Angewandte International Edition Chemie

Gold Carbenoids | Hot Paper

DOI: 10.1002/anie.201402080

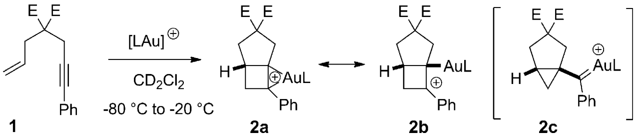
Structure of a Reactive Gold Carbenoid**

*Günter Seidel and Alois Fürstner**

Abstract: *A formal gold-for-chromium transmetalation allowed the gold carbenoid species* $[Cy_3PAuCAr_2]NTf_2$ (***11***) $(Ar = pMeOC_6H_4\text{-})$ *to be obtained in crystalline form. The structure in the solid state suggests that there is only little back donation of electron density from gold to the carbene center of **11** and hence very modest Au–C double-bond character; rather, it is the organic ligand framework that is responsible for stabilizing this species by resonance delocalization of the accumulated positive charge. Because **11** is capable of cyclopropanating p-methoxystyrene even at low temperature, the discussion of its structure is deemed relevant for a better understanding of the mechanisms of* π*-acid catalysis in general.*

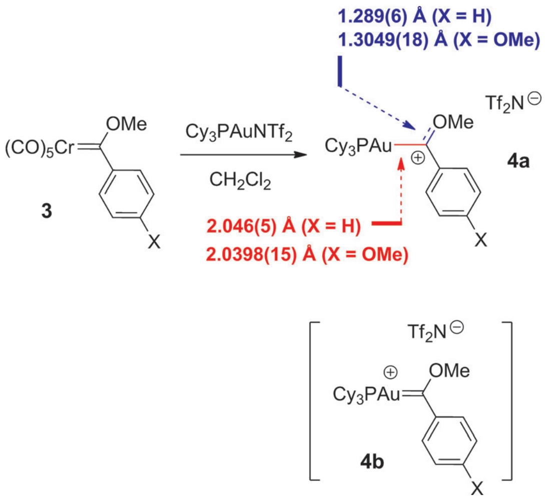
It is undisputed that many transformations induced by gold catalysts proceed via carbenoid intermediates, but the very nature of the Au–C bond in such species has been a matter of debate.[1–6] The ambiguity is basically due to the fact that structural data are largely missing and most information had to be inferred from the analysis of reactivity patterns in solution or in the gas phase.[1–6] Computational chemistry partly filled this gap, but was not considered unambiguous either with regard to its methods and conclusions.[7]

Only recently have Widenhoefer and co-workers managed to observe by NMR spectroscopy at low temperature a bare gold carbenoid formed by a prototype enyne rearrangement (Scheme 1).[8,9] Interestingly, it is the cyclobutenyl resonance extreme **2a**,**b** that describes this intermediate better than the cyclopropylmethyl form **2c**, which is prevalent in the literature otherwise. This benchmark corroborates our early interpretation of π-acid catalysis, which implied build-up of considerable charge density on the organic ligand that gets delocalized over more than one position.[10–12]



Scheme 1. Generation of a gold carbenoid, which is stable enough for NMR analysis, by enyne rearrangement (see Ref. [8]). For the sake of clarity, the noncoordinating counterion is not depicted. L = two-electron donor ligand.

Complementary information comes from the solid state structures of gold complexes of the Fischer carbene type.[13–15] However, the presence of a stabilizing heteroatom substituent at the carbene center reduces the reactivity to the extent that the relevance of the acquired knowledge for the interpretation of gold catalysis can be questioned. In fact, prototype complexes such as **4** feature little "ordinary" carbene character, as the Au–C bond order is very close to one, whereas the C–O distance is notably contracted (Scheme 2).[16] These metric data suggests that the oxocarbenium structure **4a** is the most appropriate description.[17] Even if a heteroelement substituent with largely reduced donor capacity is present, as in complex $[(Ph_3P)AuCH_2Cl]$, the Au–C distance (2.088(9) Å) does not contract; rather, the C–Cl bond becomes unusually short.[18]



