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The First Crystal Structure of a Reactive Dirhodium Carbene Complex and a Versatile Method for the Preparation of Gold Carbenes by Rhodium-to-Gold Transmetalation

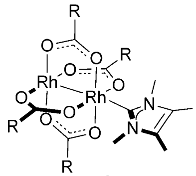
*Christophe Werlé, Richard Goddard, and Alois Fürstner**

Dedicated to Professor Steven L. Buchwald on the occasion of his 60th birthday

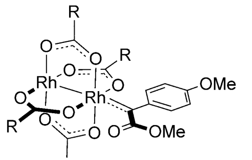
Abstract: *The dirhodium carbene derived from bis(4-methoxyphenyl)diazomethane and* $[Rh(tpa)_4]\cdot CH_2Cl_2$ *(tpa = triphenylacetate) was characterized by UV, IR, and NMR spectroscopy, HRMS, as well as by X-ray diffraction. The isolated complex exhibits prototypical rhodium carbene reactivity in that it cyclopropanates 4-methoxystyrene at low temperature. Experimental structural information on this important type of reactive intermediate is extremely scarce and thus serves as a reference point for mechanistic discussions of rhodium catalysis in general. Moreover, dirhodium carbenes are shown to undergo remarkably facile carbene transfer on treatment with* $[LAuNTf_2]$ *(L = phosphine). This formal transmetalation opens a valuable new entry into gold carbene complexes that cannot easily be made otherwise; three fully characterized representatives illustrate this aspect.*

Dirhodium carbenes, which are usually formed by decomposition of an appropriate diazo derivative with a dirhodium tetracarboxylate salt, have gained eminent importance in (asymmetric) synthesis and catalysis.[1–5] They largely owe their "superelectrophilic" character to a three-center/four-electron bonding situation at the Rh-Rh-C core,[6] which accounts for the unusually low Rh−C bond order (< 1) and the high kinetic lability of the carbenes.

As a consequence of their exceptional reactivity, however, intermediates of this type have long defied direct inspection; structural information was basically limited to computational data generated over the years at different levels of theory.[7–10] Only recently have Davies, Berry, and co-workers managed to characterize the push-pull dirhodium carbene **2** by NMR, EXAFS, and optical spectroscopy.[11]



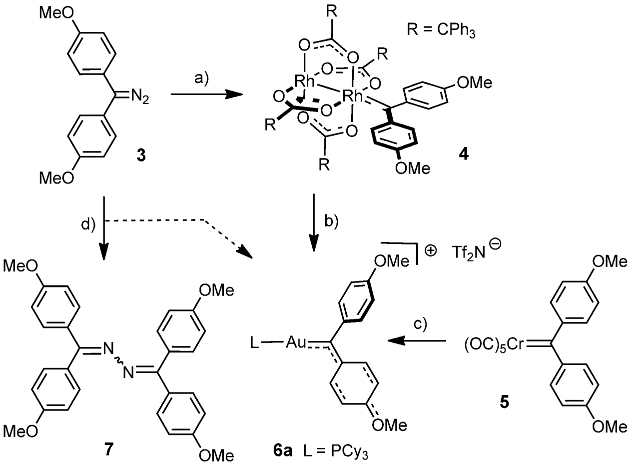
1 (R = *t*Bu)



2 (R = CPh$_3$)

The only prior information was obtained from the crystal structures of NHC adducts such as **1** (NHC = N-heterocyclic carbene).[12,13] As the coordination of the NHC ligand in **1** is reversible, however, this complex solely acts as a reservoir of $[Rh_2(tBuCOO)_4]$ and lacks the prototypical reactivity of an electrophilic rhodium carbene; in other complexes, the NHC serves as an ancillary ligand. As a result, the implications of this type of structure remained unclear. In contrast, the dirhodium carbene complex **4** (see below) readily cyclopropanates standard olefin substrates, but is kinetically stable enough to allow for its full characterization by spectroscopic as well as crystallographic means. For this reason, we consider this structure to be an important milestone for understanding rhodium catalysis in general.

Key to success was the use of the bis(4-methoxyphenyl)-carbene backbone; our previous work on reactive gold carbenes had taught us that this particular structural motif is capable of imparting *meta*-stability onto highly electrophilic and, hence, very reactive species (Scheme 1).[14,15] Under the premise that this conclusion is applicable to the rhodium



Scheme 1. a) $[Rh_2(tpa)_4]\cdot CH_2Cl_2$, CH_2Cl_2, −10 °C; b) $[(Cy_3P)AuNTf_2]$, CH_2Cl_2, −78 °C→−10 °C, 64 %; c) $[(Cy_3P)AuNTf_2]$, CH_2Cl_2, −50 °C, see Ref. [14]; d) $[LAuNTf_2]$, CH_2Cl_2, see text. Cy = cyclohexyl, Tf = trifluoromethanesulfonyl, tpa = triphenylacetate.

