Gold Complexes

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Enhanced π-Backdonation from Gold(I): Isolation of Original Carbonyl and Carbene Complexes**

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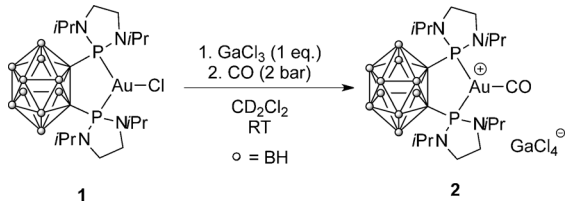
Abstract: *The specific electronic properties of bent o-carborane diphosphine gold(I) fragments were exploited to obtain the first classical carbonyl complex of gold [(DPCb)AuCO]$^+$ (ν(CO) = 2143 cm^{-1}) and the diphenylcarbene complex [(DPCb)Au(CPh$_2$)]$^+$, which is stabilized by the gold fragment rather than the carbene substituents. These two complexes were characterized by spectroscopic and crystallographic means. The [(DPCb)Au]$^+$ fragment plays a major role in their stability, as substantiated by DFT calculations. The bending induced by the diphosphine ligand substantially enhances π-backdonation and thereby allows the isolation of carbonyl and carbene complexes featuring significant π-bond character.*

The tremendous progress achieved recently in gold catalysis[1] has stimulated renewed interest in the coordination chemistry and reactivity of gold complexes.[2] Compared with other transition metals, the variety of gold complexes has long remained very limited. However, increasing efforts have been made over the past few years to isolate and characterize important classes of gold compounds such as π complexes,[3–6] vinyl complexes,[7] hydrides,[8] fluorides,[9] hydroxides and peroxides,[10] carbonyls,[11] and carbenoids.[12–14] Accordingly, our fundamental knowledge of gold organometallic chemistry has significantly progressed from both synthetic and bonding standpoints.

Owing to our interest in the development of new reactivity patterns for gold complexes,[15] we recently designed bent (L$_2$Au)$^+$ fragments to achieve oxidative addition of aryl iodides, a transformation so far considered highly disfavored, if not impossible, with gold.[16] We took advantage of *o*-carborane diphosphines (DPCb)[17] and discovered that the ensuing cationic gold(I) fragments [(DPCb)Au]$^+$ indeed readily activate C$_{sp^2}$–I bonds under mild conditions.[18] The bending induced by the DPCb diphosphine ligand was shown to play a key role in this process. We were keen to further explore the peculiar properties of [(DPCb)Au]$^+$ fragments, and we herein report a joint experimental/theoretical study of corresponding carbonyl and carbene complexes. Enhanced π-backdonation from [(DPCb)Au]$^+$ allows the isolation of unusual carbonyl and carbene complexes with significant π-bond character.

First, we sought to prepare and characterize the [(DPCb)AuCO]$^+$ complex. Although carbonyl complexes of gold are exceedingly rare, several examples of cationic gold(I) have recently been isolated and the nature of the Au–CO bonding interaction has been analyzed computationally.[11e–g] The tricoordinate cationic gold carbonyl complex **2** was prepared by reacting the gold(I) chloride complex **1** with $GaCl_3$ and then with CO in dichloromethane (Scheme 1). NMR monitoring shows selective and quantitative formation of complex **2**. A single ^{31}P NMR signal is observed at δ = 134.4 ppm, thus indicating symmetric coordination of the two phosphorus atoms.

X-ray diffraction analysis of **2** (Figure 1) showed that the gold atom sits in a distorted trigonal-planar environment. The



Scheme 1. Synthesis of the cationic bis(phosphine) gold(I) carbonyl complex **2**.

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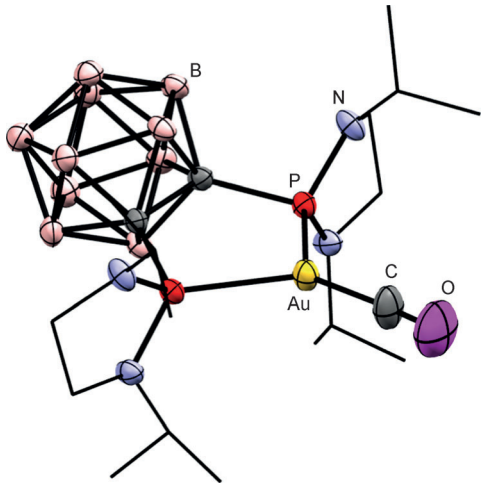


Figure 1. Molecular structure of complex **2**. Hydrogen atoms, counter anion, and solvate molecules are omitted; isopropyl and methylene groups are simplified for clarity.