Scheme 2. Representative Fischer-type gold carbenoids formed by facile gold-for-chromium exchange. Tf = trifluoromethylsulfonyl.[16]

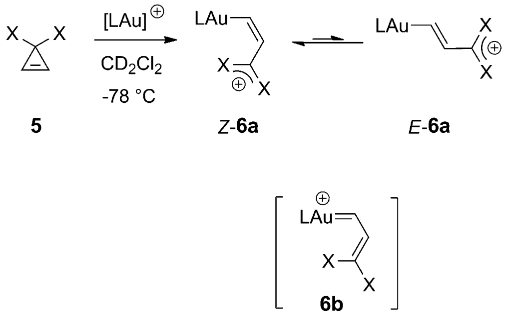
This picture does not change either upon shifting the heteroelement substituents to the vinylogous position, although the resulting carbenoids have lost much of their thermal stability and must be prepared and handled at low temperature (Scheme 3).[20,21] Detailed NMR analysis revealed surprisingly low barriers to rotation about the Au–C and the vinylogous $C{-}C(OR)_2$ bonds in **6** (X = OMe). The carbene resonance extreme **6b** obviously contributes very little to the ground state structure of this species, which is basically a regular alkenyl gold complex bearing a cationic ligand (**6a**).[20] Attempts at making analogous complexes devoid of the heteroatoms were largely unsuccessful. Subsequent computations indicated that the rotational barriers in putative species of type **6** (X = alkyl) would be higher, as one

---

[*] Ing. G. Seidel, Prof. A. Fürstner
Max-Planck-Institut für Kohlenforschung
45470 Mülheim/Ruhr (Germany)
E-mail: fuerstner@kofo.mpf.de

[**] Generous financial support by the MPG and the Fonds der Chemischen Industrie is gratefully acknowledged. We thank J. Rust, E. Dreher, and Prof. C. W. Lehmann for solving the X-ray structure and W. Wisniewski and Dr. C. Farès for support with NMR analyses.

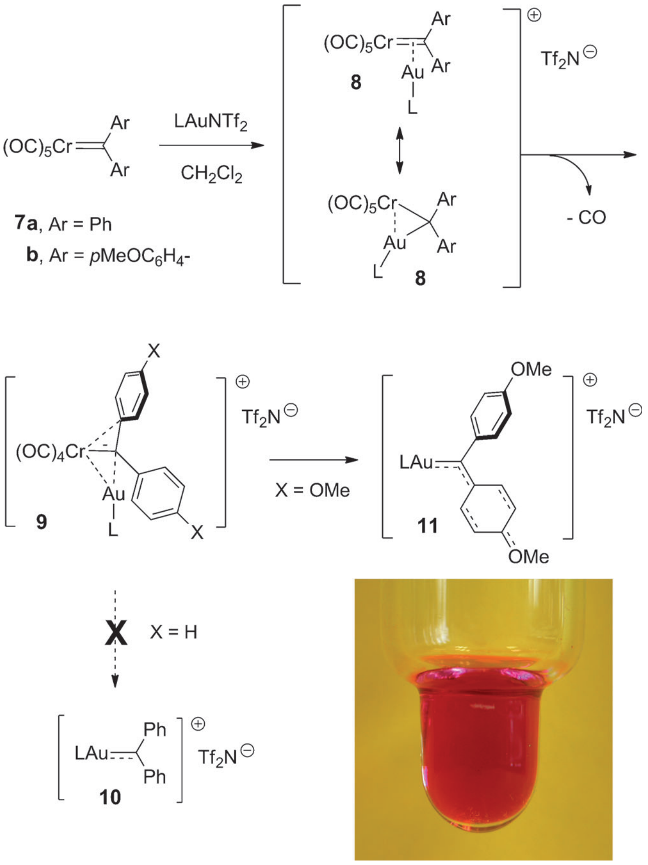
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201402080.



