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Oxidative Addition of Carbon–Carbon Bonds to Gold**

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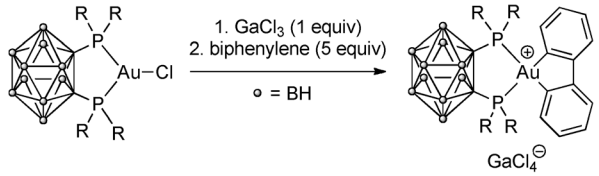
Abstract: *The oxidative addition of strained C–C bonds (biphenylene, benzocyclobutenone) to DPCb (diphosphino-carborane) gold(I) complexes is reported. The resulting cationic organogold(III) complexes have been isolated and fully characterized. Experimental conditions can be adjusted to obtain selectively acyl gold(III) complexes resulting from oxidative addition of either the C(aryl)–C(O) or C(alkyl)–C(O) bond of benzocyclobutenone. DFT calculations provide mechanistic insight into this unprecedented transformation.*

The carbon–carbon bond cleavage by transition-metal complexes is one of the most challenging reactions in organometallic chemistry.[1] The oxidative addition of C–C bonds is hampered thermodynamically by the strength of C–C σ-bonds and kinetically by steric and orbital factors (the C–C σ-bond is hindered and highly directional, which prevents its interaction with metal centers).[2] In comparison with other types of nonpolar E–E and E–H σ-bonds, the oxidative addition of C–C bonds by transition metals under stoichiometric or catalytic conditions is much less developed.[3,4] Only few efficient complexes, all based on late transition metals (mostly Rh and Pt), have been described to date.

In the field of transition-metal-mediated σ-bond activation, gold was considered inappropriate and thus left aside for a long time. However, the ability of gold(I) complexes to an undergo oxidative addition of σ-bonds, such as S–S, Si–Si, Sn–Sn, and C(aryl)–X bonds, has been recently demonstrated in intramolecular[5] as well as intermolecular versions.[6] In particular, we recently reported that rationally designed two-coordinate cationic gold(I) complexes $[(DPCb)Au]^+$ (DPCb = diphosphino-carborane) with a bent PAuP angle (ca. 100°) readily achieve the oxidative addition of aryl iodides, a transformation that was so far considered highly disfavored, if not impossible, with gold.[6c] These results prompted us to investigate the oxidative addition of C–C σ-bonds to gold as the archetype example of nonpolar σ-bond activation at transition metals. Herein we report that $[(DPCb)Au]^+$ complexes activate biphenylene and benzocyclobutenone to form stable cationic organogold(III) complexes. The selectivity and reversibility of the oxidative addition process with benzocyclobutenone has been thoroughly studied experimentally and theoretically.

Several features make biphenylene a prototypical substrate for C–C bond activation at transition metals (ring strain, formation of strong M–C(aryl) bonds, possible π-coordination of the metal prior to oxidative addition).[7] Its reactivity with 1,2-diphosphino-1,2-dicarba-*closo*-dodecaborane (DPCb) gold complexes[8] was thus explored. The neutral precursor **1** was treated with $GaCl_3$ at −30 °C and five equivalents of biphenylene were added to the resulting cationic species. The reaction mixture was heated at 120 °C in dichloromethane in a pressurizable Schlenk flask. ^{31}P NMR monitoring indicated the formation of a major species (δ = 69.9 ppm), that is, the cyclometallated gold(III) complex **3** derived from the oxidative addition of biphenylene (Scheme 1). The reaction is complete within 3 h at 120 °C.



1: R = Ph
2: R = *i*Pr

3: R = Ph, 63 %
4: R = *i*Pr, 95 %

Scheme 1. Oxidative addition of biphenylene to gold.

