

Preparation and reactivity of terminal gold(I) amides and phosphidest

Cite this: *Chem. Sci.*, 2013, **4**, 1023

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Received 13th September 2012

Accepted 28th November 2012

DOI: 10.1039/c2sc21519e

www.rsc.org/chemicalscience

Nucleophilic terminal gold(I) amides have been prepared and their reactivity toward a variety of electrophiles has been explored. For the first time these frequently proposed intermediates were isolated and shown to be unreactive in the amination of π -bonds. The first crystallographically determined terminal group 11 metal phosphide was also synthesized. Preliminary DFT studies have been conducted to understand the structure and reactivity of these complexes.

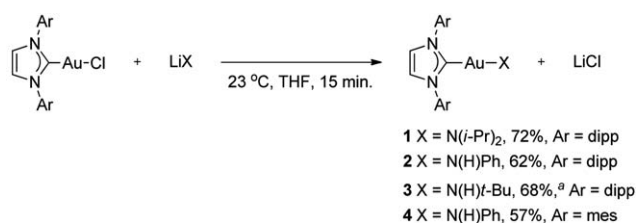
Introduction

Terminal transition metal amides represent an important class of compounds that has been explored throughout the d-block elements.¹ Late-metal amido complexes are of particular interest because they are proposed as key intermediates in important transformations such as Buchwald–Hartwig coupling,² hydroamination of olefins³ and amination of C–H bonds.⁴ Additionally, they are used as model systems for studying biological active sites⁵ and are precursors to imido complexes.⁶ However, no terminal gold(I) amides have been structurally characterized⁷ with the exception of those possessing amido ligands that act as loosely coordinating anions.^{8,9} Nonetheless, these species have been invoked as reactive intermediates in the addition of amines to π -bonds,^{10,11} a field that has undergone tremendous growth in the past decade.¹² From the perspective of coordination chemistry, gold amides are peculiar among transition metal amido complexes as they should possess the most covalent transition metal–nitrogen bond and yet the greatest hard-soft mismatch,¹³ presenting a unique opportunity to understand factors that dictate their reactivity.¹⁴ The paucity of data surrounding gold amides motivated us to pursue their synthesis and chemistry. We now report examples of terminal gold(I) amides, their reactivity, and the viability of their participation in catalytic reactions. Additionally, we were able to synthesize and characterize crystallographically the first terminal gold phosphide, further expanding our understanding of transition metal pnictogenides.

Results and discussion

Identifying a suitable neutral ancillary ligand and means of installing the amido functionality were the first challenges in this investigation. The N-heterocyclic carbene IPr (1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) was chosen as a supporting ligand due to its strong binding and common use in gold catalysis.^{15,16} A metathetical approach was needed to form the Au–N bond as an oxidative route was precluded by the desire to make a gold(I) complex. Three gold amides were thus synthesized from IPrAuCl and the corresponding lithium amide (Scheme 1). The diisopropyl amide **1** (Fig. 1) and anilide **2** were characterized by X-ray diffraction, revealing that both are monomeric in the solid state. Compound **3** was only characterized spectroscopically due to decomposition upon purification. The gold(I) anilide **4** was also accessible by this route using the sterically less demanding IMes (1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) ligand.

The diisopropyl amide **1** was of particular interest. Some transition metal amides are known to undergo β -hydride elimination; however, complex **1** undergoes no such decomposition pathway even after prolonged heating.¹⁷ That two aliphatic groups are present on the amido nitrogen is noteworthy in that most other group 11 metal amides to our knowledge require aryl substitution for stability.¹⁸ The



^a Yield was determined by ¹H NMR with hexamethylbenzene as an internal standard.

Scheme 1 Synthesis of gold(I) amides.

