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S Supporting Information

ABSTRACT: Dinuclear silver(I) complexes with bridging Nphosphorylated azolylidene ligands have been synthesized. Subsequent transfer of the ligands to other group 11 metal centers (Cu, Au) has been accomplished, highlighting the usefulness of the silver complexes as an easy to handle, air- and moisture-stable source of these ligands. Preliminary results indicate that dinuclear copper(I) complexes with Nphosphorylated imidazolylidene ligands display notable catalytic efficiency in nitrene transfer reactions.

INTRODUCTION

N-Heterocyclic carbenes $(NHC)^{1,2}$ represent a recent but extremely valuable addition to the arsenal of supporting ligands for metal complexes available to the organometallic chemist.^{1,3} However, although a lot of different NHC ligand structures have been proposed, modular NHC-based ligand systems, the steric and electronic properties of which can be easily and extensively tuned by substitution of one of the moieties making out the ligand, are still underdeveloped.⁴ In this connection, a yet almost unexplored class of NHC-based ligands with these characteristics is represented by phosphorylated azolylidenes with a direct N–P bond (Scheme 1). In the past few years, several original synthetic approaches to such free carbenes have been developed by some of us as well as by others.⁵ Furthermore, very recently the first examples of dinuclear complexes with these carbenes as ligands have been reported by

Scheme 1. N-Phosphorylated Azolylidene Ligands Employed in This Work



1 R = Me, R = H, T = CH**2** $<math>R^{1}$ = Et; R^{2} = Ph; Y = N **3** R^{1} = i-Pr; R^{2} = Ph; Y = N



us⁶ (with Ag) as well as by the group of Hofmann (with Cu).⁷ In light of our continuing research interest on the synthesis and application of NHC complexes of coinage metals,⁸ we wish now to report on the development of a general strategy for the mild and productive synthesis of complexes of such ligands with group 11 metal centers, as well as on preliminary data concerning the properties of such complexes.

RESULTS AND DISCUSSION

Free N-phosphorylated azolylidenes can be distilled without decomposition under high vacuum, but they are quite unstable and tend to decompose with time even when kept under strict exclusion of air and moisture. Therefore, in order to have more practical, stable, and easy to handle reagents for the preparation of metal complexes of such carbene ligands, we considered the use of the corresponding Ag(I) complexes. Such complexes should serve as stable transmetalating agents, easily transferring the NHC ligand to other metal centers in analogy to Ag(I) complexes with more traditional NHC ligands.⁹

The commonly employed route for the preparation of Ag(I)-NHC complexes, upon direct reaction of the azolium NHC precursor with $Ag_2O_7^9$ can be readily applied to our novel phosphorylated ligands, and we have very recently reported on the success of this synthetic strategy for the preparation of stable Ag complexes with ligands 2 and 3 (Scheme 1).⁶ Similarly, treatment of a solution of the imidazolium precursor of 1 (Scheme 1) in dichloromethane with 0.5 equivalent of Ag₂O at room temperature yielded cleanly the dinuclear



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complex 1-Ag as a crystalline, colorless, air-stable solid (Scheme 2). The same complex was formed even when an excess of Ag_2O was used.

We were able to determine the crystal structure of complex **1-Ag** (Figure 1). The imidazolylidene rings and the silver atoms



Figure 1. ORTEP view of complex 1-Ag (left) and view along the Ag-Ag direction (right). Thermal ellipsoids are at the 50% probability level. Hydrogen atoms and triflate anions are omitted for clarity. Selected bond lengths [Å] and angles [deg]: C10-N1 1.372(3), N2-C10 1.343(4), P1-Ag1 2.3852(6), C10-Ag1 2.111(2), P1-N1 1.739(2), Ag1··Ag1' 2.8221(3), N2-C10-N1 104.5(2), C10-Ag1-P1 166.99(7), Ag1-Ag1'-C10 88.13(6), Ag1-Ag1'-P1 87.92(2), P1-N1-C10 121.8(2).

connected to them are found almost in a plane (the sum of N2–C10–N1, N1–C10–Ag1, and N2–C10–Ag1 angles is 359.7°). The phosphorus atoms connected to Ag protrude instead above and below this plane as the angle C10–Ag1–P1 is 166.99(7)° (torsion angles C10–Ag1–Ag1'–P1 12.40(7)°; P1–Ag1–C10'–N1'–87.3(4)°, N1'–P1'–Ag1'–C10 85.2(3)°). The Ag–C and Ag–P bond lengths are in the

