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NHC-Coordinated Diphosphene Stabilized Gold(I) Hydride and its Reversible Conversion to Gold(I) Formate with CO_2

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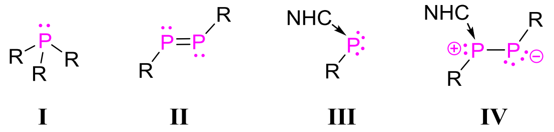
Dedicated to Professor C. N. R. Rao on occasion of his 85th birthday.

Abstract: An NHC-coordinated diphosphene is employed as ligand for the synthesis of a hydrocarbon-soluble monomeric Au(I) hydride, which readily adds CO_2 at room temperature yielding the corresponding Au(I) formate. The reversible reaction can be expedited by the addition of NHC, which induces *β*-hydride shift and the removal of CO_2 from equilibrium through the formation of an NHC-CO_2 adduct. The Au(I) formate is alternatively formed by dehydrogenative coupling of the Au(I) hydride with formic acid (HCO_2H), thus in total establishing a reaction sequence for the Au(I) hydride mediated dehydrogenation of HCO_2H as chemical hydrogen storage material.

Tertiary phosphines, **I** (Scheme 1) are ubiquitous ligands and thus play an important role in the organometallic chemistry of transition metals[1] and thereby also in the area of homogenous catalysis.[2] Celebrated examples of the use of phosphines include, Wilkinson's catalyst,[3] Noyori's catalyst,[4] and the first generation Grubbs catalyst.[5] Other phosphorus-based species such as diphosphenes **II**,[6] and base-stabilized phosphinidenes **III**[7] (Scheme 1) have also found applications as ligands in transition metal complexes. In contrast, Bertrand's base-free phosphino phosphinidene is electrophilic in nature.[8] None of these *P*-centered donors (**I**-**III**), however, can compete with carbenes in terms of the stabilization of reactive intermediates.[9]

Recently, we have reported the reversible coordination of an NHC to a diphosphene to yield **IV** (Scheme 1), which possesses two nonbonding electron pairs at the dicoordinate *P*-center.[10] Frontier orbital analysis revealed that the HOMO almost exclusively consists of a *p*-orbital at the formally negatively charged dicoordinate phosphorus center. Theoretical calculations further suggest that the NHC-coordinated diphosphene should be a stronger donor than Ph_3P.[11] Moreover, the calculated binding energy of **IV** to AuCl is −61.1 kcal/mol which is higher in comparison to **I** (−50.1 kcal/mol), **II** (−38.5 kcal/mol), and **III** (−55.8 kcal/mol).[11] Armed with this knowledge, we sought to utilize **IV** as a ligand towards gold(I) hydride. The monomeric parent Au(I) hydride (AuH) is kinetically unstable and has only been observed in cold matrices[12] and considered as an intermediate in numerous gold-catalyzed organic transformations.[13] With an NHC as a stabilizing ligand, it was isolated as a room temperature stable compound.[14]

Herein, we thus disclose the use of **IV** as a new *P*-centered neutral ligand that ultimately allowed for the isolation of a monomeric Au(I) hydride complex, which in turn is shown to undergo the first hydroauration reaction of CO_2 to form the corresponding Au(I) formate. Surprisingly, the Au(I) formate spontaneously releases CO_2 even at room temperature, a process that is facilitated by the presence of NHC. We further show that the Au(I) formate is also accessible by the dehydrogenation of HCO_2H (a chemical hydrogen storage material)[15] by the Au(I) hydride, thus stoichiometrically demonstrating its principal potential as dehydrogenation catalyst. Reversible hydrogenation of CO_2 is known by the bacterial enzyme carbondioxide reductase.[16] In an analogous manner we report a synthetic system that shows reversible hydroauration behavior of a Au(I) hydride.



Scheme 1. Chemical structures of **I**-**IV** (R = monoanionic ligand, NHC = *N*-heterocyclic carbene).

