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Gold Carbenoids: Lessons Learnt from a Transmetalation Approach**

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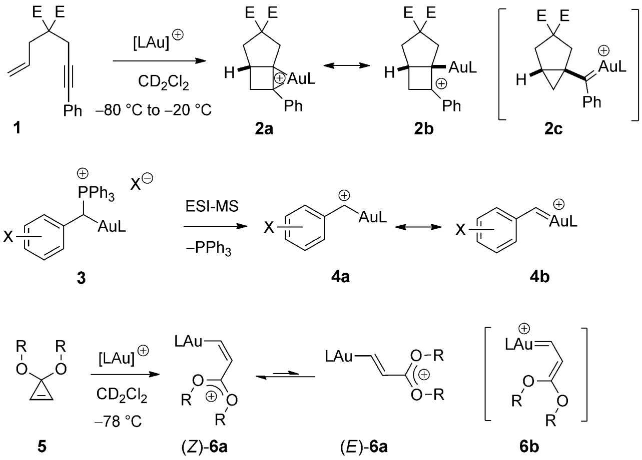
Abstract: *Carbophilic catalysts that are based on Au^I allow a host of different nucleophiles to be added across various π systems.[1–3] Although many of these reactions are thought to proceed via gold carbenoids, the challenge to observe and characterize these putative intermediates has basically been unmet.[4] The current mechanistic interpretation therefore largely relies on indirect evidence and computational data, some of which are subject to debate.[5] In an attempt to fill this gap, we pursued a potential route to gold carbenoids by formal transmetalation of chromium or tungsten Fischer carbene complexes with [LAu]$^+$. Whereas this transformation proceeds with exceptional ease as long as a stabilizing heteroelement is present on the carbene center, it stops half-way in its absence. Rather unusual bimetallic arrays are formed, which allow the charge density to delocalize over several positions. The obvious difficulty of releasing an "unstabilized" gold carbenoid has potential mechanistic implications for the understanding of π-acid catalysis in general.*

Amongst the few pertinent experimental studies on gold carbenoids known in the literature, a recent investigation by Widenhoefer and co-workers is arguably of the highest relevance.[6] For the first time, these authors managed to observe the actual intermediate of a prototype enyne cycloisomerization reaction by NMR spectroscopy; this intermediate resembles the cyclobutenyl resonance extreme **2a**,**b** rather than the cyclopropylmethyl form **2c** (Scheme 1). This observation validates an earlier mechanistic interpretation of π-acid catalysis that implied a build-up of delocalized positive charge density on the organic ligand.[1,7,8]

Other relevant data come from mass spectrometric investigations of (substituted) gold benzylidene species and their reactivity with various types of olefins.[9] Hammett correlations suggest that the resonance form **4a** significantly contributes to their ground-state structure, although a final conclusion as to whether the positive charge resides on carbon or on gold (**4b**) could not be drawn (Scheme 1). These studies also revealed that cyclopropanations of olefins by gold carbenoids, though stereospecific, likely proceed in a stepwise rather than in a concerted manner.



Scheme 1. Experimentally observed "gold carbenoids" pertinent to the mechanistic discussion of π-acid catalysis; for the sake of clarity, the non-coordinating counterions are not depicted; L = two-electron-donor ligand. E = COOMe; R,R = Me, Me or -$(CH_2)_3$-.

In a complementary approach, our group studied the rearrangement of cyclopropene derivatives, which is known to be an excellent entry point into the metal carbene series.[10] On treatment with $[(R_3P)Au]NTf_2$ at −78 °C, substrates of type **5** were transformed into discrete alkenyl gold complexes **6a** that carry a charged ligand (Scheme 1). Surprisingly small rotational barriers indicate that the carbene resonance extreme **6b** hardly contributes to the ground-state structure. We had emphasized that the vinylogous oxygen substituents in **6** might not be innocent, but favor build-up of positive charge density on the ligand.[10,11] Subsequent computational studies that were calibrated against our experimental data confirmed that the carbene resonance extreme becomes more significant as the oxygen substituents are replaced by alkyl groups, and strong ancillary donor ligands L are chosen.[12] Because of a peculiar three-center/four-electron bonding situation, however, increased π-electron back-donation from the metal to the ligand weakens the C−Au σ-bond to the extent that the overall bond order remains close to one.