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series, a precooled dark-purple solution of the diazo derivative **3**[16] in CH_2Cl_2 was added to a cold solution of $[Rh_2(tpa)_4]\cdot CH_2Cl_2$ in the same solvent under rigorously inert conditions. This caused an instantaneous evolution of nitrogen gas and a color change to dark turquoise. In line with our expectations, the resulting major product turned out to be sufficiently stable at low temperature for characterization by UV, IR, and NMR spectroscopy as well as by HRMS (see the Supporting Information). The recorded data are fully consistent with the expected dirhodium complex **4**. Particularly informative is the chemical shift of the carbene C atom at $\delta_C = 268.9$ ppm, which is markedly downfield from that of the push-pull dirhodium carbene **2** observed by Davies, Berry, and co-workers ($\delta_C = 242$ ppm).[11] Control experiments proved that this exceptionally sensitive compound is reactive and able to cyclopropanate 4-methoxystyrene at low temperature; thus the structural features of **4** are deemed relevant for mechanistic discussions.

After considerable experimentation, we managed to grow single crystals of **4** that were suitable for X-ray diffraction. The complex is stable in crystalline form for only less than 12 h at −20 °C and appears to require CH_2Cl_2 solute to be present. While the diffraction data of single crystals grown from CH_2Cl_2/toluene could only be refined by restraining all the atoms, except Rh and Cl, to be isotropic with an effective standard deviation of 0.001 (764 restraints; $R = 7.6\,\%$),[17] crystals obtained from fluorobenzene/toluene/CH_2Cl_2[18] were of better quality, such that all the atoms of the complex could be refined anisotropically ($R = 5.9\,\%$). Although the CH_2Cl_2 solute is still disordered, all the conformational features as well as the metric parameters of the reactive dirhodium carbene complex itself are unambiguous (Figure 1).

Complex **4** crystallizes as a coordination polymer in which the OMe group of one monomer unit ligates Rh2 of the next monomer (for details, see the Supporting Information). As expected, the carbene moiety occupies the axial coordination site on the dirhodium core. One of the flanking arene rings adopts an almost coplanar orientation with the (empty) 2p carbene orbital, which represents the major lobe of the LUMO.[6,9] This arrangement ensures an effective overlap and hence imposes just enough stability to this highly electrophilic entity to allow for the isolation and short-term handling of the complex. The tight Ar–C: contacts lead to remarkably short bonds between the carbene center and the *ipso*-C(arene) atoms. At only 1.426(8) and 1.438(8) Å, these bonds are shorter than those in the electron-deficient gold carbene **6a** previously described by our group (Scheme 1).[14] The bond lengths suggest that significant charge density resides on the organic backbone and nicely illustrate the exceptional electron demand of the "superelectrophilic" carbene center.[1–5] This view concurs with the low-field ^{13}C NMR shift (see above) as well as the unusual reactivity of this complex even towards electrophilic gold sources (see below).

To relieve steric pressure, the entire carbene moiety in **4** adopts a staggered conformation relative to the tetracarboxylate dirhodium core, although this conformer has previously been computed for model compounds to be the (low-lying) transition state of rotation about the Rh1−C bond, with the eclipsed orientation being the minimum energy structure.[9] In this context, one has to consider that the D_4 symmetry of the dimetallic cage renders the $4d_{xz}$ and $4d_{yz}$ orbitals of Rh1 degenerate: either one—as well as a linear combination thereof—is able to engage with the (empty) 2p carbene orbital to some degree, such that back-donation will never completely cease in any conformer.[6–8] As a result, the barrier to rotation about the Rh1−C bond in **4** is also expected to be low. This conclusion concurs with previous computations on the simplified model dirhodium carbenes **8** and **9** formally derived from diazomethane or diazoacetate, respectively (Figure 2).[9]