PAuP bite angle is rather small [93.95(5)°] and the AuCO skeleton is quasi-linear [176.7(9)°]. The Au–C and C–O distances [1.971(7) Å and 1.126(10) Å, respectively] fall within the same range as those of the few structurally characterized gold carbonyl complexes.[19]

More salient features of complex **2** are the ^{13}C NMR and IR data. The ^{13}C NMR spectrum of **2** displays a resonance signal at $\delta = 191.8$ ppm for the carbonyl ligand bound to gold, which is shifted downfield compared to the signal for free CO ($\delta = 184$ ppm). This situation contrasts with the upfield shift observed for gold carbonyl complexes known so far ($\delta = 164.0$ to 182.6 ppm).[11] The ν(CO) stretching frequency of **2** is also remarkable at 2113 cm^{-1}. In fact, complex **2** stands as the first classical carbonyl complex of gold, i.e., one with a CO stretching frequency lower than that of free CO (2143 cm^{-1}). Indeed, all gold carbonyl complexes reported to date display CO stretching frequencies higher than that of free CO (from 2144 to 2237 cm^{-1}),[11] whatever the coordination number of gold and the charge of the complex (neutral and cationic complexes). Theoretical studies performed on these complexes have highlighted the importance of electrostatic effects and the small contribution of Au→CO π-backdonation compared with other transition metals.[11e–g]

A different bonding situation is apparently met in complex **2** and this was analyzed in detail computationally. Calculations were carried out on the real $[(DPCb)Au(CO)]^+$ cation (**2***). The optimized geometry of **2*** well reproduces the key Au–C, C–O bond lengths (< 0.03 Å) and PAuP angle.[20] The stretching of CO in complex **2*** was compared to that of free CO and the computed harmonic frequencies indicate a red shift of −35 cm^{-1} upon coordination to gold, which also compares very well with experimental observations.

Molecular orbital analysis of **2*** (Figure 2) provides further insight into the nature of the Au–CO interaction. The HOMO corresponds to a bonding combination of the occupied d_{xz}(Au) orbital with the vacant π^*_{CO} orbital. This bonding interaction is retrieved in the corresponding natural localized molecular orbital (NLMO), thus indicating substantial Au→CO π-backdonation. The *o*-carborane diphosphine plays a major role here. It imparts a three-coordinate environment to gold, and bending of the $[PAuP]^+$ fragment raises the energetic level of the occupied d_{xz} orbital at gold[17] and thereby enhances its interaction with the vacant π^*_{CO} orbital (an energy gap $\Delta E_{d_{xz}(Au)/\pi^*CO}$ of 8.4 eV is computed for **2***).[20] The linear dicoordinate phosphine gold carbonyl complex $[(Mes_3P)Au(CO)]^+$[11e] behaves very differently. The corresponding occupied d_{xz} orbital at gold is significantly lower in energy ($\Delta E_{d_{xz}(Au)/\pi^*CO} = 11.4$ eV),[20] and Au→CO π-backdonation is therefore much weaker. The difference in Au–CO bonding between the two complexes is also apparent from: 1) the donation/backdonation ratio, as estimated by charge decomposition analysis (CDA; $d/b = 2.13$ for **2*** vs. 3.25 for $[(Mes_3P)Au(CO)]^+$), and 2) the charge transfer between the CO and gold fragments as deduced from NPA charges (CO acquires positive charge upon coordination to $[(Mes_3P)Au]^+$, with a net charge transfer of 0.14 e^-, but remains neutral in complex **2***). Together, these data indicate that the bent dicoordinate fragment $[(DPCb)Au]^+$ features singular electronic properties. The presence of the high-energy occupied d_{xz} orbital at gold enhances π-backdonation in **2*** and this counterbalances the electrostatic effect associated with the positive charge of the complex.[11e–g]

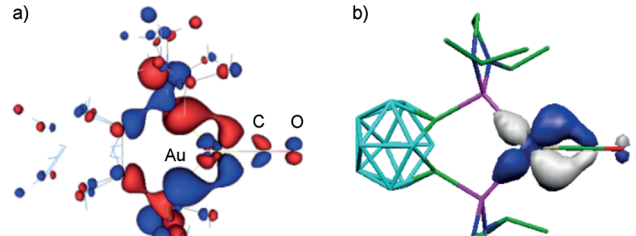


Figure 2. a) HOMO plot for complex **2*** (cutoff: 0.04). b) NLMO plot accounting for the $d_{xz}(Au)\rightarrow\pi^*_{CO}$ interaction in complex **2*** (cutoff: 0.04).