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† Electronic supplementary information (ESI) available: Synthetic, spectroscopic, crystallographic, and computational details. CCDC 906061 and 901602–901607. For ESI and crystallographic data in CIF or other electronic format See DOI: 10.1039/c2sc21519e

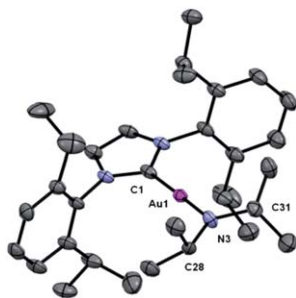


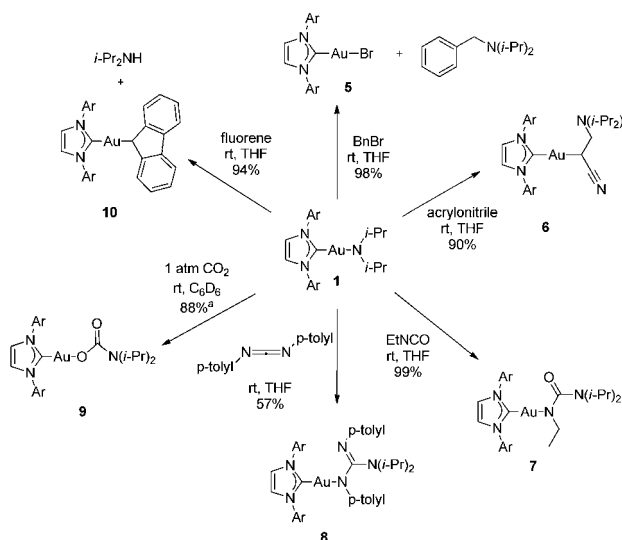
Fig. 1 Solid state structure of amido complex **1** (50% probability ellipsoids). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Au(1)–N(3), 1.967(4); Au(1)–C(1), 1.995(4); Au(1)–N(3)–C(28), 122.0(3); Au(1)–N(3)–C(31), 124.8(3); C(28)–N(3)–C(31), 124.8(3).

conjugate acid of **1** was also synthesized and characterized crystallographically to examine the difference in Au–N bond lengths between the two compounds (see ESI[†]). Complex **1** was found to have a shorter Au–N bond than that of the corresponding amine complex, 2.0921(2) Å compared to 1.967(4) Å, consistent with observations made on ruthenium amides.¹⁹ Additionally, a calculated gas-phase structure of **1** matched that found in the solid state (Fig. 2), arguing against the possibility that crystal packing effects affect the complex's structure (see the ESI[†]). These data when taken together suggest that the planarity of late transition metal amides with aryl substitution may not be attributed to delocalization alone (*vide infra*).²⁰

Reactivity studies began with a survey of the interactions between various electrophiles and **1** with the intention of gauging the nucleophilicity and basicity of this complex (Scheme 2). The reaction of **1** with benzyl bromide led to immediate alkylation of the amide ligand, resulting in full conversion to *N,N*-diisopropylbenzylamine and isolation of IPrAuBr (**5**) in 98% yield. Compound **1** was competent in the amination of acrylonitrile, a typical substrate for

hydroamination by transition metals,^{3,21} to form the net Au–N insertion product **6**. The regiochemistry of this reaction was verified unambiguously through single crystal X-ray diffraction. The stability of this complex may provide insight as to why anti-Markovnikov hydroamination of acrylonitrile is less effective using gold catalysts than copper ones.²² Complex **1** also reacts with the heteroallenes ethyl isocyanate, di(*p*-tolyl) carbodiimide, and carbon dioxide to form complexes **7**, **8**, and **9**, respectively. Product **9** could only be identified spectroscopically due to decomposition upon concentration.²³ A labeling experiment using ¹³C₂O₂ allowed for identification of the carbonyl carbon resonance at δ 161 ppm in the ¹³C NMR spectrum. The solution IR spectrum exhibited a strong absorbance at ν = 1578 cm⁻¹ and the assignment of this band was confirmed by its shift to 1527 cm⁻¹ when the ¹³C-enriched analogue was analyzed. Both of these results are in agreement with the spectral properties of other late transition metal carbamates.²³ This result is interesting in that gold hydrocarbyl complexes have been shown to be unreactive toward CO₂, suggesting that formation of **9** takes place *via* nucleophilic attack rather than insertion.²⁴

