

N-Heterocyclic Carbenes

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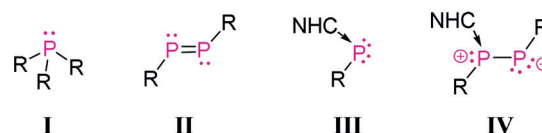
NHC-Coordinated Diphosphene-Stabilized Gold(I) Hydride and Its Reversible Conversion to Gold(I) Formate with CO₂

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Dedicated to Professor C. N. R. Rao on the 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 CO₂ 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 CO₂ from equilibrium through the formation of an NHC-CO₂ adduct. The Au^I formate is alternatively formed by dehydrogenative coupling of the Au^I hydride with formic acid (HCO₂H), thus in total establishing a reaction sequence for the Au^I hydride mediated dehydrogenation of HCO₂H 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 homoge-



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

nous 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 Ph₃P.^[11] Moreover, the calculated binding energy of **IV** to AuCl is –61.1 kcal mol^{–1} which is higher in comparison to **I** (–50.1 kcal mol^{–1}), **II** (–38.5 kcal mol^{–1}), and **III** (–55.8 kcal mol^{–1}).^[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 CO₂ to form the corresponding Au^I formate. Surprisingly, the Au^I formate spontaneously releases CO₂ 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 HCO₂H (a chemical hydrogen storage material)^[15] by the Au^I hydride, thus stoichiometrically

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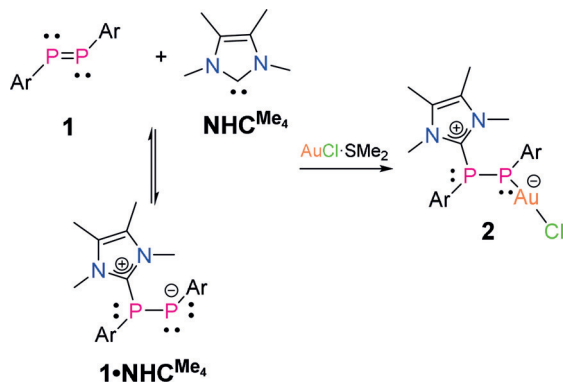
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demonstrating its principal potential as dehydrogenation catalyst. Reversible hydrogenation of CO₂ is known by the bacterial enzyme carbon dioxide reductase.^[16] In an analogous manner we report a synthetic system that shows reversible hydroauration behavior of a Au^I hydride.

The reaction of AuCl·SMe₂ with a 1:1 solution of NHC^{Me₄}^[17] and diphosphine **1**^[18] in THF at –78 °C yields the NHC^{Me₄}/diphosphine-coordinated Au^I chloride complex **2** (Scheme 2).^[11] Formation of **2** reveals the ability of the diphosphine motif to act simultaneously both as a Lewis acid



Scheme 2. Synthesis of NHC^{Me₄}-coordinated diphosphene-stabilized Au^I-Cl complex **2** (Ar = 2,6-Mes₂C₆H₃, Mes = 2,4,6-Me₃C₆H₂).

and a Lewis base in analogy to compounds with heavier Group 14 multiple bonds.^[19] The ³¹P NMR spectrum of **2** exhibits two doublets at δ = 1.34 and –31.46 ppm with ¹J_{PP} = 462 Hz, which is in between the values of **1**·NHC^{Me₄} (¹J_{PP} = 423 Hz)^[10] and the monoaurated adduct, Mes*(AuCl)P = PMes* (¹J_{PP} = 539 Hz).^[20]

Interestingly, in solution, the coordinated NHC^{Me₄} does not dissociate unlike **1**·NHC^{Me₄}, which exists in equilibrium with **1** and NHC^{Me₄}.^[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^{Me₄}. This is also supported by DFT calculations on the highly endergonic dissociation of NHC^{Me₄} from **2** (21.8 vs. 6.7 kcal mol^{–1} from **1**·NHC^{Me₄}) 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 Ph₃P·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^{Me₄} (2.134 Å).^[10]

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 ³¹P NMR spectrum of **3** exhibits two resonances at δ = 1.6 ppm as doublet (¹J_{PP} = 470 Hz) and at δ = –14.5 ppm as a doublet of doublets (¹J_{PP} = 470 Hz, ²J_{PH} = 138 Hz).

In the ¹H NMR spectrum, the doublet at δ = 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).^[14a] The IR spec-

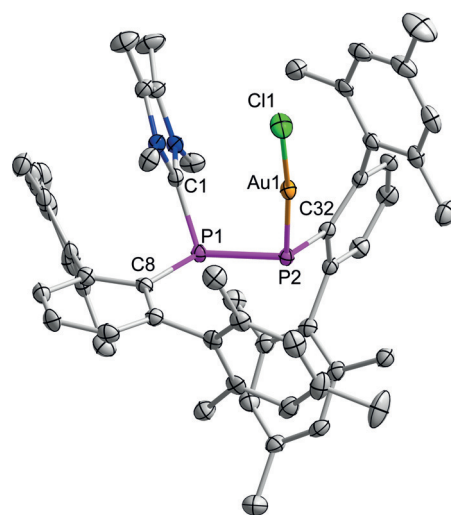
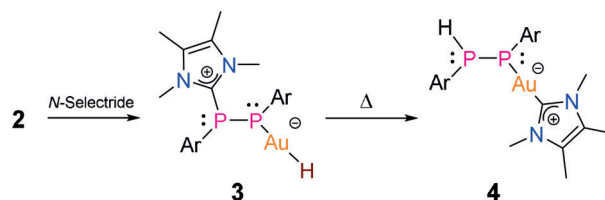