The reaction of $AuCl{\cdot}SMe_2$ with a 1:1 solution of $\mathbf{NHC^{Me_4}}$[17] and diphosphene **1**[18] in THF at −78 °C yields the NHC^{Me_4}/diphosphene-coordinated Au(I) chloride complex **2** (Scheme 2).[11] Formation of **2** reveals the ability of the diphosphene motif to act simultaneously both as a Lewis acid and a Lewis base in analogy to compounds with heavier Group 14 multiple bonds.[19] The ^{31}P NMR spectrum of **2** exhibits two doublets at $\delta = 1.34$ and −31.46 ppm with $^{1}J_{PP} = 462$ Hz, which is in between the values of $\mathbf{1{\cdot}NHC^{Me_4}}$ ($^{1}J_{PP} = 423$ Hz)[10] and the monoaurated adduct, Mes*(AuCl)P=PMes* ($^{1}J_{PP} = 539$ Hz).[20]

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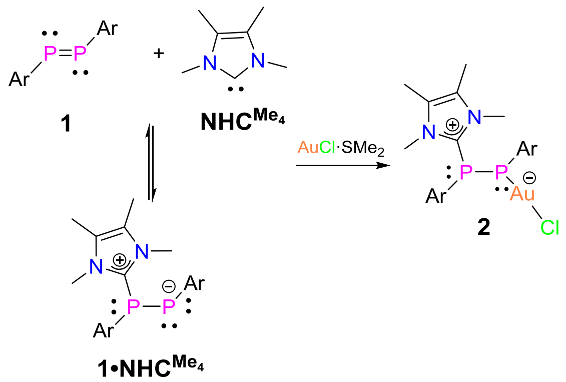


Scheme 2. Synthesis of NHC^{Me_4}-coordinated diphosphene stabilized Au(I)-Cl complex, **2** (Ar = 2,6-Mes$_2$C$_6$H$_3$, Mes = 2,4,6-Me$_3$C$_6$H$_2$).

Interestingly, in solution, the coordinated **NHC^{Me_4}** does not dissociate unlike **1·NHC^{Me_4}** that exists in equilibrium with **1** and **NHC^{Me_4}**.[10] The stability of **2** is probably due to the coordination of the diphosphene moiety to AuCl, which enhances the electrophilicity of the second *P* center resulting in stronger binding to **NHC^{Me_4}**. This is also supported by DFT calculations on the highly endergonic dissociation of **NHC^{Me_4}** from **2** (21.8 *vs.* 6.7 kcal/mol from **1·NHC^{Me_4}**) in THF.[11]

The molecular structure of **2** was confirmed by single crystal X-ray diffraction (Figure 1). The P–Au bond distance (2.2540(8) Å) in **2** is longer than those of Ph$_3$P·AuCl (Au–P 2.235 Å)[21] and the corresponding diaurated adduct of Mes*-substituted diphosphene, Mes*(AuCl)P=P(AuCl)Mes* (2.201 Å).[20] The P1–P2 bond distance is 2.219(1) Å and thus considerably longer than in free diphosphene **1** (2.029 Å)[22] or **1·NHC^{Me_4}** (2.134 Å).[10]

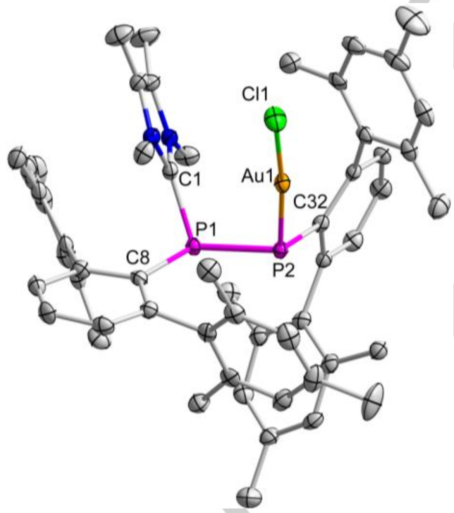
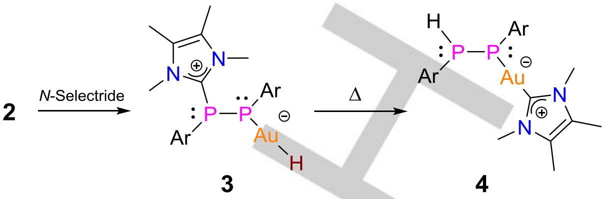


Figure 1. Molecular structure of **2** with thermal ellipsoids at 50% probability level. All hydrogen atoms and one molecule of co-crystallized toluene are omitted for clarity.

The 1:1 reaction of **2** with *N*-selectride at −78 °C affords the NHC/diphosphene-stabilized Au(I) hydride, **3** in 90 % yield as light yellow crystals (Scheme 3). The ^{31}P NMR spectrum of **3** exhibits two resonances at $\delta = 1.6$ ppm as doublet ($^1J_{PP} = 470$ Hz) and at $\delta = -14.5$ ppm as a doublet of doublets ($^1J_{PP} = 470$ Hz, $^2J_{PH} = 138$ Hz).



Scheme 3. Synthesis of NHC-coordinated diphosphene stabilized Au(I)-hydride, **3** and it's rearrangement to **4**.