The unusual electronic structure of the gold carbonyl complex **2** prompted us to investigate related gold carbenoid species. The preparation and characterization of cationic gold carbenoid species has recently attracted considerable attention (Figure 3) and analysis of their bonding has also stimulated much fundamental interest.[13g,21] Most of the complexes reported to date are stabilized by π conjugation of the electrodeficient carbenoid center with heteroatoms,[13]

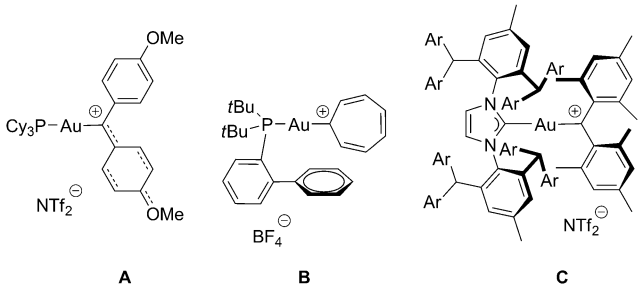
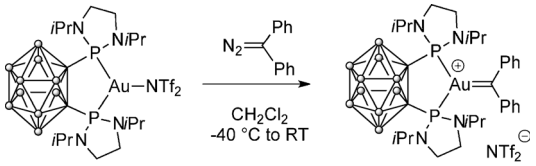


Figure 3. Recently isolated gold carbenoid complexes.

as nicely illustrated by complex **A**.[13g] Two examples of non-heteroatom-stabilized complexes have also been reported very recently.[14] In complex **B**,[14a] the carbene moiety is incorporated into an aromatic cycloheptatrienylidene framework and is thereby stabilized by π delocalization. In complex **C**,[14b] the dimesityl carbene moiety $CMes_2$ is combined with a bulky $[(NHC)Au]^+$ fragment, thus resulting in very strong steric shielding of the gold carbenoid motif.

The peculiar electronic properties of the $[(DPCb)Au]^+$ fragment may open a new way to stabilize such carbene complexes, with significant participation of the gold fragment via π-backdonation. To test this hypothesis, we decided to target the $[(DPCb)Au(CPh_2)]^+$ carbene complex. All attempts to generate $[(L)Au(CPh_2)]^+$ complexes, either by decomposition of diphenyldiazomethane or by transmetallation from tungsten Fischer carbene complexes, have so far been unsuccessful.[13f,g,14a] Gratifyingly, the $[(DPCb)AuNTf_2]$ complex **3** was found to rapidly and cleanly react with diphenyldiazomethane at temperatures as low as −40 °C (Scheme 2). Complex **4** was isolated (93 % yield) as a dark violet solid. It is highly thermally stable [mp.: 158–160 °C (decomp)] and was fully characterized.



3 4

Scheme 2. Synthesis of the bis(phosphine) gold carbene complex **4**.

The ^{31}P NMR spectrum of **4** displays a single ^{31}P NMR resonance at $\delta = 144.7$ ppm, shifted slightly downfield compared to the starting complex **3** (138.3 ppm). The carbene center of **4** resonates in ^{13}C NMR as a triplet ($J_{CP} = 75.2$ Hz) at $\delta = 316.2$ ppm, a chemical shift at the upper range of those observed previously in gold carbenoid complexes (δ 225–321 ppm).[13,14]

According to X-ray diffraction analysis (Figure 4), complex **4** adopts a discrete ion pair structure and the gold center is arranged in a trigonal-planar environment. The DPCb ligand chelates the gold center and the PAuP fragment is strongly bent [90.26(4)°]. The carbene center is perfectly planar and essentially perpendicular to the PAuP coordination plane (with a twist angle of 85.2°). This orientation minimizes steric repulsion and enables optimal interaction between the high-energy occupied d_{xz}(Au) orbital in the plane of the $[DPCbAu]^+$ fragment and the vacant 2p orbital at the carbene center (see above). The Au–C bond length [1.984(4) Å] is consistently slightly contracted compared to those of complexes **A**–**C** (2.014–2.035 Å). Note also that the bonds between the carbene center and the C_{ipso}(Ph) carbons are not contracted [1.454(6) and 1.464(5) Å] and the two phenyl rings are twisted by 58° from the carbene plane, thus indicating very weak, if any, π interaction.