In addition to **3**, the four-coordinate complex $[(DPCb)_2Au]^+$ (δ = 42.0 ppm) stemming from the decomposition of the cationic complex $[(DPCb)Au]^+$, $GaCl_4^-$ was detected in minor quantity. Complex **2** bearing isopropyl substituents at phosphorus also reacts with biphenylene under these conditions. In this case, complete conversion is achieved within 5 h and oxidative addition proceeds very cleanly. Gold(III) complex **4** is obtained as the sole product according to ^{31}P NMR spectroscopy (δ = 89.5 ppm).

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Complexes **3** and **4** were isolated as stable crystalline solids (63% and 95%, respectively). Molecular structures were unambiguously established by spectroscopic and crystallographic analyses. Most diagnostic is the ^{13}C NMR signal observed in the typical region for C(aryl) atoms bound to gold(III)[5d,6c] ($\delta = 165.1$ ppm for **3** and 165.6 ppm for **4**). These signals appear as doublets of doublets because of the coupling of the carbon atom with the two phosphorus atoms in *trans* and *cis* positions ($J_{PC} = 111.2/9.0$ Hz for **3**, 114.3/9.7 Hz for **4**; Figure 1, left). Recrystallization provided

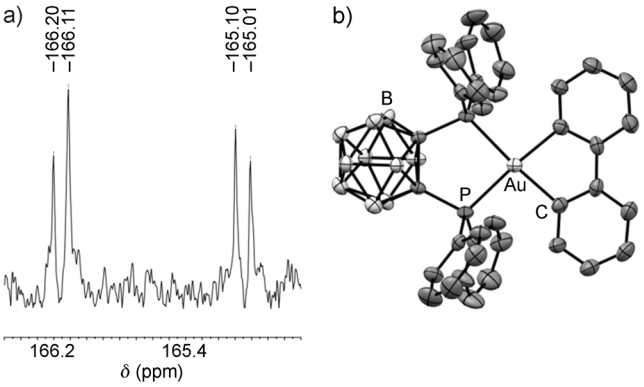


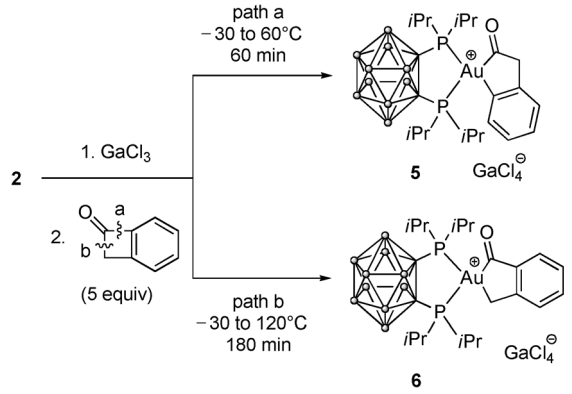
Figure 1. Complex **3**. a) Characteristic ^{13}C NMR signal associated with the C(aryl) carbon atom bound to gold. b) Molecular structure determined by single-crystal X-ray diffraction. The $GaCl_4^-$ counter anion and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Au–C 2.073(7), Au–P 2.369(2), C-Au-C 81.1(4), P-Au-P 89.43(8).

crystals of **3** and **4** suitable for X-ray diffraction analyses (Figure 1, right).[9] The two complexes display very similar structures in the solid state. The gold center is four-coordinated (the $GaCl_4^-$ counter anion remains at long distance) and adopts a square-planar geometry (P-Au-P = 87 ± 2°, C-Au-C = 81 ± 1°). The Au–P and Au–C distances are comparable to those previously reported for gold(III) complexes (2.30–2.38 Å and 2.02–2.08 Å, respectively).[10] The only noticeable structural difference between **3** and **4** is the arrangement of the three contiguous rings of the metallafluorene moiety, which remains almost perfectly coplanar in **3**, but adopts a bowl-shape conformation in **4** (the lateral aromatic rings are tilted away from the gold coordination plane probably because of the steric shielding of the isopropyl substituents at P).[11]