In the ^{1}H NMR spectrum, the doublet at $\delta = 4.60$ ppm ($^2J_{PH} = 138$ Hz) can be unambiguously assigned to the Au–*H* resonance, which is upfield shifted in comparison to that of NHC^{Dip}-stabilized Au(I)-hydride (5.11 ppm).[12a] The IR spectrum of **3** shows a strong sharp band at 1893 cm^{-1} for the Au-H motif, in good agreement with the calculated value (1880.2 cm^{-1}).[11]

The molecular structure of **3** (Figure 2) reveals a P–P bond distance of 2.197(1) Å, which is slightly shorter than the P–P bond distance in **2** due to less pronounced π-back-donation. Indeed, the P–Au bond distance in **3** of 2.3297(9) Å is larger than the 2.2540(8) Å in **2** suggesting a stronger trans influence of the hydride compared to the chloride ligand. The Au(I) hydride **3** is stable in presence of degassed water in toluene overnight; a solid-crystalline sample even persists in open air at least for two days.

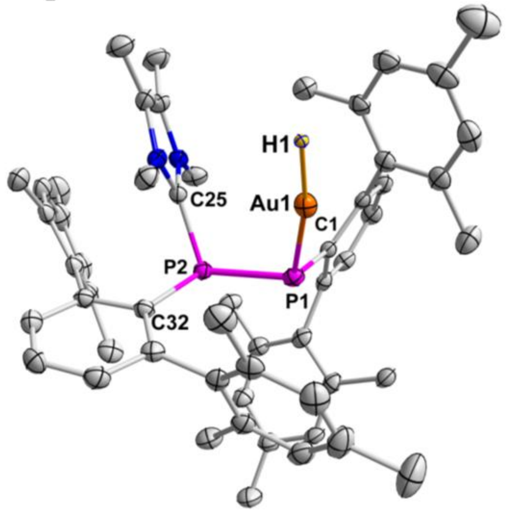


Figure 2. Molecular structure of **3** with thermal ellipsoids at 50% probability level. All H atoms except Au-H and one co-crystallized molecule of benzene are omitted for clarity.

In solution, however, **3** slowly undergoes a 1,3-hydrogen shift from the Au center to the β-phosphorus atom resulting in the Au(I) phosphinophosphide **4** as shown by the appearance of a ^{1}H NMR doublet of doublets at $\delta = 4.19$ ppm (dd, $^1J_{PH} = 214$. Hz, $^2J_{PH} = 9$ Hz). The concomitant migration of the NHC ligand from the phosphorus to the gold center is evident from the significantly smaller coupling of the ^{13}C{^{1}H} signal at $\delta = 193.6$ ppm of the carbenic carbon atom to the nearest ^{31}P nucleus

($^{2}J_{CP}$ = 53 Hz for **4** *vs.* $^{1}J_{CP}$ = 99 Hz for **2**). Conversion is completed by heating to 65 °C for one hour. According to our DFT results, the rearrangement of **3** to **4** is exergonic by 26.1 kcal/mol.[11] The structure of the NHC-stabilized Au(I) phosphinophosphide **4** was finally confirmed by X-ray diffraction on single crystals (Figure 3). The P–P bond distance of **4** is 2.218(1) Å and thus slightly longer than in the one of the reported boryl substituted lithium phosphinophosphide (2.1775 Å).[23]

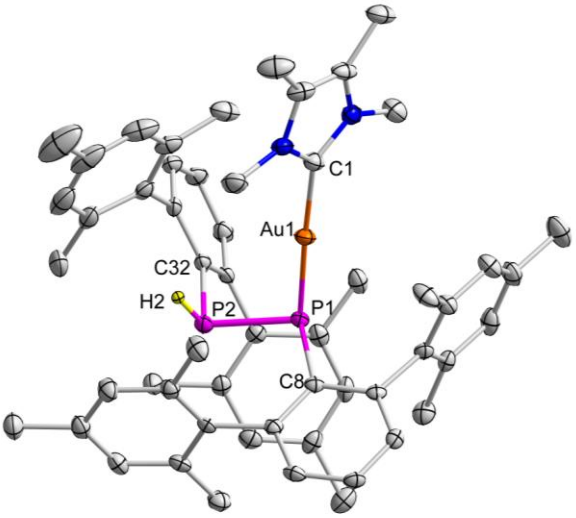
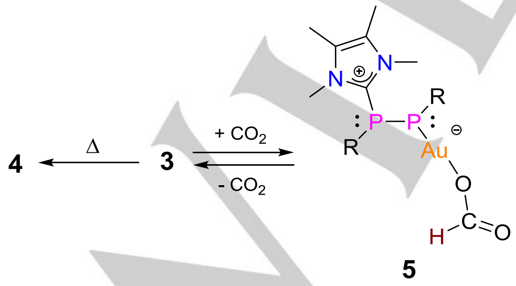


Figure 3. Molecular structure of **4** with thermal ellipsoids at 50% probability level. All hydrogen atoms and one molecule of co-crystallized hexane solvent molecule are omitted for clarity.