Scheme 3. Gold carbenoids formed by cyclopropene rearrangement. The species are stable enough for characterization by NMR spectroscopy, provided X = OR (see the main text).[20]

might expect, although the overall Au–C bond order remains close to one.[22] A peculiar three-center/four-electron bonding mode was made accountable for this situation; the proposed model suggests that the character of these intermediates lies on a continuum between cations and carbenes, depending on the ancillary ligands and the particular substitution patterns.

In another attempt to prepare gold carbenoids devoid of any stabilizing heteroelements, we relied on a transmetalation approach (Scheme 4).[23] Because Fischer carbene complexes of chromium or tungsten are known to undergo exceptionally facile carbene transfer upon treatment with an appropriate Au$^{\text{I}}$ source (the complexes **4** were prepared this way),[13] the analogous reaction of $Ph_2C{=}Cr(CO)_5$ (**7a**) with $LAuNTf_2$ ($L = Cy_3P$, Me_3P, Ph_3P, IMes) was investigated. Surprisingly though, formation of the putative gold carbenoid of type **10** could not be enforced. η^2-Coordination of the gold fragment was observed instead, which deprives the chromium carbene unit of electron density to the extent that the primary adduct **8a** has to abandon one of the electron-withdrawing CO ligands even at −50 °C. The resulting bimetallic species **9a** escapes breakdown to the targeted gold carbenoid **10** by using one of the neighboring phenyl rings for protection. Despite the close contact, the electronic gain for the $[Cr(CO)_4]$ fragment is small as any significant bonding interaction would deprive this aryl group of its resonance stabilization; the proximal phenyl ring therefore mainly serves as a steric guard.[23] Nevertheless, this unorthodox situation is preferred over release of the "unstabilized" gold carbenoid **10**. When allowed to reach ambient temperature, the bimetallic complex **9a** simply decomposed.



Scheme 4. Transmetalation of chromium carbenes with Au$^{\text{I}}$. The outcome of the reaction is dependent on the nature of the aryl groups (Ar) flanking the carbene center. The photograph shows the characteristic pink color of the gold carbenoid **11** dissolved in CD_2Cl_2. $L = Cy_3P$.

The reluctance of **7a** to gold-for-chromium exchange stands in striking contrast to the ease with which the more stabilized Fischer carbenes **3** underwent this transformation (see Scheme 2).[23] This antagonistic situation insinuates that a [LAu] fragment alone is not able to impart sufficient stability onto a gold carbenoid to allow spectroscopic or structural interrogation. Even two flanking phenyl groups, if unsubstituted, do not suffice to compensate the evidently only small contribution of the [LAu] fragment. More effective ways to satisfy the empty orbital are needed to ensure appreciable lifetimes. With this idea in mind, we set out to prospect the borderline at which gold carbenoids transition from fleeting to discrete intermediates by subjecting various complexes of the type $Ar_2C{=}Cr(CO)_5$ (**7**, Ar ≠ Ph), which solely differ in the electronic properties of their aryl rings, to transmetalation.

The known complex **7b**[24] seemed to be a promising candidate en route to a gold carbenoid that remains reactive, yet becomes stable enough for structural inspection. Hence, it was treated with $[(Cy_3P)Au]NTf_2$ in CD_2Cl_2 at −78 °C to give a mixture of the expected bimetallic adducts **8b** and **9b** as the primary products, which were easily discerned by their characteristic spectroscopic fingerprints.[25] However, an additional species with a distinctive low-field signal at $\delta_C = 284.5$ ppm (d, $J_{C,P} = 95$ Hz) was present. This spectral signature suggested that the new compound might be the sought-after gold carbenoid **11**,[26] whose unsubstituted analogue **10** had remained elusive. Upon raising the temperature to −50 °C, the initial adduct **8b** disappeared; careful fractional crystallization of the resulting mixture of **9b** (ca. 40 % by ^{31}P NMR spectroscopy) and **11** as the major constituent (ca. 60 %) at low temperature furnished bright-red crystals of the latter compound suitable for X-ray diffraction.