Herein, we report further efforts to characterize germane gold carbenoids that are devoid of stabilizing heteroelement substituents. As the cyclopropene rearrangement had failed in such cases,[11] a different entry was sought. Attempts at reacting the diazo compound $Ph_2C{=}N_2$ with an appropriate gold precursor were equally unsuccessful, affording only the corresponding azine $Ph_2C{=}N{-}N{=}CPh_2$.[13–15] We then turned our attention to the carbene transfer method that is known to

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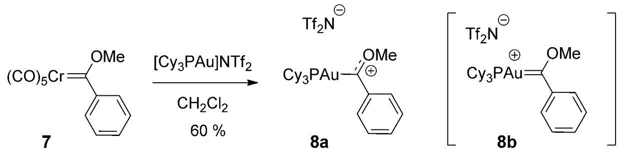


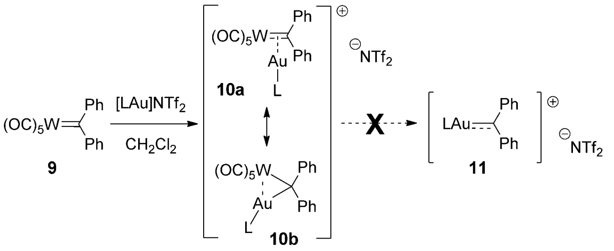
Scheme 2. Preparation of a prototype Fischer gold carbenoid by metal exchange. Cy = cyclohexyl.

work exceedingly well for the preparation of stabilized Fischer-type carbene complexes of gold.[16–18]

Indeed, reaction of **7** with [(Cy$_3$P)Au]NTf$_2$ furnished **8** in good yield (Scheme 2). Although the preparative experiments were carried out at ambient temperature, NMR spectroscopy revealed that this formal transmetalation proceeds even at −50 °C. As expected, the structure of **8** in the solid state (see the Supporting Information)[19] shows that the bond order of the C–Au bond (2.046(5) Å) is very close to one, whereas the C–OMe bond (1.289(6) Å) is notably contracted. This metric implies that the oxocarbenium resonance form **8a** is dominant.[20,21]

The remarkable ease with which this Fischer-type gold carbenoid is formed stands in striking contrast to the outcome of the attempted transmetalation of the diphenylcarbene complexes **9** and **12**, which were thought to provide the same gold carbenoid **11** devoid of stabilizing heteroatom donors. Yet, **11** could never be detected, irrespective of the ancillary ligand L bound to the cationic gold reagent.

In the tungsten series, the only detectable products are heteroleptic *gem*-dimetallic complexes of type **10**, which form rapidly even at −50 °C (Scheme 3). In CD$_2$Cl$_2$ solution, **10** (L = IMes) is stable at ambient temperature for hours before it eventually decomposes,[22] and this complex even persists under a CO atmosphere for more than two hours; the tungsten fragment could not be removed, and hence, free **11** could not be released under any of the chosen conditions.



Scheme 3. Attempted transmetalation of a tungsten carbene with [LAu]$^+$ affords hetero-bimetallic complexes **10** rather than the gold carbenoids **11**: 67 % (L = IMes), 93 % (L = PPh$_3$), quant. (by NMR spectroscopy; L = PCy$_3$, PMe$_3$). IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene.

Crystals that are suitable for X-ray analysis could be grown for two members of this series. The solid-state structure of **10** (L = IMes) is representative (Figure 1).[19] The C–W bond (2.1996(13) Å) is only slightly longer than that in the starting complex **9** (2.15(2)/2.13(2) Å);[23] the C–Au bond length (2.1445(13) Å) is comparable to that in other *gem*-metalated species.[24] The W⋯Au contact (2.7751(2) Å) suggests that the unusual hetero-bimetallic structure of **10** is stabilized by an attractive force between the two metal centers that is reminiscent of the well-known aurophilic interactions in homoleptic gold clusters.[25–27]