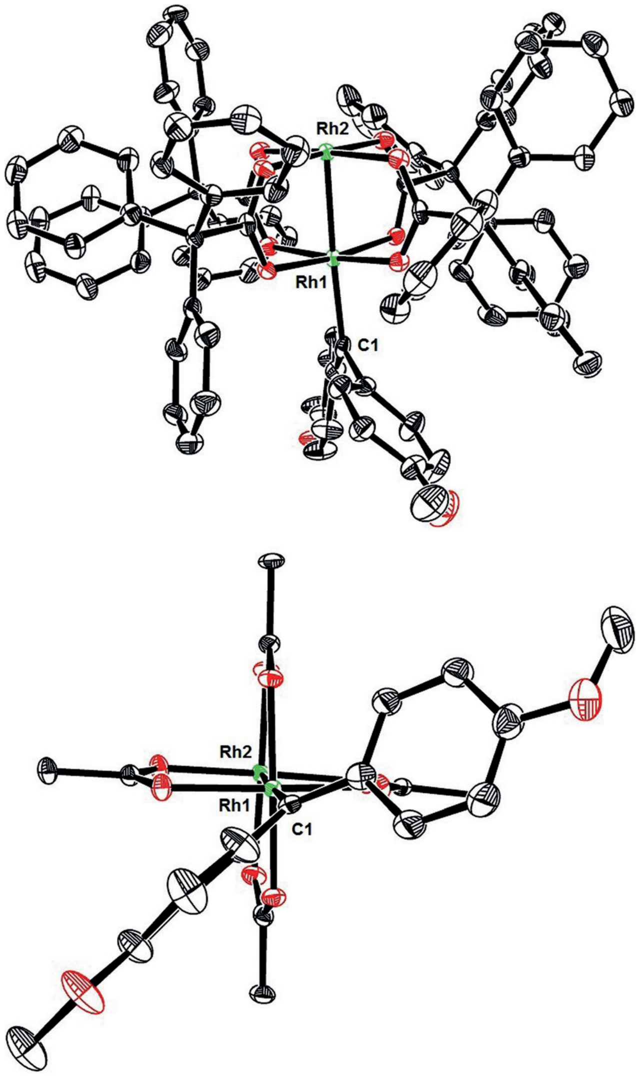


Figure 1. Top: Structure of the dirhodium tetracarboxylate carbene **4** in the solid state; cocrystallized CH_2Cl_2 and toluene molecules are omitted for clarity; the complex is a coordination polymer (see the Supporting Information); bottom: Newman-type projection along the C1-Rh1-Rh2 axis, which shows the alignment of one of the *p*-$MeOC_6H_4$ rings with the carbene center and the eclipsed orientation of the entire carbene moiety relative to the dirhodium cage (its lateral phenyl rings are removed for clarity).

The bonding situation within the central Rh2-Rh1-C1 unit of dirhodium carbene complexes is best described by a three-center/four-electron interaction, which infers low bond orders

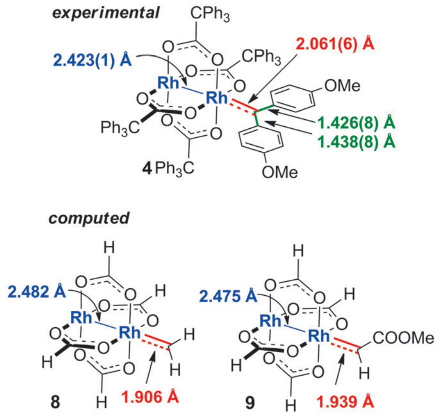
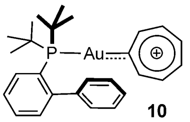


Figure 2. Relevant bond lengths in **4**; comparison with the computed distances of two simplified model compounds; see Ref. [9].

and long distances between all partners.[6,9,11] In line with this notion, the Rh1–Rh2 bond in **4** is longer (2.423(1) Å) than the average distance observed in ordinary dirhodium tetracarboxylate complexes (ca. 2.35 Å) and similar to the one found in the NHC adduct **1** (2.424 Å),[12] but notably shorter than in the computed structures.[9] Arguably more striking is the Rh1–C1 bond length of 2.061(6) Å, which clearly exceeds the computed 1.906 Å for **8** or 1.939 Å for **9**.[9] Once again, the corresponding bond length in the dirhodium-NHC adduct **1** is comparable (2.057 Å), even though this complex shows different reactivity as mentioned previously. We presume that the remarkably long experimental Rh1–C distances in both complexes reflect the preference of the carbene center to engage primarily with the flanking arene rings in **4** or with the neighboring N atoms of the NHC in **1** rather than with the d electrons that Rh1 could provide. Since **4** exhibits the reactivity profile of an ordinary dirhodium carbene, however, this finding is thought to be an important reference and calibration point for further experimental and computational investigations into this flourishing field of catalysis.[1–5]