The reactions of $[(DPCb)Au]^+$ complexes with biphenylene represent the first examples of the oxidative addition of C–C bonds to gold.[12] These transformations are reminiscent of those reported earlier with neutral Pt^0 fragments and actually occur under nearly the same conditions. Indeed, depending on the precursor, insertion of Pt into biphenylene was shown to require heating at 55–120 °C for a few hours up to several days.[7]

Encouraged by the results obtained with biphenylene, we then turned our attention to benzocyclobutenone. The presence of a strained and functionalized four-membered ring makes this substrate particularly valuable for transition-metal-mediated C–C bond cleavage, as demonstrated previously with Rh complexes.[13] The reaction of complex **2** with benzocyclobutenone (10 equiv) was investigated in the presence of $GaCl_3$ as chloride abstractor. Strikingly, a reaction takes place spontaneously at room temperature, as apparent from the ^{31}P NMR spectrum. The starting material **2**/$GaCl_3$ ($\delta = 74$ ppm) slowly converts into a new complex **5**, which displays two doublets at $\delta = 79.7$ and 78.3 ppm with a J_{PP} coupling constant of 13.9 Hz. The desymmetrization of the diphosphine environment is consistent with the oxidative addition of benzocyclobutenone.

Complete conversion of **2**/$GaCl_3$ requires about 24 h at room temperature. In the late stage of the reaction, another set of doublets ($\delta = 91.8$ and 74.4 ppm, $J_{PP} = 14.4$ Hz) appears in the ^{31}P NMR spectrum. This observation suggests the formation of another gold(III) complex **6**, possibly an isomer of **5** resulting from the oxidative addition of another C–C bond of benzocyclobutenone. Based on ^{13}C NMR analyses,[11] the molecular structures of **5** and **6** were unequivocally assigned to the acyl gold(III) complexes resulting from oxidative addition of the C(aryl)–C(O) and C(alkyl)–C(O) bonds of benzocyclobutenone, respectively (Scheme 2,



Scheme 2. Oxidative addition of benzocyclobutenone to gold: selective formation of the two acyl–gold(III) complexes **5** and **6** upon activation of either the C(aryl)–C(O) or the C(alkyl)–C(O) bond.

paths a and b). Acyl complexes of gold are extremely rare. A few $[(Ph_3P)Au(COR)]$ complexes have been prepared by acyl transfer,[14] and to the best of our knowledge, the only related gold(III) species are $[(Ph_3P)AuMe_2(COOR)]$ complexes obtained by carbonylation.[15]

At room temperature, complex **5**, arising from C(aryl)–C(O) bond activation, is formed as the major species, and only traces of **6**, resulting from C(alkyl)–C(O) bond activation is observed. By optimizing the reaction conditions, both complexes could be obtained selectively and were isolated. Reaction of **2**/$GaCl_3$ with five equivalents of benzocyclobutenone for 1 h at 60 °C exclusively gives complex **5** (the kinetic product), while complex **6** (the thermodynamic product) is formed selectively when the same reaction mixture is heated for 3 h at 120 °C.

The behavior of the gold complex $[(DPCb)Au]^+$ toward benzocyclobutenone differs markedly from that of rhodium complexes.[16,17] Liebeskind demonstrated early on the ability of Wilkinson's complex $[RhCl(PPh_3)_3]$ to react with benzo-

cyclobutenones at high temperature (130 °C). However, the process is not selective and gives a mixture of acyl Rh^{III} complexes as a result of the competitive insertion of Rh into the C(alkyl)–C(O) and C(aryl)–C(O) bonds.[16] Moreover, activation of the C(aryl)–C(O) bond was favored thermodynamically with $[ClRh(PPh_3)_3]$, contrary to what we noticed with $[(DPCb)Au]^+$. Very recently, Yamashita, Nozaki, and Murakami described the site-selective oxidative addition of benzocyclobutenone to an original T-shaped PBP-pincer Rh complex.[17] In this case, the reaction occured at room temperature and proceeded selectively at the sterically less hindered C(alkyl)–C(O) bond, probably because of the bulky *t*Bu substituents at P. Thus, $[(DPCb)Au]^+$ is the only complex to cleave selectively either the C(aryl)–C(O) or the C(alkyl)–C(O) bond of benzocyclobutenone as a result of kinetic/thermodynamic control.

