Selective Reduction of CO₂ to a Formate Equivalent with Heterobimetallic Gold---Copper Hydride Complexes

Alexandra Hicken, Andrew J. P. White, and Mark R. Crimmin*

A series of heterobimetallic complexes containing 3-center,2-electron Au--H--Cu bonds have been prepared from addition of a parent gold hydride to a bent d⁰ copper(I) fragment. These highly unusual heterobimetallic complexes represent a missing link in the widely investigated series of neutral and cationic coinage metal hydride complexes containing Cu--H--Cu and M--H--M' moieties (M = Cu, Ag). The well-defined heterobimetallic hydride complexes act as precatalysts for the conversion of CO₂ to HCO₂Bpin using HBpin as a reductant. The selectivity of the heterobimetallic complexes for the catalytic production of a formate equivalent surpasses that of the parent monomeric group 11 complexes.

In recent years there has been increasing interest in the synthesis and catalytic applications of coinage metal hydrides (M = Cu, Ag, Au).¹⁻⁸ The majority of catalytic studies have focused on the in situ generation of terminal metal hydride complexes stabilized by N-heterocyclic carbene ligands.⁹,¹⁰ There is, however, a growing appreciation that species possessing 3-center,2-electron M--H--M bonds may play a role in catalysis. For example, Lalic and co-workers have shown that cationic dinuclear copper(I) hydride complexes are key catalytic intermediates in the hydroalkylation of alkynes.²,¹¹ The original structural characterization of these dicopper hydride complexes, along with related silver analogues, has been pioneered by Sadighi and co-workers (Figure 1).¹²,¹³

![Figure 1](image)

Figure 1. Mononuclear and Dinuclear coinage metal hydride complexes.

Despite detailed studies on the preparation and reactivity of symmetric dinuclear coinage metal hydrides, little is known about heterobimetallic compounds containing asymmetric M--H--M' interactions. Combinations of copper and gold N-heterocyclic carbene complexes catalyze the addition of phenols to internal alkynes with activities in excess of the individual components of the mixture.¹⁴

One approach to prepare complexes containing M--H--M' linkages is through addition of monomeric metal hydride complex to a suitable electrophilic metal fragment.¹⁵⁻¹⁸ For example, borane-capped copper(I) hydrides (Figure 1) have been prepared by addition of boranes to a terminal copper hydride.¹⁹,²⁰ Herein, we report the first examples of heterobimetallic complexes of the coinage metals containing 3-center, 2-electron Cu--H--Au interactions (1-3•Au). These species are prepared by the simple addition of a monomeric gold(I) hydride to a bent d¹⁰ (CuL₃) fragment and are selective catalysts for reduction of CO₂ with HBpin (HBpin = pinacolborane) to a formate equivalent..

Reaction of one equiv. of the fluorinated copper(I) β-diketiminate complexes 1tol or 2tol with [Au(H)(IPr)] in toluene at 25 °C afforded complexes 1•Au and 2•Au in 89-92 % yield. Similarly, 3•Au was prepared from reaction of the phosphine stabilized copper(I) complex 3•PPH₃ with the same gold(I) hydride complex. The heterobimetallic complexes 1-3•Au were fully characterized by NMR spectroscopy, X-ray crystallography, IR spectroscopy and CHN analysis (Scheme 1).

![Scheme 1](image)

Scheme 1. Synthesis of Au--H--Cu heterobimetallics 1-3•Au.

Single crystals of 1-3•Au could be grown from 1:3 mixtures of CuD₃/n-heptane at −35 °C. 1-2•Au afforded data of a quality that allowed the position of the hydrides to be determined from a difference electron density map (Figure 2). A notable difference in the structures of 1-3•Au lies within the Cu--Au separation. The distance between the two metal centers varies significantly across the series taking values of 2.5910(6), 2.6376(5), and 2.7525(7) Å for 2•Au < 1•Au < 3•Au respectively. The Au--C distances observed in 1•Au and 2•Au are within experimental error of one another (2.026(3) – 2.025(4) Å) and are marginally shorter than that reported for [Au(H)(IPr)] (2.045(3) Å). The data can be explained by a diminished trans-influence of the hydride ligand in 1-2•Au compared to the monomeric complex due to its involvement in a 3-centre,2-electron bond. In 3•Au, significant lengthening of the Cu--P bond is observed with respect to 3•PPH₃ (see supporting information for structural details) due to the increased coordination number at copper (3•Au, 2.2401(11) Å; 3•PPH₃, 2.1639(10) Å).