After gaining an understanding of the reactivity of these amides toward traditional electrophiles, we investigated the likelihood that these species and similar complexes intervene as intermediates in gold-catalyzed reactions. The following experiments suggest that gold amides are not viable intermediates in the gold-catalyzed addition of amines to π -bonds. Published reports of the intermolecular reaction of unsaturated substrates with gold amides are not available to determine if such complexes are competent in amination. Our compounds offer the opportunity to probe the mechanism of amination without exogenous amine present. Combining **1** with both alkynes (diphenylacetylene and 3-hexyne) (eqn (1)) and alkenes (cyclopentene and styrene) led to no reaction even at 75 °C. Additionally, the kinetic basicity of **1** is sufficiently high to deprotonate the weak acid fluorene (p*K*_a 23 in THF)²⁵ forming the alkyl gold complex **10**.²⁶ This demonstrates that a strong base must be present in order to generate a gold amide from the corresponding amine complex. These experiments suggest that gold amides are unlikely intermediates in the insertion of unsaturated C–C bonds into Au–N bonds, and support the



Scheme 2 Reactivity of complex **1** with various electrophiles.

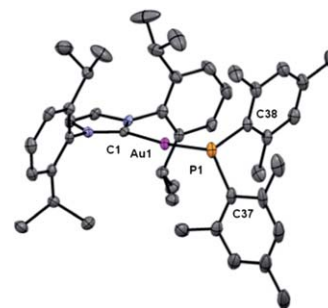
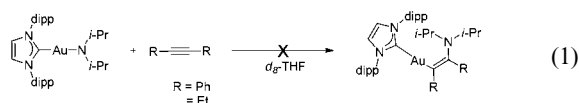


Fig. 2 Solid state structure of phosphido complex **4** (50% probability ellipsoids). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Au(1)–P(1), 2.3195(9); Au(1)–C(1), 2.042(3); Au(1)–P(1)–C(28), 101.2(1); Au(1)–P(1)–C(37), 118.0(1); C(28)–P(1)–C(37), 103.2(2).

hypothesis that the hydroamination of π -bonds takes place *via* an outersphere mechanism in gold catalysis.¹¹



Our findings concerning gold amides prompted us to explore the possibility of preparing a terminal gold phosphide. There are numerous examples of bridging gold phosphides in the literature but no terminal group 11 metal phosphides have been isolated to date.²⁷ Salt metathesis proved to be insufficient for the synthesis of the desired compounds. Instead, abstraction of the chloride from IPrAuCl in the presence of a phosphine resulted in the formation of corresponding phosphine salts **11** and **12** (Scheme 3). The former could be deprotonated to form the dimesityl phosphide **13**, which was characterized in the solid state. Complex **14** could only be characterized in solution due to its instability.²⁸ However, this compound proved to be catalytically active in the alkylation of *tert*-butyl phosphine with benzyl chloride and the intermediate phosphine complex **15**, the catalytic resting state, was fully characterized (Scheme 4).²⁹ This marks the first example of C–P bond formation by a homogeneous gold catalyst.

A density functional theory study was undertaken in order to gain insight into the bonding of these gold pnictogenides, in particular, the interactions leading to the gold–heteroatom bond and possible causes for the planarity at the amido nitrogen.³⁰ Complexes **1**, **3**, **13**, and **14** were analyzed and compared against their well defined and studied *t*-butoxide (**16**) and triflimide (**17**) analogues. Our amides were predicted to have significantly polarized Au–N bonds based on natural population analysis, with electrostatic charge differences approaching that of the gold–triflimide nitrogen bond of **17** (see Table 1).³¹ The phosphides, however, were found to have little difference in charge between the phosphorus and gold centers, indicating a highly covalent bond. In all four cases the HOMO was identified as being predominantly the phosphorus or