In order to address the hydridic character of the Au-*H* moiety of **3**, we considered the hydroauration reaction with CO_2. The hydrometallation of carbonyl compounds, in particular of CO_2, is a key step of catalytic conversions to access C1-feedstock materials.[24] In fact, the formation of **5** from **3** and CO_2 is computed to be exergonic by 11.6 kcal/mol.[11] Upon passing CO_2 gas into a toluene solution of **3** at room temperature, the quantitative formation of Au(I) formate **5** was observed based on ^{31}P NMR of the reaction mixture (Scheme 4).



Scheme 4. Synthesis of NHC-coordinated diphosphene stabilized Au(I)-formate, **5**.

The ^{1}H NMR spectrum of **5** exhibits a doublet centered at δ = 9.50 ppm ($^{4}J_{HP}$ = 7 Hz), in line with the suggested formate as is a prominent IR band at 1884 cm^{-1} for the C=O stretching frequency. The molecular structure of **5** was confirmed by X-ray crystallography (Figure 4). The Au–O bond distance in the Au(I) formate **5** of 2.140(4) Å is slightly longer than that of a reported Au(III) formate (2.102 Å).[25] To the best of our knowledge, the formation of **5** represents the first example of any gold formate obtained by *direct* hydroauration of CO_2.

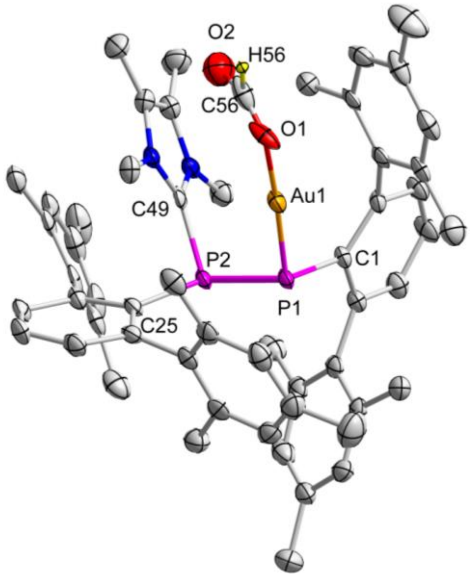
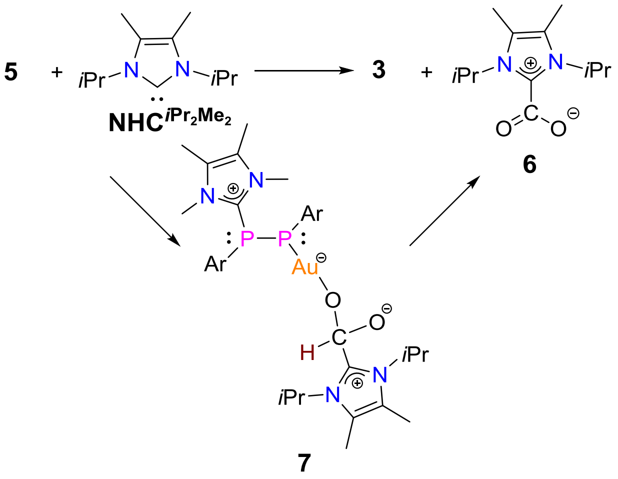


Figure 4. Molecular structure of **5** with thermal ellipsoids at 50% probability level. All hydrogen atoms and one molecule of toluene are omitted for clarity.

We had noted that the ^{31}P NMR spectrum of the residue after removal of the solvent shows the presence of about 5 % of the starting Au(I) hydride, **3**. This observation prompted us to further investigate a possible spontaneous release of CO_2 from **5**. The release of CO_2/HCO_2^- from transition-metal formates is well-known[26] and the reductive elimination of CO_2 from a binuclear Au(II)/CO_2 complex has been reported.[27] Indeed, the application of 0.12 mbar vacuum for 15 h results in the original Au(I)-hydride **3** in about 50%. Decarboxylation of **5** above 65 °C proceeds to complete conversion, but also affords **4**, the thermal isomerization product of **3** as side product.