Figure 1. Molecular structure of **2** with ellipsoids set at 50% probability. All hydrogen atoms and one molecule of co-crystallized toluene are omitted for clarity.^[33]



Scheme 3. Synthesis of NHC-coordinated diphosphene-stabilized Au^I-hydride **3** and the rearrangement to **4**.

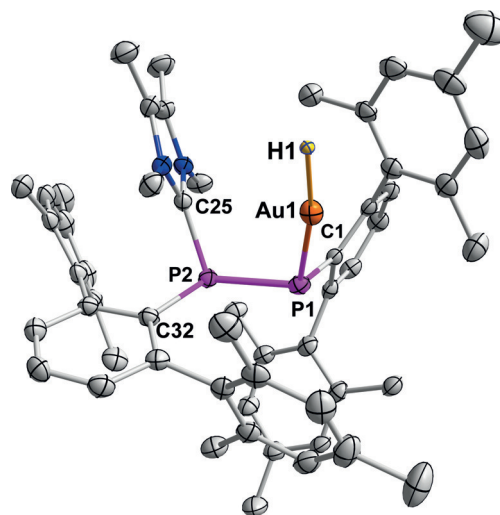


Figure 2. Molecular structure of **3** with ellipsoids set at 50% probability. All H atoms except Au–H and one co-crystallized molecule of benzene are omitted for clarity.^[33]

trum 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.

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 ¹H NMR doublet of doublets at δ = 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 ¹³C{¹H} signal at δ = 193.6 ppm of the carbenic carbon atom to the nearest ³¹P nucleus (²J_{CP} = 53 Hz for **4** vs. ¹J_{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⁻¹.^[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]

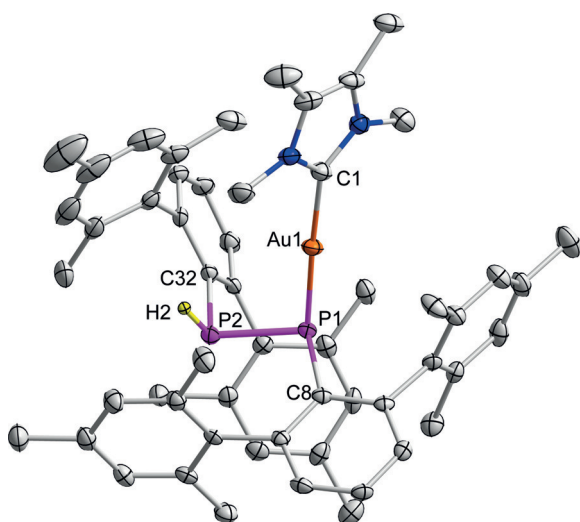
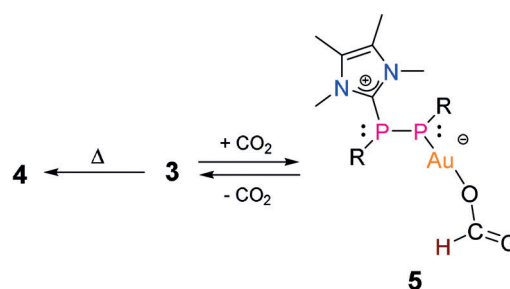


Figure 3. Molecular structure of **4** with ellipsoids set at 50% probability. All hydrogen atoms and one molecule of co-crystallized hexane solvent molecule are omitted for clarity.^[33]

To address the hydridic character of the Au–H moiety of **3**, we considered the hydroauration reaction with CO₂. The hydrometalation of carbonyl compounds, in particular of CO₂, is a key step of catalytic conversions to access C1-feedstock materials.^[24] In fact, the formation of **5** from **3** and CO₂ is computed to be exergonic by 11.6 kcal mol⁻¹.^[11] Upon passing CO₂ gas into a toluene solution of **3** at room temperature, the quantitative formation of Au^I formate **5** was observed based on ³¹P NMR of the reaction mixture (Scheme 4).

The ¹H NMR spectrum of **5** exhibits a doublet centered at δ = 9.50 ppm (⁴J_{HP} = 7 Hz), in line with the suggested formate



Scheme 4. Synthesis of NHC-coordinated diphosphene-stabilized Au^I-formate **5**.