Computational studies were carried out on complex **4** to gain insight into its bonding and assess the role of the

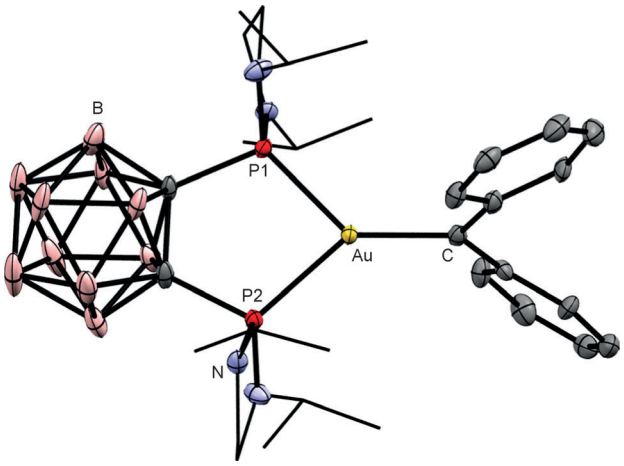


Figure 4. Molecular structure of complex **4**. Hydrogen atoms, counter anion, and solvate molecules are omitted; isopropyl and methylenegroups are simplified for clarity.

$[(DPCb)Au]^+$ fragment on its stability. Calculations were again performed on the actual complex $[(DPCb)Au(CPh_2)]^+$ (**4***) at the B3PW91/SDD + f(Au),6-31G**(B,P,N,C,H) level of theory. The optimized geometry of **4*** fits nicely with that determined crystallographically.[20] A bonding interaction between the d_{xz}(Au) and $2p^{\pi}$(C) orbitals in the coordination plane of gold is apparent in the HOMO of **4***, as well as in the related NLMO (Figure 5).[20] This indicates significant Au→carbene backdonation and thus some degree of Au–C π bonding.

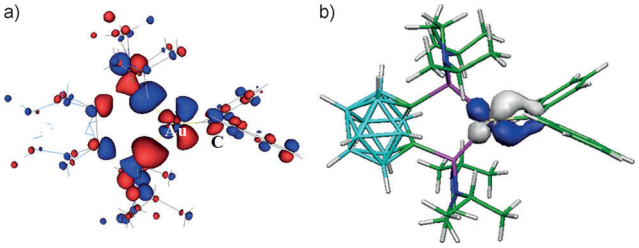


Figure 5. a) HOMO plot for complex **4*** (cutoff: 0.04). b) NLMO plot accounting for the d_{xz}(Au)→$2p^{\pi}$(C) interaction in complex **4*** (cutoff: 0.04).

The electronic structure of complex **4*** was compared with that of the related diarylcarbene complexes **A**[13g] and **C**.[14b] The respective molecular orbitals display much less interaction between the vacant $2p^{\pi}$(C) and the occupied d_{xz}(Au) orbitals, thus indicating that the $[(L)Au]^+$ fragment does not substantially contribute to the stabilization of the carbenoid species in these compounds.[20] The different bonding situations are also indicated by the donation/backdonation ratio estimated by CDA ($d/b = 1.72$ for **4*** vs. 5.67 and 3.61 for complexes **A** and **B**, respectively), and by the charge transfer between the carbene and gold fragments (no CT for **4*** vs. carbene→Au transfers of $0.35e^-$ and $0.28e^-$ computed for complexes **A** and **C**, respectively). The bonding in complex **4** is thus significantly different from that in complexes **A**–**C**.

Enhanced π-backdonation from the [(DPCb)Au$^+$] indeed results in a significant contribution from the gold fragment to the stabilization of the carbene center. In turn, this enlarges the variety of accessible carbene gold complexes, as illustrated by the isolation of the first diphenylcarbene complex **4**.

In conclusion, we have synthesized and fully characterized the first classical carbonyl complex of gold and the first carbene complex stabilized by the gold fragment rather than the carbene substituents. As substantiated by DFT studies, bending of the PAuP$^+$ fragment raises the energetic level of the occupied d_{xz}(Au) orbital and thus enhances backdonation. This induces unique bonding situations with significant Au–C π bonding. In future work, we will seek to further develop this approach to prepare new types of gold complexes.

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