The exceptionally electrophilic character of this dirhodium carbene is also reflected in its reactivity. Thus, complex **4** was found to undergo a remarkably easy Rh→Au carbene transfer on treatment with [(Cy$_3$P)AuNTf$_2$][19,20] at low temperature to give the corresponding gold carbene **6a** in good yield (Scheme 1). This result is somewhat counterintuitive, since gold complexes themselves have gained prominence as π-acid catalysts because of their pronounced electrophilic nature.[21,22] Complex **6a** had originally been prepared by transmetalation of the Fischer chromium carbene **5**,[23] because attempted decompositions of the diazo precursor **3** with various gold sources of type [LAuNTf$_2$] had invariably led to formation of azine **7** as the major product (Scheme 1).[14,15,24] Since the preparation of **5** is challenging (a speedy chromatographic purification at low temperature is the best way to purify the compound), the new entry into gold carbenes by transmetalation of a dirhodium precursor is clearly more practical. This is particularly true since the diazo derivative **3** can be readily prepared on a large scale and is safe to handle.[16] Thus, this method lends itself to a more systematic study into structure/reactivity relationships of gold carbenes, which is necessary for a better understanding of this topical branch of catalysis research.[21,22] Since the disclosure of our complex **6a** as the first reactive gold carbene to be fully characterized structurally and spectroscopically,[14,15] a small set of other well-defined gold carbenes has been published.



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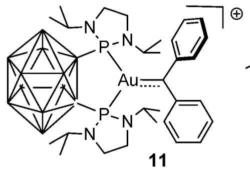

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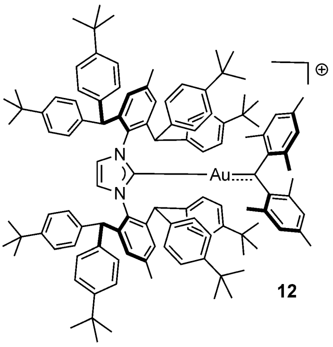

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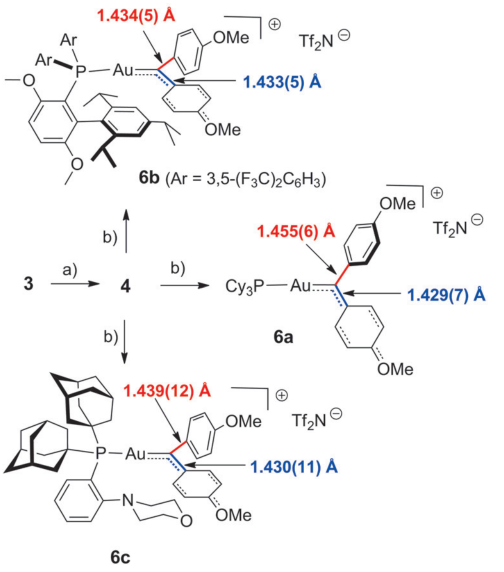
Whereas complex **10** draws its stability mainly from charge delocalization over the (aromatic) organic ligand framework,[25] complex **11** features an unusual trigonal coordination geometry about the Au$^{\text{I}}$ center,[26] while the carbene unit in complex **12** is massively shielded.[24,27] Together with other relevant data,[28–30] these species greatly help in putting the mechanistic discussions on a firmer basis, but do not allow certain subtle but important aspects of gold catalysis to be rationalized. It is well known, for example, that the reactivity of gold carbenes is tunable by proper choice of the ancillary ligand.[21,22,31] To better understand this subtle but essential chemical attribute, it is necessary in the long run to learn how changes of the *trans* ligand affect the structure of a given gold carbene.

The new method described here allows such systematic investigations to be carried out. This aspect is aptly illustrated by the preparation of two additional complexes of type **6** which differ from the parent complex **6a** (L = PCy$_3$) only in the two-electron donor L at the *trans* position (Scheme 2). Specifically, complex **6b** (Figure 3) contains a member of Buchwald's phosphine ligand family, the donor capacity of which is down-regulated by four CF$_3$ substituents on the P-Ar$_2$ groups.[32] In contrast, the Mor-DalPhos ligand[33,34] in **6c** is highly electron donating (Figure 4). The fact that the molecular structures and spectral properties of **6a–c** reflect these differences only to a limited extent is arguably telling: Although the Au–C bond lengths are responsive to the nature of L, they fall into a rather narrow range (**6a**: 2.039(5) Å, **6b**: 2.028(4) Å, **6c**: 2.020(8) Å).[35,36] In all the cases investigated, the carbene center seems to draw stability primarily from an interaction with the flanking aryl groups, as manifested in the short bonds to the *ipso*-C atoms. Although the *p*-MeOC$_6$H$_4$ rings are slightly twisted out of coplanarity in the solid state, likely to relieve steric repulsion of the *ortho* protons, they give rise to a single set of NMR signals, even at −50 °C. For the low rotational barrier, their π systems can engage with the (empty) 2p carbene lobe, and this interaction prevails over LAu→C: electron back-donation. This interpretation is consistent with the fact that the carbene centers in