Complexes **5** and **6** are the first acyl gold(III) that were characterized by single-crystal X-ray crystallography (Figure 2).[9] They both adopt ion-pair structures with the gold center positioned in a square-planar environment. The five-membered ring resulting from the insertion of gold into benzocyclobutenone adopts an envelope conformation (the gold center deviates by 0.47–0.76 Å from the C4 plane) and the C-Au-C bond angle is rather acute (78–80°). The Au–CH_2 and Au–C(aryl) bond distances are in typical ranges and the Au–C(O) bond length is similar to that reported for $[(Ph_3P)AuMe_2(COOMe)]$ (2.08(2) Å).[15]

To gain mechanistic insight, the activation of benzocyclobutenone at gold was investigated computationally. DFT calculations were carried out on the real system at the B97D/SDD + f(Au), 6-31G**(other atoms) level of theory. The results obtained taking into account counter anion ($GaCl_4^-$) and solvent (dichloromethane) effects are described herein (Figure 3).[11] Accordingly, $GaCl_3$ was predicted to readily abstract a chloride ion from complex **2** to give an ion pair complex **2′** ($\Delta G = -18.6$ kcal mol^{-1}, shortest Cl···Au contact: 2.604 Å). Oxidative addition of the C(aryl)–C(O) bond of benzocyclobutenone was explored first. Accordingly, the formation of the acyl complex **5** was found to be about thermoneutral ($\Delta G = 0.7$ kcal mol^{-1}) and to involve a rather low activation barrier ($\Delta G^{\neq} = 20.5$ kcal mol^{-1}), in line with experimental observations (spontaneous reaction at room temperature in the presence of an excess of benzocyclobutenone). Activation of the C(alkyl)–C(O) bond was then studied. Comparatively, the formation of the isomeric acyl complex **6** is more favored energetically ($\Delta G = -8.2$ kcal mol^{-1}), but the associated activation barrier is substantially larger ($\Delta G^{\neq} = 27.3$ kcal mol^{-1}). To assess the importance of steric effects on the selectivity of the reaction, calculations have been performed on a model system featuring Me instead of *i*Pr substituents at P (see Figure S4). Similar results were obtained, indicating that the kinetic preference for C(aryl)–C(O) bond activation and thermodynamic preference for C(alkyl)–C(O) bond activation are intrinsic of the $[(DPCb)Au]^+$ complex. In addition, analysis of the transition states $\mathbf{TS_5}$ and $\mathbf{TS_6}$ by the activation strain model[18] indicates minimal contribution of the $\Delta E^{\neq}_{\text{dist-[(DCPb)Au+]}}$ distortion term to the activation barrier $\Delta E^{\neq}$ (Table S3), as in the case of Ph–I activation.[6c] This result substantiates the preorganized character of the $[(DPCb)Au]^+$ fragment and the role of bending in the oxidative addition of C–C bonds to gold.

The formation of the regioisomeric complex **6** may result from the direct isomerization of **5** or from the reductive elimination of the C(aryl)–C(O) bond followed by the oxidative addition of the C(alkyl)–C(O) bond. According to the reaction profiles computed by DFT, reductive elimination of the C(aryl)–C(O) bond of benzocyclobutenone can readily