Scheme 3. Synthesis of Complexes 1-Au and 1-Cu

characteristic range for other silver(I) carbene and phosphine complexes previously reported.^{10,11} Finally, the very short recorded intermetallic distance of 2.8221(3) Å in **1-Ag** (compare the conventionally tabulated covalent radius of 1.45 \pm 0.05 Å for silver) makes it likely that closed shell d¹⁰-d¹⁰ interactions¹² are present in the complex.

We then started to investigate whether the Ag(I) complexes could indeed act as transmetalating agents. Indeed, the phosphorylated imidazolylidene ligand 1 could be cleanly transferred under mild conditions from 1-Ag to either Cu(I) or Au(I) centers (Scheme 3).

The identity of the Cu complex **1-Cu** was confirmed by comparison with its characterization data reported by Hofmann, who prepared the same complex starting from the free carbene ligand.⁷ Instead, the identity of the Au complex **1-Au** was confirmed by determination of its crystal structure (Figure 2). The structure of complex **1-Au** is as expected



Figure 2. ORTEP view of complex 1-Au (left) and view along the Au–Au direction (right). Thermal ellipsoids are at the 50% probability level. Hydrogen atoms and triflate anions are omitted for clarity. Selected bond lengths [Å] and angles [deg]: C1–N1 1.347(8), C1–N2 1.322(9), P1–Au1 2.299(2), C1–Au1 2.061(7), P1–N1 1.756(5), Au1-Au1' 2.8099(4); N1–C1–N2 106.8(5), C1–Au1–P1 177.5(2), Au1–Au1'–C1 89.4(2), Au1–Au1'–P1 89.16(4), P1–N1–C1 125.5(4).

similar to that of complex 1-Ag. Relevant bond lengths are slightly shorter than in the Ag case; for example, the metal–C and metal–P bond lengths are respectively 2.111(2) and 2.3852(6) Å in 1-Ag versus 2.061(7) and 2.299(2) Å in 1-Au. Nevertheless, such bond lengths are in agreement with those of other gold(I) carbene and phosphine complexes previously reported.¹³ The Au–Au distance of 2.8099(4) Å is very short, as it lies below the Au–Au distance in elemental gold (2.88 Å), making it likely that closed-shell $d^{10}-d^{10}$ interactions are



Scheme 4. Synthesis of Complexes 2-Au and 3-Au



present also in this case.¹² The main difference between the structures of the Ag and the Au complexes is the higher degree of planarity of the latter (Figure 2, right side), in which the coordination geometry around the two Au atoms is almost perfectly linear (C1–Au1–P1 angle 177.5(2)°) and with the coordination axes parallel to each other. Consequently, gold atoms, phosphorus atoms, and imidazolylidene rings all lie in the same plane.

The NMR spectrum of the **1-Au** complex exhibits the expected peaks, and it turns out to be very similar to that of **1-Ag**. The carbone carbon resonance in the ¹³C NMR spectrum of **1-Au** is found at 192.7 ppm, well below the value in the free ligand (223.6 ppm) and similar to the value for the Ag complex (195.1 ppm).

Transmetalation to Au was successful also with complexes 2-Ag and 3-Ag (Scheme 4) and yielded the corresponding Au complexes 2-Au and 3-Au, which once again displayed spectroscopic features analogous to the corresponding Ag complexes (see the Supporting Information) On the other hand, transmetalation to Cu apparently yielded products that were too unstable to be conveniently isolated in pure form and characterized.

The molecular structure of **2-Au** was determined by means of single-crystal X-ray diffraction analysis (Figure 3). As expected, the gold atoms are linearly coordinated (C1–Au1– P1 angle 177.6(3)°), as in the case of **1-Au**, and the Au–C and Au–P bond lengths (Au1–C1 2.03(1) Å, Au1–P1 2.288(3) Å) are also very close to those exhibited by **1-Au**. The Au1–Au1' distance (2.8554(7) Å) is slightly longer than in **1-Au**; the same trend for the metal–metal distance is observed in the corresponding silver complexes (**2-Ag**⁶ vs **1-Ag**). The structure of complex **2-Au** is also very similar to that of the parent silver complex **2-Ag**,⁶ the main difference being, as in the case of ligand **1**, the C_{carbene}–metal–P angle (177.6(3)° for Au and 166.99(7)° for Ag).