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Supporting information for this article is given via a link at the end of the document.
In order to gain a deeper understanding into the nature of the Au--H--Cu bonding, DFT calculations were performed with the ωB97x functional and a hybrid basis set (6-311G∗/SDDAl). NBO analysis confirms a common electronic structure to the three-centered core for complexes 1-3•Au. Wiberg bond indices elucidate the strongest covalent interaction occurs between the gold and hydride atoms (Au--H = 0.48 – 0.51), with weaker interactions between the remaining atoms in the core (Au--Cu, 0.08 – 0.11; Cu--H, 0.14 – 0.22). In all cases, second-order perturbation analysis reveals that donation of the σ–(Au–H) → Cu 4s orbital is far more significant than back-donation from the Cu(3d) → σ*(Au–H) (1•Au, 82 & 8 kcal mol⁻¹; 2•Au, 84 & 8 kcal mol⁻¹; 3•Au, 54 & 3 kcal mol⁻¹). QTAIM calculations describe the same bonding picture with bond critical paths present between both the Au and H and Cu and H atoms but not the metals themselves (see supporting information, Figure S17). In combination, the solid state and computational data show that the 3-centre,2-electron interaction is dominated by metal–hydride bonding and not metal–metal bonding. The conclusions are consistent with the analysis of cationic dinuclear coinage metal hydride complexes but with the key difference that the Cu–H–Au moiety is absent an asymmetric distribution of electron density.⁷⁻¹⁵,₂⁵⁻²⁶

The hydroboration of CO₂ (1 atm) with HBpin can be catalyzed by 10 mol% 1-2•Au in C₆D₆ to produce predominantly the formoxyborane, HCO₂Bpin.⁷⁻²⁸ The absolute activity and selectivity of the heterobimetallic catalysts are greatly inferior to a number of transition metal systems.⁷⁻²⁸,²⁹⁻³⁰ For example, palladium complexes supported by silyl-pincer ligands have recently reported for the selective hydroboration of CO₂ with TON > 60,000, while copper-NHC complexes show similar selectivity but TON < 10. Importantly, in the current case the monometallic complexes 1-2-tol and [Au(H)(IPr)] show negligible activity for CO₂ reduction and neither complex produces significant amounts HCO₂Bpin in the absence of its coinage metal counterpart.³₀⁻³¹ On comparison of the data in Figure 3, it seems clear that both metals are required for the selective conversion of CO₂ and HBpin to HCO₂Bpin.³²⁻³⁵

Additional reactions were run to explore the generality of the heterobimetallic effect. The frontier molecular orbitals of 1-2³² are isolobal with bent (ML₂) d⁵⁰ fragments (M = Ni, Pd). Both [[Ni(PCy₃)₂(μ-N₂)] and [Pd(PCy₃)₂] were investigated in catalysis, with and without added [Au(H)(IPr)]²¹,³³³ Comparing the product distribution from the group 10 pre-catalysts revealed that the heterobimetallic effect was also observed for the Pd/Au ad-mixtures (Figure 3). Ni/Au ad-mixtures, while catalytically competent, resulted in CO₂ reduction with a similar selectivity to the parent nickel complex (Supporting Information, Table S6).

Repeating catalytic runs with ¹³C₀₂ provided evidence for the generation of ¹²CO expected from the production of PinBOBpin.[]⁻⁴⁶ [Ni(PCy₃)₂(CO)] was observed by ¹³C(¹H) NMR spectroscopy following completion of the catalytic reaction (δ = 203.1 ppm, ¹µc = 3.3 Hz).¹⁴⁻¹⁵ Formation of H₂ was also observed by ¹H NMR spectroscopy (δ = 4.77 ppm).


**Figure 3.** (a) Selective catalytic reduction of CO₂ with 1-2•Au and Pd / Au and Ni / Au ad-mixtures, values based on an average taken from two repeat catalytic runs. (b) Isoelectronic relationship of transition metal fragments.
Interrogation of the solution dynamics of 1-2•Au provides insight relevant to the plausible mechanisms of CO₂ reduction. On dissolution of the heterobimetallic complexes in C₆D₆, an equilibrium is established between the heterobimetallic complex and the parent copper and gold complexes (Scheme 1). In toluene-d₈ at 298 K, the components are in fast exchange and a single set of resonances are observed in the ^{19}F(¹H) and ^{1}H NMR spectra due to a time averaged contribution of both sides of the equilium. VT NMR of 1-2•Au resulted in observation of both sides of the equilibrium at low temperature (1•Au = 213 K, 2•Au = 253 K) and with 2•Au allowed van’t Hoff analysis to give the thermodynamic parameters: ΔH° = –0.1 kcal mol⁻¹, ΔS° = –9.3 cal K⁻¹ mol⁻¹. ΔG°₂₉₈ = +2.7 kcal mol⁻¹. These values are consistent with weak and reversible binding previously reported for α-complexes of copper(I).[21,44,45] The reversible dissociation of 2•Au was confirmed by reaction with PCy₃, resulting in trapping of the copper(I) fragment as 2•PCy₃ (see supporting information, Figure S4).