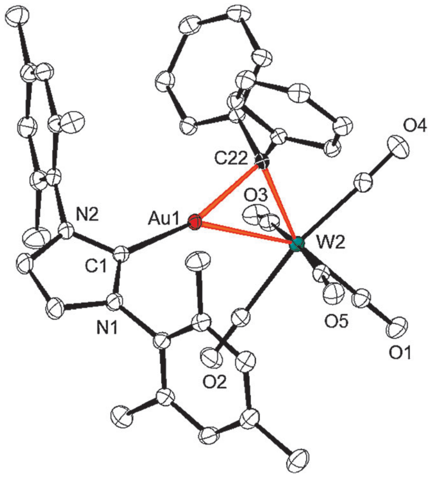
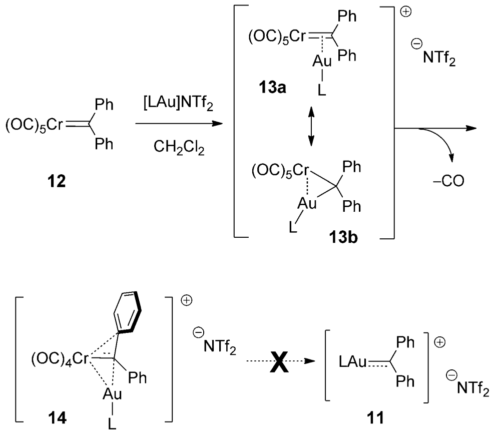


Figure 1. Structure of complex **10** (L = IMes) in the solid state; only the cationic entity is shown, whereas the escorting [NTf$_2$]$^-$ and co-crystallized solvent have been removed for clarity. For the entire structure, see the Supporting Information.

A salient feature of **10** (L = IMes) is the almost planar "carbene" center, even though the C–Au distance of 2.1445(13) Å suggests that this site engages in four (rather than three) bonding interactions. Likewise, the considerable high-field shift of the carbene carbon atom from 326.5 ppm in the tungsten precursor **9** to 262.6 ppm in **10** (L = PPh$_3$), together with a clearly discernible $J_{C,P} = 36$ Hz, indicates that the carbene site interacts with the coordinated gold fragment. To consolidate these data, we assume that the bonding in **10** is best described as a side-on complex of [LAu]$^+$ onto the π bond of the starting tungsten carbene, with moderate back-donation of electron density from gold into the antibonding orbitals of this entity. Overall, the complex seems closer to a tungsten carbene bearing an η^2-bound [LAu]$^+$ unit, as drawn in **10a**, than to the resonance extreme **10b** with a truly bridging carbene site.[28]

The reaction of the corresponding chromium carbene complex **12**[19,29] with [LAu]$^+$ at −50 °C primarily leads to the same type of hetero-bimetallic complex **13**, as deduced from the characteristic spectroscopic signature (Scheme 4).[30] Yet, this product rapidly converts into a more involved species **14** that retains the chromium carbonyl fragment but exhibits only four CO ligands that are magnetically inequivalent.[31] The bridging "carbene" center is strongly shielded [for L = PCy$_3$: 243.1 ppm (d, $J_{P,C} = 47$ Hz)], and the *ipso* carbon atom of one of the two arene rings resonates at unusually high field (93.6 ppm); this latter phenyl group is locked, whereas the second one rotates freely at temperatures ≥ −30 °C.[32]

The unusual constitution is apparent from the structure of complexes **14** (L = PCy$_3$, IMes) in the solid state; the structure of one of them is shown in Figure 2.[19] The Cr–C1 bond length (1.994(3) Å) is almost identical to that of the starting complex **12** (1.9877(12) and 1.9973(13) Å; two independent molecules



Scheme 4. Attempted transmetalation of **12** with $[LAu]^+$ also affords hetero-bimetallic complexes, even though the chromium entity has to abandon one of the CO ligands; the resulting complex **14** is stabilized by charge delocalization over Cr, Au, the carbene center, and, to a small extent, even one of the arene C_{ipso} positions.

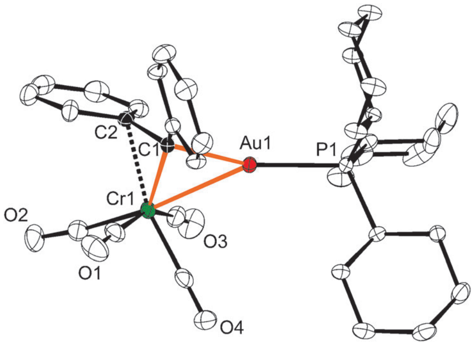


Figure 2. Structure of complex **14** (L = PCy$_3$) in the solid state; only the cationic entity is shown, whereas the escorting $[NTf_2]^-$ has been removed for clarity. For the entire structure, see the Supporting Information.