Finally, we have preliminarly investigated the properties of the newly synthesized complexes **1-Cu** and **1-Au**. The photophysical properties of the Au complex were evaluated in the solid state under conditions previously employed by some of us for investigating related dinuclear dicarbene complexes of gold(I).^{8b} Unfortunately, it was determined that despite the very short Au–Au distance the complex displayed negligible emission under these conditions ($\Phi < 0.01$). On the other hand, the catalytic efficiency of **1-Cu** in nitrene transfer reactions was also preliminarly evaluated (Scheme 5). Once again reaction protocols previously developed by some of us for related dinuclear dicarbene copper(I) catalysts^{8a} were employed. Excellent results were obtained in the aziridination of styrene with *in situ* formed *N*-tosyliminophenyliodinane, in



Figure 3. ORTEP view of complex **2-Au** (left) and view along the Au–Au direction (right). Thermal ellipsoids are at the 50% probability level. Hydrogen atoms and triflate anions are omitted for clarity. Selected bond lengths [Å] and angles [deg]: C1–N1 1.38(1), C1–N3 1.35(2), P1–Au1 2.288(3), C1–Au1 2.03(1), P1–N1 1.75(1), Au1–Au1' 2.8554(7); N1–C1–N3 102.6(9), C1–Au1–P1 177.6(3), Au1–Au1'–C1 88.5(3), Au1–Au1'–P1 89.45(8), P1–N1–C1 125.9(8).

Scheme 5. Nitrene Transfer Reactions Catalyzed by Complex 1-Cu



which the new complex displayed higher catalytic efficiency (94% yield) compared to more conventional dinuclear dicarbene copper(I) complexes.^{8a} Moderate yields were recorded also in the more challenging C–H insertion of the nitrene into the α -C–H bond of dioxane (41% yield).

CONCLUSIONS

In conclusion, we have shown with the present work that Nphosphorylated azolylidenes can act as bridging ligands in dinuclear metal complexes of group 11 metals. In particular, we have demonstrated that disilver(I) complexes of such ligands behave as convenient, air-stable reagents that transfer the carbene ligand to other metal centers. Further studies on the properties of such complexes as well as on the preparation and characterization of complexes with other metals are currently under way.

ASSOCIATED CONTENT

S Supporting Information

Full experimental procedures and X-ray crystallographic data in CIF format for **1-Ag**, **1-Au**, and **2-Au**. 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

 General references on NHC ligands: (a) Diez-Gonzalez, S., Ed. N-Heterocyclic Carbenes: From Laboratory Curiosities to Efficient Synthetic Tools; RSC Catalysis Series; RSC: Cambridge, 2010.
 (b) Cazin, C. S. J., Ed. N-Heterocyclic Carbenes in Transition Metal Catalysis and Organocatalysis. Catalysis by Metal Complexes, Vol. 32; Springer: Heidelberg, 2010. (c) Kühl, O. Functionalised N-Heterocyclic Carbene Complexes; John Wiley and Sons: New York, 2010. (d) Nolan, S. P., Ed. N-Heterocyclic Carbenes in Synthesis; Wiley-VCH: Weinheim, 2006.

(2) Selected reviews on NHCs: (a) Melaimi, M.; Soleilhavoup, M.; Bertrand, G. Angew. Chem., Int. Ed. 2010, 49, 8810–8849. (b) Dröge, T.; Glorius, F. Angew. Chem., Int. Ed. 2010, 49, 6940–6952. (c) Hahn, F. E.; Jahnke, M. C. Angew. Chem., Int. Ed. 2008, 47, 3122–3172.

(3) Selected reviews on NHC metal complexes: (a) Corberan, R.; Mas-Marza, E.; Peris, E. Eur. J. Org. Chem. 2009, 1700-1716.
(b) Glorius, F., Ed. N-Heterocyclic Carbenes in Transition Metal Catalysis. Topics in Organometallic Chemistry, Vol. 21; Springer: Heidelberg, 2007. (c) Herrmann, W. A. Angew. Chem., Int. Ed. 2002, 41, 1290.