Inspection of the structure of **11** in the solid state (Figure 1) shows that the Au–C1 "carbene" bond (2.039(5) Å) has the exact same length as that in **4** (X = OMe, 2.0398(15) Å), which bears the OMe substituent directly at the carbene center.[19,27] This striking insensitivity of the Au–C distance to a substantial change in the first coordination sphere of the metal stands in marked contrast to

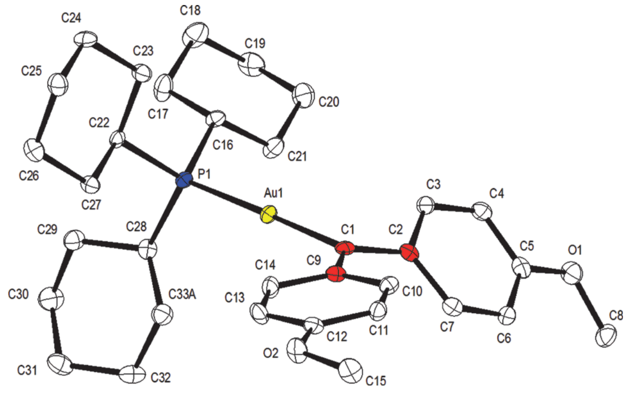


Figure 1. Structure of the gold carbenoid **11** in the solid state. Only the cationic entity is shown, the counterion [NTf$_2$]$^-$ was removed for clarity. For the entire structure, see the Supporting Information. For selected bond lengths, see Figure 2. Selected bond angles [°]: Au1-C1-C2 115.8(3), Au1-C1-C9 122.8(3), C2-C1-C9 120.9(4), P1-Au1-C1 176.78(13).

the unmistakable shortening of the bonds between the carbenoid center and the aryl groups (C1–C9, 1.429(7) Å; C1–C2, 1.455(6) Å). The more contracted C1−C9 bond connects to an aryl ring that is nearly co-planar with the carbene center to enable efficient orbital overlap and seems to carry much of the electronic burden for the stabilization of **11**; the other arene is somewhat tilted to relieve the van der Waals repulsion of the protons in *ortho* position. However, this conformational situation averages out in solution because the two aromatic rings give rise to only a single set of signals, even at −50 °C. Further lowering of the temperature to −80 °C allowed the barrier of the rotation about the C1−C$_{ipso}$ bonds to be roughly estimated as 35 kJ mol^{-1}; the truly carbenoid-like character of **11** is nicely manifested in this value.[28]

It is also informative to compare the solid-state structure of **11** with those of other species that contain an sp^2-hybridized carbon center carrying two anisyl rings (Figure 2). Two ruthenium carbenes of this type are known;[29–31] interestingly, neither **13** nor **14** show any significant shortening of the C1−C$_{ipso}$ bonds, the lengths of which are comparable to those of the parent ketone **12**.[32] In contrast, the pattern in **11** echoes the situation in a series of prototype diarylcarbenium ions, such as **15**–**18**.[33] Manifestly, the substituted arene rings play the dominant role in stabilizing the gold carbenoid. This conclusion is consistent with the fact that the bimetallic array **9b** (X = OMe) does release complex **11**, whereas the parent complex **10** with a carbenoid center flanked by unsubstituted and hence somewhat less electron-rich phenyl rings could not be set free as a discrete species from the analogous precursor complex **9a** (X = H).[23] Thus, electron back donation from the filled d-orbitals of gold to the empty π-orbital of the carbene alone is not sufficient to impart a finite lifetime onto such species, even if the metal carries an electron-donating trialkylphosphine ligand such as Cy$_3$P.[34,35]