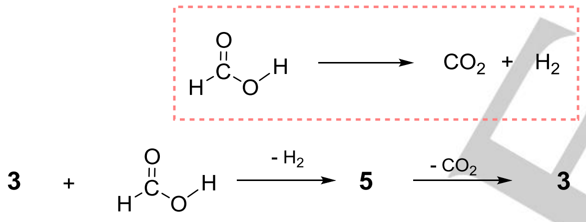


Scheme 5. **NHC^{iPr_2Me_2}**-mediated release of CO_2 from Au(I)-formate, **3**.

To facilitate the release of CO_2, we added **NHC**^{iPr_2Me_2}[14] in the anticipation that it might induce the required 1,3-H shift (β-hydride elimination)[28] by coordination to the carbonyl group and removal of CO_2 from equilibrium as NHC^{iPr_2Me_2}-CO_2 adduct **6**.[29] Addition of one equivalent of **NHC**^{iPr_2Me_2} to a solution of **5** at room temperature indeed resulted in the immediate formation of **3** (Scheme 5).

In order to verify the CO_2 release at lower temperatures and to check for intermediates, we carried out a VT-NMR study of a 1:1 toluene-d_8 solution of **NHC**^{iPr_2Me_2} and **5**. At −78 °C, the ^{31}P NMR spectrum does not show any indication for the release of CO_2. At −10 °C, we observed one new set of peaks at $\delta = -35.2$ and 0.9 ppm ($^1J_{PP} = 465$ Hz). These resonances disappear while approaching room temperature with the concomitant appearance of the resonances of **3**. The occurrence of an intermediate suggests that the reaction may indeed proceed through the initial coordination of **NHC**^{iPr_2Me_2} to the carbonyl carbon centre of **5** to give the thermally unstable adduct **7**; in analogy to the nucleophilic coordination of NHC to aldehydes.[30] Subsequent hydride migration (β-hydride elimination) would lead to the **NHC**^{iPr_2Me_2} adduct of CO_2 **6** and Au(I) hydride **3** (Scheme 5). The calculated Gibbs free energy values confirm that the reaction **5** + **NHC**^{iPr_2Me_2} → **3** + **6** is endergonic by 7.4 kcal/mol.[11]

Finally, we contemplated the use of the NHC/diphosphene coordinated Au(I) hydride **3** for the dehydrogenation of HCO_2H. The stoichiometric reaction of **3** and HCO_2H indeed results in the Au(I) formate **5** with elimination of H_2 (Scheme 6). Computationally, the formation of **5** from **3** and HCO_2H is thermodynamically favourable by 13.5 kcal/mol.[11]



Scheme 6. Au(I)-hydride, **3** mediated release of H_2 and CO_2 from HCO_2H (Inset: Reaction of HCO_2H to CO_2 and H_2).

In conclusion, we herewith disclosed a water-stable monomeric terminal Au(I)-hydride coordinated by an NHC/diphosphene adduct. Like other heavier Group 14 multiple bonds, the diphosphene can simultaneously act as a Lewis acid and as a Lewis base. The Au(I) hydride exhibits pronounced hydridic character and thus reacts with CO_2 to the corresponding Au(I)-formate, which spontaneously releases CO_2 at room temperature, a feature that typically requires much higher temperatures.[31] The alternative formation of formate from Au(I)-hydride and HCO_2H with release of H_2 suggests that a thermally more stable Au(I)-hydride might indeed be a competent catalyst for the release of H_2 from HCO_2H, a chemical hydrogen storage material at ambient conditions.[32]

Acknowledgements

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Keywords: carbon dioxide • diphosphene • gold • ligand design • phosphorus

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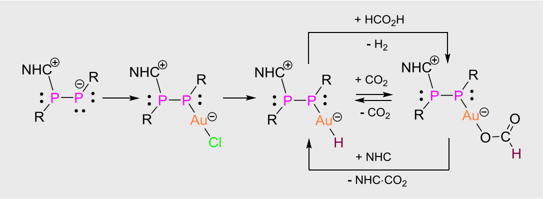
COMMUNICATION



NHC-coordinated diphosphene has been used as a ligand for the isolation of monomeric gold(I) hydride which readily converted to the corresponding Au(I) formate in either by hydroauration of CO_2 or by dehydrogenative coupling with formic acid. The Au(I) formate in turn loses CO_2 at room temperature upon application of vacuum and this process can be expedited at lower temperatures by using NHC.

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NHC-Coordinated Diphosphene Stabilized Gold(I) Hydride and its Reversible Conversion to Gold(I) Formate with CO_2