(4) For a comprehensive account on efforts to overcome this limitation, see: Benhamou, L.; Chardon, E.; Lavigne, G.; Bellemin-Laponnaz, S.; Cesar, V. *Chem. Rev.* **2011**, *111*, 2705–2733.

(5) (a) Marchenko, A. P.; Koidan, H. N.; Huryeva, A. N.; Zarudnitskii, E. V.; Yurchenko, A. A.; Kostyuk, A. N. *J. Org. Chem.* **2010**, 75, 7141–7145. (b) Marchenko, A. P.; Koidan, H. N.; Pervak, I. I.; Huryeva, A. N.; Zarudnitskii, E. V.; Tolmachev, A. A.; Kostyuk, A. N. *Tetrahedron Lett.* **2012**, 53, 494–496. (c) Marchenko, A. P.; Koidan, H. N.; Hurieva, A. N.; Pervak, I. I.; Shishkina, S. V.; Shishkin, O. V.; Kostyuk, A. N. *Eur. J. Org. Chem.* **2012**, 4018–4033. (d) Herrlich (neé Blumbach), U. Dissertation, Universität Heidelberg, 2007.

(6) Marchenko, A. P.; Koidan, H. N.; Zarudnitskii, E. V.; Hurieva, A. N.; Kirilchuk, A. A.; Yurchenko, A. A.; Biffis, A.; Kostyuk, A. N. *Organometallics* **2012**, *31*, 8257–8264.

(7) Kühnel, E.; Shishkov, I. V.; Rominger, F.; Oeser, T.; Hofmann, P. Organometallics **2012**, *31*, 8000–8011.

(8) (a) Tubaro, C.; Biffis, A.; Gava, R.; Scattolin, E.; Volpe, A.; Basato, M.; Diaz-Requejo, M. M.; Perez, P. J. *Eur. J. Org. Chem.* **2012**, 1367–1372. (b) Baron, M.; Tubaro, C.; Basato, M.; Biffis, A.; Graiff, C.; Poater, A.; Cavallo, L.; Armaroli, N.; Accorsi, G. *Inorg. Chem.* **2012**, *51*, 1778–1784. (c) Baron, M.; Tubaro, C.; Basato, M.; Biffis, A.; Graiff, C. J. Organomet. Chem. 2012, 714, 41–46. (d) Baron, M.; Tubaro, C.; Basato, M.; Biffis, A.; Natile, M. M.; Graiff, C. Organometallics 2011, 30, 4607–4615. (e) Biffis, A.; Tubaro, C.; Scattolin, E.; Basato, M.; Santini, C.; Papini, G.; Alvarez, E.; Conejero, S. Dalton Trans. 2009, 7223–7229. (f) Tubaro, C.; Biffis, A.; Scattolin, E.; Basato, M. Tetrahedron 2008, 64, 4187–4195. (g) Biffis, A.; Gioia Lobbia, G.; Papini, G.; Pellei, M.; Santini, C.; Scattolin, E.; Tubaro, C. J. Organomet. Chem. 2008, 693, 3760–3766. (h) Baron, M.; Tubaro, C.; Basato, M.; Natile, M. M.; Graiff, C. J. Organomet. Chem. 2013, 723, 108–114.

(9) (a) Wang, H. M. J.; Lin, I. J. B. Organometallics **1998**, 17, 972–975. (b) Lin, I. J. B.; Vasam, C. S. Coord. Chem. Rev. **2007**, 251, 642–670.

(10) Ma, Y.; Wei, S.; Lan, J.; Wang, J.; Xie, R.; You, J. J. Org. Chem. 2008, 73, 8256-8264.

(11) Radloff, C.; Weigand, J. J.; Hahn, F. E. Dalton Trans. 2009, 9392-9394.

(12) Pyykkö, P. Chem. Rev. 1997, 97, 597-636.

(13) (a) Baker, M. V.; Barnard, P. J.; Berners-Price, S. J.; Brayshaw, S. K.; Hickey, J. L.; Skelton, B. W.; White, A. H. J. Organomet. Chem. **2005**, 690, 5625–5635. (b) Gaillard, S.; Nun, P.; Slawin, A. M. Z.; Nolan, S. P. Organometallics **2010**, 29, 5402–5408.