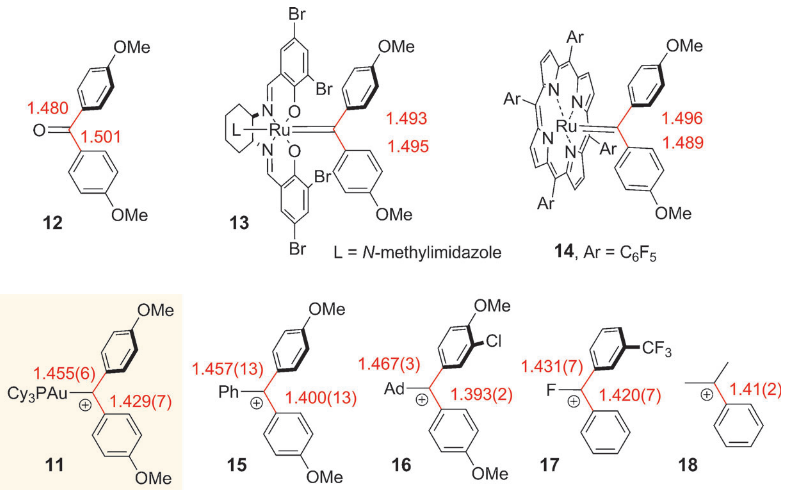
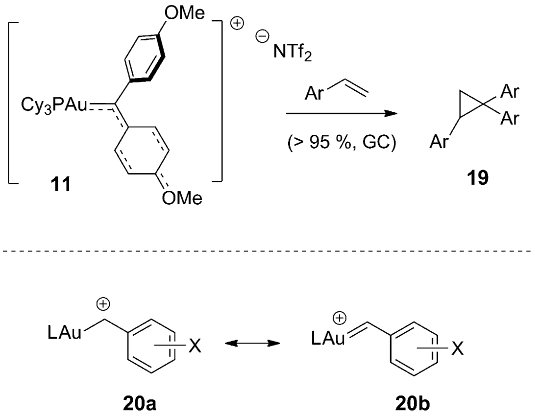


Figure 2. Characteristic C1−C$_{ipso}$ bond lengths in the solid-state structures of different species comprising a [C(sp^2)Ar$_2$] core. The counterions are not shown for clarity. Ad = 1-adamantyl.



Scheme 5. Cyclopropanation by the gold carbenoid **11** and comparison with gold benzylidene species previously proposed in the literature. Ar = *p*MeOC$_6$H$_4$-, L = neutral two-electron donor ligand.

Complex **11** is a close relative of a series of putative gold benzylidene species of type [ArCHAuL]$^+$ (**20**) that were implicated in cyclopropanation reactions of various olefins (Scheme 5).[36–38] To probe the functional link, excess *p*-methoxystyrene was added to the intensely pink-colored solution of the carbenoid **11** at −78 °C and the mixture was then slowly warmed. The characteristic color (see Scheme 4) started to fade away at −20 °C, and full conversion (> 95 %, GC/MS) to the corresponding cyclopropane **19** was observed when room temperature was reached.[39] This observation confirms that the discussion of the structural features of **11** is relevant for the mechanistic understanding of π-acid catalysis.

Carbon species that carry a formal positive charge (or a good leaving group) and a carbon–metal bond at the same site are commonly called "carbenoids". Evidently, complex **11** and analogues fall into this category.[40–42] Yet, it remains a semantic question if one prefers the expressions "gold carbenes" or "gold-stabilized carbocations" over the terminus "gold carbenoids" in an attempt to emphasize certain aspects of their reactivity. What is not a matter of taste, however, is the fact that the popular notion of gold–carbon "double bonds" is currently not supported by any structural or spectral evidence. Back donation of electron density from gold to the vacant carbene π-orbital is certainly operative and may even be tuned to some extent by proper choice of the ancillary ligand,[22,43] but this effect alone is evidently too small to impart finite lifetimes onto such species. Rather, the charge density at the carbenoid site has to obtain stabilization from the organic ligand framework by other means, such as resonance or delocalization (see the intermediate **2**).[8] We recommend to acknowledge this attribute by not using the [Au=C] notation whenever referring to distinct intermediates of this type in condensed phase.

Received: February 4, 2014

Keywords: bonding · carbenoids · catalysis · cyclopropanation · gold

---

[1] a) A. Fürstner, P. W. Davies, *Angew. Chem.* **2007**, *119*, 3478–3519; *Angew. Chem. Int. Ed.* **2007**, *46*, 3410–3449; b) A. Fürstner, *Chem. Soc. Rev.* **2009**, *38*, 3208–3221.

[2] D. J. Gorin, F. D. Toste, *Nature* **2007**, *446*, 395–403.