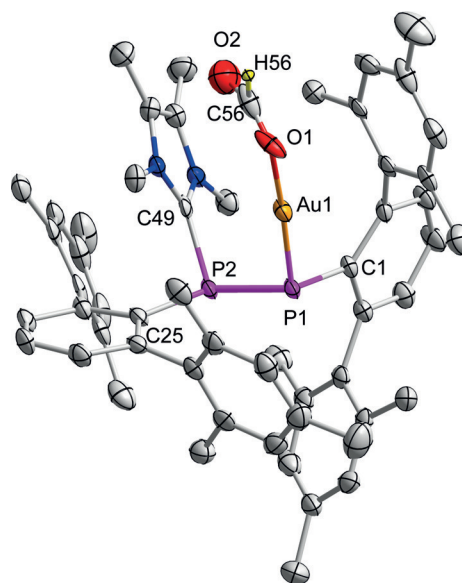
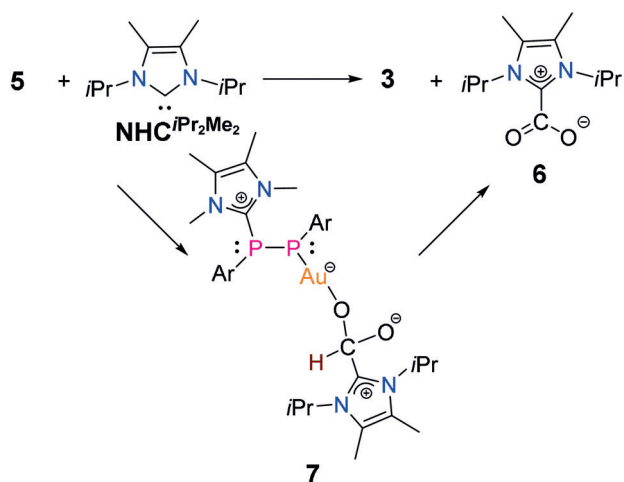


Figure 4. Molecular structure of **5** with ellipsoids set at 50% probability. All hydrogen atoms and one molecule of toluene are omitted for clarity.^[33]

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 CO₂.

We had noted that the ³¹P 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 CO₂ from **5**. The release of CO₂/HCO₂⁻ from transition-metal formates is well-known^[26] and the reductive elimination of CO₂ from a binuclear Au^{II}/CO₂ 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.

To facilitate the release of CO₂, we added NHCⁱPr₂Me₂^[14] in the anticipation that it might induce the required 1,3-H shift

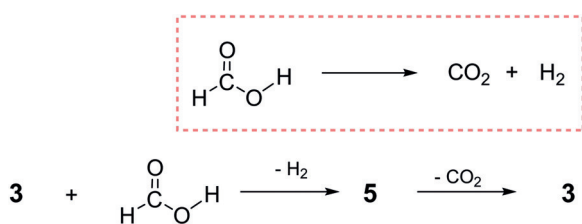


Scheme 5. NHC^{iPr₂Me₂}-mediated release of CO₂ from Au^I-formate **3**.

(β-hydride elimination)^[28] by coordination to the carbonyl group and removal of CO₂ from equilibrium as NHC^{iPr₂Me₂}-CO₂ adduct **6**.^[29] Addition of one equivalent of NHC^{iPr₂Me₂} to a solution of **5** at room temperature indeed resulted in the immediate formation of **3** (Scheme 5).

To verify the CO₂ release at lower temperatures and to check for intermediates, we carried out a VT-NMR study of a 1:1 [D₈]toluene solution of NHC^{iPr₂Me₂} and **5**. At −78 °C, the ³¹P NMR spectrum does not show any indication for the release of CO₂. At −10 °C, we observed one new set of peaks at δ = −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^{iPr₂Me₂} to the carbonyl carbon center 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^{iPr₂Me₂} adduct of CO₂ **6** and Au^I hydride **3** (Scheme 5). The calculated Gibbs free energy values confirm that the reaction **5** + NHC^{iPr₂Me₂} → **3** + **6** is endergonic by 7.4 kcal mol^{−1}.^[11]

Finally, we contemplated the use of the NHC/diphosphine coordinated Au^I hydride **3** for the dehydrogenation of HCO₂H. The stoichiometric reaction of **3** and HCO₂H indeed results in the Au^I formate **5** with elimination of H₂ (Scheme 6). Computationally, the formation of **5** from **3** and HCO₂H is thermodynamically favourable by 13.5 kcal mol^{−1}.^[11]



Scheme 6. Au^I-hydride **3** mediated release of H₂ and CO₂ from HCO₂H (inset: Reaction of HCO₂H to CO₂ and H₂).

In conclusion, we have disclosed a water-stable monomeric terminal Au^I-hydride coordinated by an NHC/diphosphine adduct. Like other heavier Group 14 multiple bonds, the diphosphine can simultaneously act as a Lewis acid and as a Lewis base. The Au^I hydride exhibits pronounced hydridic character and thus reacts with CO₂ to the corresponding Au^I formate, which spontaneously releases CO₂ at room temperature, a feature that typically requires much higher temperatures.^[31] The alternative formation of formate from Au^I hydride and HCO₂H with release of H₂ suggests that a thermally more stable Au^I hydride might indeed be a competent catalyst for the release of H₂ from HCO₂H, a chemical hydrogen storage material at ambient conditions.^[32]

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Conflict of interest

The authors declare no conflict of interest.

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