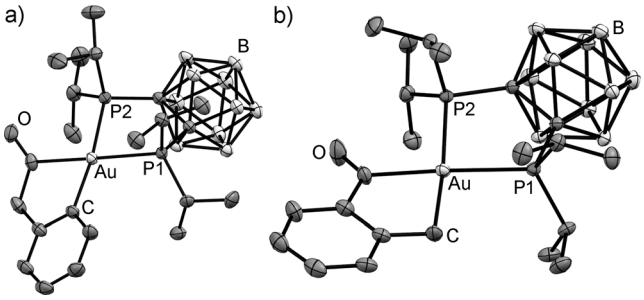


Figure 2. Molecular structures of the acyl gold(III) complexes **5** (a) and **6** (b) determined by single-crystal X-ray diffraction. The $GaCl_4^-$ counter anions and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: **5** C(O)–Au 2.112(3), Au–C_{Ar} 2.081(3), Au–P1 2.454(1), Au–P2 2.393(1), C–O 1.187(4), C-Au-C 77.98(13), P-Au-P 85.61(3); **6** C(O)–Au 2.106(4), CH_2–Au 2.107(4), Au–P1 2.436(1), Au–P2 2.388(1), C–O 1.205(5), C-Au-C 80.81(17), P1-Au-P2 89.69(3).

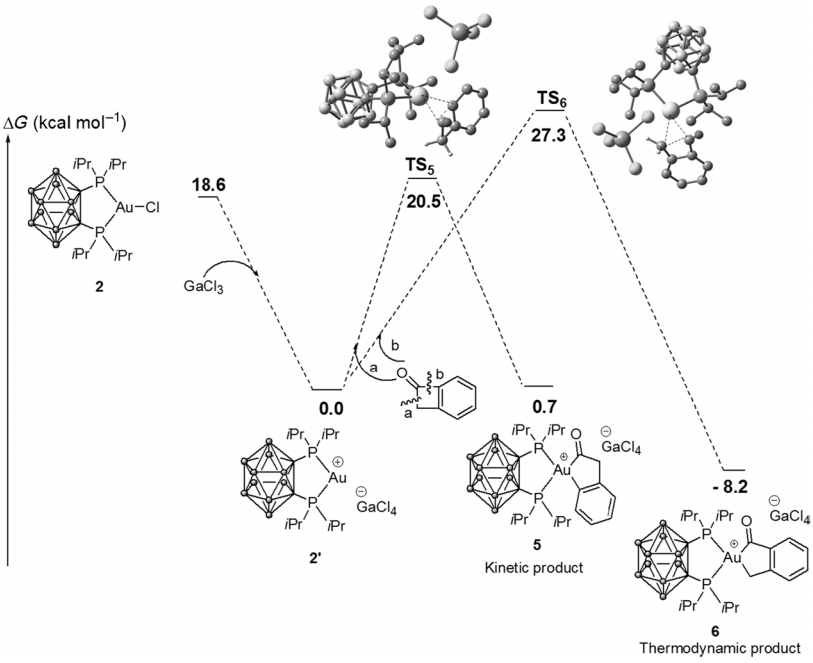


Figure 3. Energy profile in dichloromethane (Gibbs free energy, in kcal mol^{-1}) for the reaction of benzocyclobutenone with the gold complex **2** in the presence of $GaCl_3$.

occur from the gold(III) complex **5** on both kinetic and thermodynamic grounds. Experimentally, the acyl complex **5** was found to be stable in the solid state, but to evolve slowly back to the cationic gold(I) complex **2′** and benzocyclobutenone in dichloromethane at room temperature. Over time or upon heating, the oxidative addition of the C(alkyl)–C(O) bond takes place and the acyl complex **6** is obtained as thermodynamic product. These observations support the latter mechanistic hypothesis and corroborates the ability of the $[(DPCb)Au]^+$ fragment to activate both the C(aryl)–C(O) and C(alkyl)–C(O) bonds of benzocyclobutenone.