[3] C. Obradors, A. M. Echavarren, *Chem. Commun.* **2014**, *50*, 16–28.

[4] A. S. K. Hashmi, *Angew. Chem.* **2008**, *120*, 6856–6858; *Angew. Chem. Int. Ed.* **2008**, *47*, 6754–6756.

[5] For reviews on structurally characterized intermediates in gold catalysis, see: a) A. S. K. Hashmi, *Angew. Chem.* **2010**, *122*, 5360–5369; *Angew. Chem. Int. Ed.* **2010**, *49*, 5232–5241; b) L.-P. Liu, G. B. Hammond, *Chem. Soc. Rev.* **2012**, *41*, 3129–3139; c) H. G. Raubenheimer, H. Schmidbaur, *S. Afr. J. Sci.* **2011**, *107*, 31–43.

[6] A. Fürstner, *Acc. Chem. Res.* **2014**, DOI: 10.1021/ar4001789.

[7] For a comment, see: D. A. Dixon, *J. Am. Chem. Soc.* **2011**, *133*, 19257.

[8] R. E. M. Brooner, T. J. Brown, R. A. Widenhoefer, *Angew. Chem.* **2013**, *125*, 6379–6381; *Angew. Chem. Int. Ed.* **2013**, *52*, 6259–6261.

[9] A. Fürstner, P. W. Davies, T. Gress, *J. Am. Chem. Soc.* **2005**, *127*, 8244–8245.

[10] a) A. Fürstner, H. Szillat, B. Gabor, R. Mynott, *J. Am. Chem. Soc.* **1998**, *120*, 8305–8314; b) A. Fürstner, F. Stelzer, H. Szillat, *J. Am. Chem. Soc.* **2001**, *123*, 11863–11869.

[11] A. Fürstner, C. Aïssa, *J. Am. Chem. Soc.* **2006**, *128*, 6306–6307.

[12] A. Fürstner, L. Morency, *Angew. Chem.* **2008**, *120*, 5108–5111; *Angew. Chem. Int. Ed.* **2008**, *47*, 5030–5033.

[13] a) R. Aumann, E. O. Fischer, *Chem. Ber.* **1981**, *114*, 1853–1857; b) E. O. Fischer, M. Böck, R. Aumann, *Chem. Ber.* **1983**, *116*, 3618–3623; c) E. O. Fischer, M. Böck, *J. Organomet. Chem.* **1985**, *287*, 279–285.

[14] U. Schubert, K. Ackermann, R. Aumann, *Cryst. Struct. Comm.* **1982**, *11*, 591–594.

[15] a) M. Fañanás-Mastral, F. Aznar, *Organometallics* **2009**, *28*, 666–668; b) F. Kessler, N. Szesni, C. Maaß, C. Hohberger, B. Weibert, H. Fischer, *J. Organomet. Chem.* **2007**, *692*, 3005–3018; c) S.-T. Liu, T.-Y. Hsieh, G.-H. Lee, S.-M. Peng, *Organometallics* **1998**, *17*, 993–995; d) see also: M. Gómez-Gallego, M. J. Mancheño, M. A. Sierra, *Acc. Chem. Res.* **2005**, *38*, 44–53.

[16] For the structure of **4** (X = H), see Ref. [23]; for the structure of the analogous complex **4** (X = OMe), which was prepared to allow an even better comparison with **11**, see the Supporting Information.

[17] We have already emphasized that a complex previously formulated as [ClAu = C(Ph)(NMe$_2$)] (see Ref. [14]) might be more adequately viewed as an iminium cation in the coordination sphere of a gold fragment, see Ref. [1,20].

[18] D. Steinborn, S. Becke, R. Herzog, M. Günter, R. Kircheisen, H. Stoeckli-Evans, C. Bruhn, *Z. Anorg. Allg. Chem.* **1998**, *624*, 1303–1307.

[19] For comparison, the Au–C bond length in [Ph$_3$PAu-Ph] is 2.045(6) Å, see E. J. Fernández, A. Laguna, M. E. Olmos, *Adv. Organomet. Chem.* **2005**, *52*, 77–141.