Scheme 2. Preparation of gold carbenes differing only in the *trans* ligand by transmetalation of the dirhodium carbene precursor **4**: a) $[Rh_2(tpa)_4]\cdot CH_2Cl_2$, CH_2Cl_2, −10 °C; b) $[LAuNTf_2]$, CH_2Cl_2, −78 °C→ −10 °C, 64 % (**6a**), 29 % (**6b**), 47 % (**6c**).

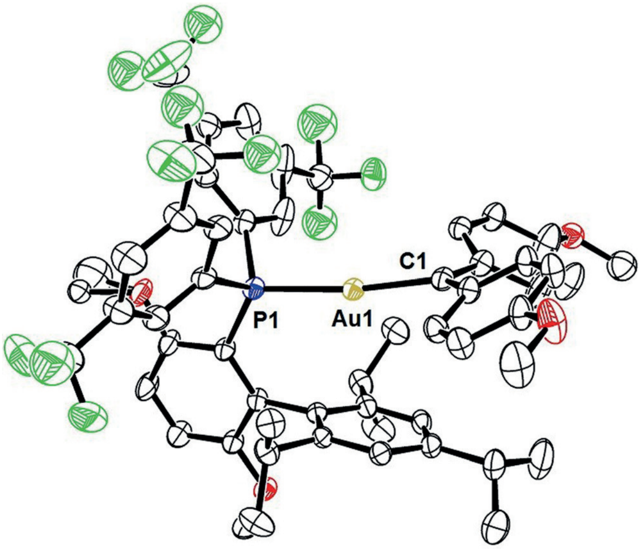


Figure 3. Structure of the gold carbene **6b** in the solid state; only the complex cation is shown for clarity.

6a (285 ppm), **6b** (275 ppm), and **6c** (290 ppm) respond to the donor ability of the *trans* ligand, yet resonate within a fairly narrow shift range. Only when an effective electronic communication between the flanking arene rings and the carbene is precluded on steric grounds does the shift of the carbene C atom unmistakably show the change: this is the case in complex **12**, which bears mesityl rings that are necessarily twisted out of coplanarity.[27] The resulting more pronounced deshielding ($\delta_C = 321$ ppm) also suggests that LAu→C: back-donation does not fully compensate for the largely missing interaction with the arene π clouds.

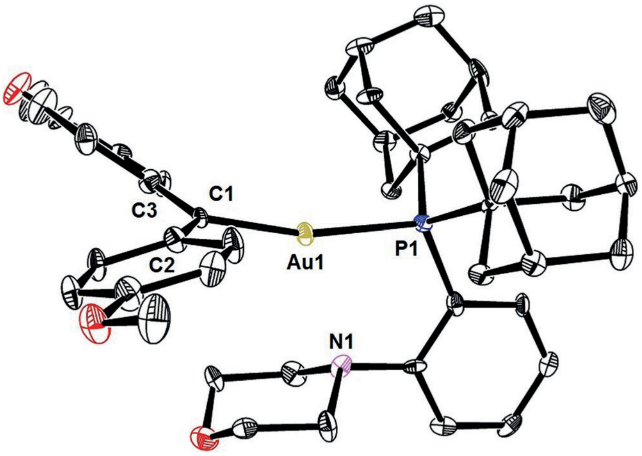


Figure 4. Structure of the gold carbene **6c** in the solid state; only one complex cation of the two independent molecules in the asymmetric unit is shown for clarity.

We conclude that the dirhodium carbene complex outlined above constitutes a calibration point for further investigations into this vibrant field of research as it is the first representative which features the prototypical reactivity of intermediates of this type that has been fully characterized by spectroscopic as well as crystallographic means. Moreover, it readily engages in transmetalation with other late-transition elements, which opens a new window for studies into gold carbenes and beyond.

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Keywords: carbene complexes · gold · homogeneous catalysis · rhodium · transmetalation

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[36] Secondary interactions between the Au center and the lateral aryl ring in **6b** or the N atom of the morpholino substituent in **6c** force the P-Au-C axes in these complexes to bend away from linearity (173° and 166°, respectively).

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