Dissociation of 1-2•Au creates a pair of nucleophilic and electrophilic coinage metal complexes reminiscent of a frustrated Lewis pair. One plausible mechanism for CO₂ reduction involves coordination of the C₁ reagent to the d₁₀ metal fragment following by nucleophilic attack by either the gold- or boron-hydride species.[46]

(a) Heterobimetallic Binding

Substrate Binding

Product Binding

(b) Reaction of Aresta’s complex with HBpin.

Figure 4. (a) Gibbs free binding energies of [Au(H)₃PPh₃]⁻, substrate and product to the bent Cu(I) fragment. (b) Reaction of Aresta’s complex with HBpin.

The putative complex 2•CO₂ is thermodynamically uphill based on DFT calculations and could not be prepared by addition of CO₂ to 2•tol. This metal bound CO₂ adduct is isoelectronic with Aresta’s complex Ni•CO₂ (Figure 4b).[51]

Ni•CO₂ is stable in solution, and was independently synthesised and used as a mechanistic probe. Reaction of Ni•CO₂ with 10 equivalents of HBpin leads to mixtures containing HCO₂Bpin, Ni•CO and O(Bpin)₂.[82] Furthermore, Ni•CO₂ is catalytically competent for CO₂ reduction with HBpin (Supporting information, Figure 12-14). These experiments demonstrate that metal bound CO₂ is a plausible C₁ source during catalytic turnover.

In summary, we have reported the synthesis, characterization and reactivity of the first heterobimetallic complexes of the coinage metals containing a Au–H–Cu 3-centre, 2-electron interaction. These complexes have been shown to be selective in the formation of HCO₂Bpin, a formate equivalent, from CO₂ and HBpin. A consistent heterobimetallic effect is observed and both metal centers are required for the selective formation of formoxyborane. Preliminary mechanistic experiments and DFT calculations suggest that activation of CO₂ by coordination to the d₁₀ metal fragment is feasible under the catalytic conditions. The precise mechanism of CO₂ reduction and origin of heterobimetallic selectivity remain unclear and will be the subject of future studies.

Supporting Information

Full experimental details, including experimental procedures, details of DFT calculations and Xray data (.cif) are available. Further, editable versions of the NMR data for 3•PPh₃ and 1-3•Au are provided as .mmna and .nmpub files (DOI: 10.14469/hpc/3010). Dr. Sebastian D. Pike is thanked for his help with preliminary experiments with CO₂.

Acknowledgements

We are grateful for generous support from the Leverhulme Trust (RPG – 2015 – 248) and the NERC Science and Solutions for a Changing Planet Doctoral Training Programme.

Keywords: heterobimetallic • hydride • copper • gold • carbon dioxide

References

We considered ligand scrambling of 1•2Au could lead to catalytically active [HCu(Ipr)] which would be expected to selectively produce HCO\textsubscript{2} HBpin.\footnote{After 14h, ratio of boron-containing species calculated by \textsuperscript{1}H NMR; 7.6:1.5:1 HBPin:HCO\textsubscript{2} HBpin:PinBOBpin} While we cannot unambiguously rule it out at this stage, the possibility of ligand exchange appears prohibitive based on DFT. \textsuperscript{[BD]Au(Au)(Cu(Ipr))] was found to be significantly higher in energy than 2•2Au (\Delta E_{\text{rxn}} \approx \pm 20 \text{ kcal mol}^{-1}). Monitoring the reaction of 2•2Au with CO\textsubscript{2} and HBpin as a function of time (See Supporting Information, Figure S9) supports a subtle induction period for catalysis and suggests that 2•2Au is off cycle.

Monitoring catalysis with 2•2Au by \textsuperscript{19}F NMR spectroscopy using a fluorinated internal standard, showed that 90% of the fluoroine containing starting material converts to an as yet unknown product. (See Supporting Information, Figure S9)

\textbf{Y. Yang, M. Xu, D. Song, Chemical Communications} 2015, 51, 11293–11296.


NH\textsubscript{C}Cs are known to act as catalysts in the reduction of CO\textsubscript{2} with boranes and silanes. To the best of our knowledge these reaction are selective for the formation of methanol equivalents. Y. Yang, M. Xu, D. Song, Chem. Comm. 2015, 51, 11293–1129. S. N. Riduan, Y. Zhang, J. Y. Ying, Angew. Chem. Int. Ed. 2009, 48, 3322–3325.


\textbf{L. P. Wolters, F. M. Bickelhaupt, ChemistryOpen 2013, 2, 106–114.}


The golden touch: A series of heterobimetallic complexes containing 3-center, 2-electron Au–H–Cu bonds have been prepared. These unusual molecules represent a missing link in the widely investigated series of neutral and cationic coinage metal hydride complexes containing Cu–H–Cu and M–H–M+ moieties (M = Cu, Ag). The well-defined heterobimetallic hydride complexes act as pre-catalysts for the selective reduction of CO₂ to HCO₂Bpin using HBpin as a reductant.

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