[20] G. Seidel, R. Mynott, A. Fürstner, *Angew. Chem.* **2009**, *121*, 2548–2551; *Angew. Chem. Int. Ed.* **2009**, *48*, 2510–2513.

[21] For a more stabilized variant in which the vinylogous heteroatom donor is part of a heterocyclic ring, see: C. E. Strasser, E. Stander-Grobler, O. Schuster, S. Cronje, H. G. Raubenheimer, *Eur. J. Inorg. Chem.* **2009**, 1905–1912.

[22] D. Benitez, N. D. Shapiro, E. Tkatchouk, Y. Wang, W. A. Goddard, F. D. Toste, *Nat. Chem.* **2009**, *1*, 482–486.

[23] G. Seidel, B. Gabor, R. Goddard, B. Heggen, W. Thiel, A. Fürstner, *Angew. Chem.* **2014**, *126*, 898–901; *Angew. Chem. Int. Ed.* **2014**, *53*, 879–882.

[24] J. Pfeiffer, K. H. Dötz, *Organometallics* **1998**, *17*, 4353–4361.

[25] For details, see the Supporting Information.

[26] For comparison, the carbenoid center of the Fischer-type complex **4** (X = OMe) resonates at $\delta_C = 279.7$ ppm (d, $J_{P,C} = 101.8$ Hz).

[27] CCDC 984123 (**4**, X = OMe) and 984124 (**11**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Short crystallographic abstracts can also be found in the Supporting Information.

[28] According to ab initio calculations, planar [C_6H_5-CH_2^+] has a notably contracted central bond (1.356 Å) compared with the corresponding singlet carbene [C_6H_5-CH] (1.462 Å); moreover, the rotational barrier of the cation was computed to be about four times higher than that of the carbene, see: W. Kirmse, K. Kund, E. Ritzer, A. E. Dorigo, K. N. Houk, *J. Am. Chem. Soc.* **1986**, *108*, 6045–6046. In this context, one should note that the difference between the estimated 35 kJ mol^{-1} for the barrier in **11** and the rotational barriers in prototype diarylcarbenium cations is not anywhere close to a factor of four; the latter have barriers in the order of 41.5–56.5 kJ mol^{-1}, see: G. A. Olah, M. I. Watkins, *Proc. Natl. Acad. Sci. USA* **1980**, *77*, 703–707.

[29] Y. Li, J.-S. Huang, G.-B. Xu, N. Zhu, Z.-Y. Zhou, C.-M. Che, K.-Y. Wong, *Chem. Eur. J.* **2004**, *10*, 3486–3502.

[30] G.-Y. Li, J. Zhang, P. W. H. Chan, Z.-J. Xu, N. Zhu, C.-M. Che, *Organometallics* **2006**, *25*, 1676–1688; note that the unit cell of complex **13** contains two independent molecules with rather different but uniform C1–C$_{ipso}$ bond lengths (1.493/1.1.495 and 1.443/1.458 Å).

[31] The structure of a copper carbene of type LCu=CAr$_2$ (Ar = *p*-nitrophenyl) is also relevant in this context. Although the species is highly electrophilic, the Cu=C distance definitely represents a double bond and the two C1–C$_{ipso}$ bonds are of the same length (1.457(3) and 1.467(3) Å), see: P. Hofmann, I. V. Shishkov, F. Rominger, *Inorg. Chem.* **2008**, *47*, 11755–11762.

[32] a) H. G. Norment, I. L. Karle, *Acta Crystallogr.* **1962**, *15*, 873–878; b) for a different polymorph, see: H.-K. Fun, S. Franklin, S. R. Jebas, T. Balasubramanian, *Acta Crystallogr. Sect. E* **2008**, *64*, o1256.