Table 1 Charge distribution and population analysis of Au–heteroatom complexes^a

X ^b		<i>q</i> (Au) ^c	<i>q</i> (X) ^c	Δq (Au–X) ^d	% Contribution ^e
N(<i>i</i> -Pr) ₂	1	0.25	–0.81	1.06	63
NH(Ph)	2	0.34	–0.91	1.25	39
P(Mes) ₂	13	0.11	–0.22	0.11	52
P(<i>t</i> -Bu) ₂	14	0.04	–0.23	0.19	69
O <i>t</i> -Bu	16	0.35	–0.88	1.23	71
NTf ₂	17	0.20	–1.25	1.51	0

^a Natural charge based on NBO analysis and occupancy on population analysis BPV86/LANL2DZ/6-311++G(d,p). ^b X = pnictogen. ^c *q* = charge. ^d Δq = difference in charge between Au and heteroatom. ^e Percent contribution of X to the HOMO.

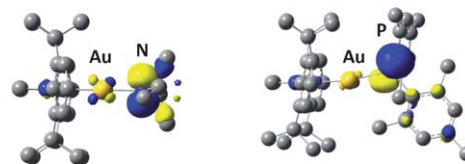
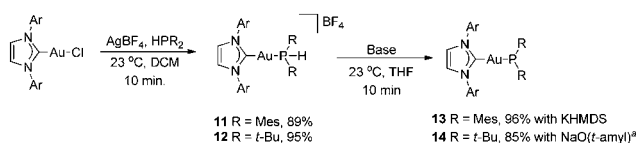


Fig. 3 Calculated HOMO (BPV86/LANL2DZ/6-311++G(d,p), 0.06 isocontour) of complexes **1** and **13**.

nitrogen lone pair, with the respective lone pairs residing in *sp* and *p* orbitals (Fig. 3). These results contrast with the HOMO of **17** that consisted of <13% contribution from the amido nitrogen. Additionally, natural localized molecular orbital (NLMO) calculations for **1** and **2** indicate that in both cases the Au–N bond consists of 82% contribution from an *sp*²-hybridized nitrogen. All second order interactions between gold and nitrogen were less than 3% of the primary interactions, signifying that multiple bond character is not present. These data suggest that the planarity at nitrogen can be attributed to the electrostatic benefit of concentrating the amide nitrogen's electron density at an orbital of high *s*-character.²⁰ Phosphides **13** and **14** exhibit much more contribution from gold in the Au–P bond, 30% and 33%, respectively, corroborating the small difference in electronegativity between the two centers.

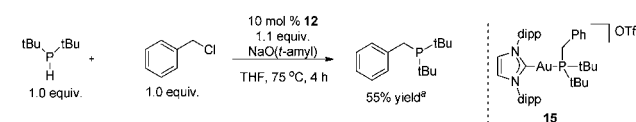
Conclusions

In summary, a number of terminal gold amides have been synthesized and their reactivity explored. High nucleophilicity was observed with traditional electrophiles, including carbon dioxide. Despite this nucleophilicity, these amides were unreactive toward unactivated π -bonds, lending further support for the outer sphere mechanism for addition of amines to unsaturated bonds. Additionally, we isolated and identified crystallographically the first terminal group 11 metal phosphide



^aYield determined by ¹H NMR with hexamethylbenzene as an internal standard.

Scheme 3 Synthesis of gold(i) phosphides.



^aYield determined by ¹H NMR with hexamethylbenzene as an internal standard.

Scheme 4 Catalytic benzylation of di-*tert*-butyl phosphine.

and demonstrated catalytic reactivity with another gold phosphide. Computational work was conducted as well to gain an understanding of the bonding and geometries of these unique complexes.

Acknowledgements

R. G. B. and F. D. T. thank the U.S. Air Force (ID # 11RSA093) for a research grant. M.W.J acknowledges the NSF (no. DGE1106400) and UC Berkeley for pre-doctoral fellowships. Drs Neal Mankad, Jürgen Koller, and Antonio DiPasquale are thanked for helpful discussion and assistance with X-ray crystallographic studies. Dr Erika Cobar, Mark Lipke, Dr Xinzhen Yang, and Dr Kathleen Durkin provided helpful discussion concerning the computational portion of this manuscript.

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