in the unit cell).[19] The carbene center is only slightly pyramidalized by the additional contact with the gold atom; the C1−Au distance (2.135(3) Å) falls into the range observed in related *gem*-bimetallic arrays.[24,25] The gold fragment is notably slipped away from the chromium center, residing almost perpendicularly over the carbene carbon atom (Cr1–C1–Au1, 82.28(12)°).[33] The rather long Cr···Au distance (2.7185(6) Å) speaks for an only weakly attractive interaction between the early- and late-transition-metal atoms.

The most unusual structural aspect of **14** is the contact between the chromium and the *ipso* carbon atom of the phenyl ring, which explains why this position is strongly shielded, and why the arene cannot rotate. Although the Cr1−C2 distance (2.281(10 Å) is too long for an efficient electronic communication, the interaction must be somehow constructive, because it prevents the collapse of the complex with release of the targeted free gold carbenoid **11**, even though one CO ligand has been spontaneously lost at −50 °C.

Qualitatively, this outcome can be rationalized as follows: Side-on coordination of $[LAu]^+$ deprives the Cr=C bond of **12** of a significant amount of electron density that is only partly compensated by back-donation from gold into the antibonding orbital (otherwise, rehybridization expressed by pyramidalization of C1 would be more prominent). The imparted partial positive charge reduces the ability of the chromium center to share its electrons with five electron-withdrawing CO ligands. To counterbalance this deficit, one of them is released and replaced by the best donor in vicinity, which turns out to be the π lobe of the *ipso* carbon atom of the adjacent aromatic ring. Although the electronic gain is likely to be minute,[34] the formation of an unstabilized gold carbenoid must be even less favorable. This interpretation also explains why the reaction of $[LAu]^+$ with the analogous tungsten complex **9**, which has a much higher core electron density, does not result in loss of CO, but stops at the initially formed pentacarbonyl complexes of type **10**.

DFT calculations at the RI-BP86/def2-TZVP + D3 level of theory substantiate the conclusions drawn from the structural and spectral data.[35] The calculated and experimental structures of **10**, **13**, and **14** are in excellent agreement; likewise, the NMR shifts were well reproduced with the B3LYP hybrid functional using an extended basis set and added relativistic corrections. In case of **14** (L = PCy$_3$), fragment molecular orbital analyses show that the LUMO of the gold entity accepts substantial electron density (ca. 0.45 electrons) from the HOMO and HOMO-1 of the $\{(CO)_4Cr{=}CPh_2\}$ fragment; nevertheless, the latter retains true carbene character as evident from simultaneous σ donation and π back-donation. Thus, the overall bonding situation in **14** is in fact best described as a chromium carbene that carries an η^2-bound, but visibly slipped, gold unit. Small Wiberg bond indices suggest that the Au–Cr, Au–C1, and Cr–C2 interactions are feeble. Likewise, natural bond order analysis and the topological characteristics of the electron density confirm that the *ipso* carbon atom, though remarkably shielded, is not engaged in a significant bonding interaction with the metal center.[35]

Our investigations confirm that gold-for-chromium carbene transfer is exceptionally facile, but only in the Fischer carbene series. As soon as stabilization of charge density by an adjacent heteroatom substituent is lacking, the transmetalation derails. Bimetallic complexes are formed instead, which have little in common with the unstabilized gold carbenoids that were invoked in many mechanistic discussions of π-acid catalysis. At this point, such species basically remain elusive from the experimental vantage point, as three of the very best entries into carbene complexes so far failed to deliver these species (diazo decomposition, cyclopropene rearrangement, carbene transfer). Even the cyclobutenyl intermediate **2**,[6] as the example that comes closest to this ideal, benefits from charge delocalization over several positions of a non-classical cation.[1,7] In future studies, we will strive to learn how much stabilization is necessary to enable full characterization of a pertinent donor-free gold carbenoid.

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[31] Some $[Cr(CO)_6]$ precipitated from the solution; other by-products could not be identified.

[32] The complex decomposes at RT within a few hours to give tetraphenylethene (89%) and benzophenone (11%) as the major products according to GC–MS analysis.

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[35] For detailed information, see the Supporting Information.