[33] a) C. Bleasdale, W. Clegg, S. B. Ellwood, B. T. Golding, *Acta Crystallogr. Sect. C* **1991**, *47*, 550–553; b) R. Rathore, S. V. Lindeman, A. S. Kumar, J. K. Kochi, *J. Am. Chem. Soc.* **1998**, *120*, 6931–6939; c) K. O. Christe, X. Zhang, R. Bau, J. Hegge, G. A. Olah, G. K. S. Prakash, J. A. Sheehy, *J. Am. Chem. Soc.* **2000**, *122*, 481–487; d) T. Laube, G. A. Olah, R. Bau, *J. Am. Chem. Soc.* **1997**, *119*, 3087–3092; e) for the computed structure of $[\mathrm{ArCHAr}]^+$ (Ar = -C_6H_4OMe), see: C. Schindele, K. N. Houk, H. Mayr, *J. Am. Chem. Soc.* **2002**, *124*, 11208–11214.

[34] A recent study suggested that electron donation from a LAu center (L = P(*t*Bu)$_2$(*o*-biphenyl)) might be similar to that of a cyclopropyl group. See: R. E. M. Brooner, R. A. Widenhoefer, *Chem. Commun.* **2014**, *50*, 2420–2423.

[35] This lack of any substantial π-electron back donation is reminiscent of the bonding situation in gold carbonyl cations, such as $[\mathrm{Au(CO)}]^+\,[\mathrm{SO_3F}]^-$, which basically feature a $\mathrm{OC}\rightarrow\mathrm{Au}$ σ-bond only, despite the excellent π-acceptor properties of the CO ligands. We thank one of the referees for bringing this analogy to our attention. See: H. Willner, F. Aubke, *Chem. Eur. J.* **2003**, *9*, 1668–1676.

[36] a) A. Fedorov, L. Batiste, A. Bach, D. M. Birney, P. Chen, *J. Am. Chem. Soc.* **2011**, *133*, 12162–12171; b) A. Fedorov, P. Chen, *Organometallics* **2009**, *28*, 1278–1281; c) A. Fedorov, P. Chen, *Organometallics* **2010**, *29*, 2994–3000; d) D. H. Ringger, P. Chen, *Angew. Chem.* **2013**, *125*, 4784–4787; *Angew. Chem. Int. Ed.* **2013**, *52*, 4686–4689.

[37] a) C. R. Solorio-Alvarado, A. M. Echavarren, *J. Am. Chem. Soc.* **2010**, *132*, 11881–11883; b) Y. Wang, P. R. McGonigal, B. Herlé, M. Besora, A. M. Echavarren, *J. Am. Chem. Soc.* **2014**, *136*, 801–809.

[38] A study of complexes of type **20** with different *para* substituents showed clear Hammett correlations, but a definitive conclusion as to whether the positive charge resides on carbon or on gold could not be drawn (see Ref. [36]). Our data for **11** suggest that the resonance extreme **20a** is the better description of their ground-state structure.

[39] Whereas the reaction of **11** with *p*-methoxystyrene occurred at low temperature, the retro-Buchner reaction/cyclopropanation described in Ref. [37] typically required 120 °C to proceed.

[40] For an instructive qualitative discussion of the bonding in metal carbene species of different types, see: P. J. Brothers, W. R. Roper, *Chem. Rev.* **1988**, *88*, 1293–1326.

[41] Qualitatively, π-acid catalysts based on Pt and Au often induce similar chemistry; a recent study unequivocally showed that platinum carbenoids are also exceptionally electrophilic species. See: J. Campos, R. Peloso, E. Carmona, *Angew. Chem.* **2012**, *124*, 8380–8383; *Angew. Chem. Int. Ed.* **2012**, *51*, 8255–8258.

[42] Like gold carbenoids, dirhodium donor–acceptor carbene complexes are highly electrophilic, and have a low carbene bond order and only a weak π-contribution to the carbon–metal bonding interaction, see: K. P. Kornecki, J. F. Briones, V. Boyarskikh, F. Fullilove, J. Autschbach, K. E. Schrote, K. M. Lancaster, H. M. L. Davies, J. F. Berry, *Science* **2013**, *342*, 351–354.

[43] For an instructive example, see: M. Alcarazo, T. Stork, A. Anoop, W. Thiel, A. Fürstner, *Angew. Chem.* **2010**, *122*, 2596–2600; *Angew. Chem. Int. Ed.* **2010**, *49*, 2542–2546.