It is also important to note that the backward reaction from **5** to **2′** provides evidence for a spontaneous reductive elimination of a C(aryl)–C(O) bond at gold. Reductive eliminations of C–C bonds from square-planar complexes are common in organometallic chemistry, but very rare with gold and so far limited to C(aryl)–C(aryl) bond formation.[19–21]

In conclusion, the oxidative addition of C–C bonds to gold was disclosed. Bent gold(I) complexes $[(DPCb)Au]^+$ readily insert into the four-membered rings of biphenylene and benzocyclobutenone. Remarkably, $[(DPCb)Au]^+$ is the only complex to cleave selectively either the C(aryl)–C(O) or the C(alkyl)–C(O) bond of benzocyclobutenone as a result of kinetic/thermodynamic control. The resulting acyl gold(III) regioisomers have been isolated and fully characterized. A reverse reaction, namely the reductive elimination of a C(aryl)–C(O) bond has also been substantiated from a well-defined gold(III) complex.

These results further confirm that contrary to what was long believed, gold(I) complexes do undergo oxidative additions and are thus promising candidates for σ-bond activation.[22] The properties of the thereby generated cationic organogold(III) complexes are currently under investigation.

Keywords: C–C bond activation · gold chemistry · oxidative addition · reductive elimination · selectivity

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[1] *C–C Bond Activation*, *Vol. 346* (Ed.: G. Dong), Springer, Berlin, **2013**, pp. 1–258.

[2] a) M. Murakami, Y. Ito in *Activation of Unreactive Bonds and Organic Synthesis* (Eds.: P. S. Murai, H. Alper, R. A. Gossage, V. V. Grushin, M. Hidai, Y. Ito, W. D. Jones, F. Kakiuchi, G. van Koten, Y.-S. Lin, et al.), Springer, Heidelberg, **1999**, pp. 97–129; b) M. Etienne, A. S. Weller, *Chem. Soc. Rev.* **2014**, *43*, 242–259.

[3] For selected reviews on C–C bond activation, see: a) W. D. Jones, *Nature* **1993**, *364*, 676–677; b) B. Rybtchinski, D. Milstein, *Angew. Chem. Int. Ed.* **1999**, *38*, 870–883; *Angew. Chem.* **1999**, *111*, 918–932; d) M. Murakami, Y. Ito, *Top. Organomet. Chem.* **1999**, *3*, 97–129; e) M. E. van der Boom, D. Milstein, *Chem. Rev.* **2003**, *103*, 1759–1792; f) C.-H. Jun, *Chem. Soc. Rev.* **2004**, *33*, 610–618; g) T. Satoh, M. Miura, *Top. Organomet. Chem.* **2005**, *14*, 1–20; h) C.-H. Jun, J.-W. Park, *Top. Organomet. Chem.* **2007**, *24*, 117–143; i) D. Necas, M. Kotora, *Curr. Org. Chem.* **2007**, *11*, 1566–1591; j) T. Seiser, N. Cramer, *Org. Biomol. Chem.* **2009**, *7*, 2835–2840; k) C. Aïssa, *Synthesis* **2011**, 3389–3407; l) N. Cramer, T. Seiser, *Synlett* **2011**, 449–460; m) M. Murakami, T. Matsuda, *Chem. Commun.* **2011**, *47*, 1100–1105; n) A. Korotvicka, D. Necas, M. Kotora, *Curr. Org. Chem.* **2012**, *16*, 1170–1214; o) A. Dermenci, J. W. Coe, G. Dong, *Org. Chem. Front.* **2014**, *1*, 567–581; p) I. Marek, A. Masarwa, P. O. Delaye, M. Leibeling, *Angew. Chem. Int. Ed.* **2015**, *54*, 414–429; *Angew. Chem.* **2015**, *127*, 424–439.

[4] For recent examples of C–C bond activation with transition metals, see: a) J. M. Darmon, S. C. E. Stieber, K. T. Sylvester, I. Fernández, E. Lobkovsky, S. P. Semproni, E. Bill, K. Wieghardt, S. DeBeer, P. J. Chirik, *J. Am. Chem. Soc.* **2012**, *134*, 17125–17137; b) M. A. Bowring, R. G. Bergman, T. D. Tilley, *J. Am. Chem. Soc.* **2013**, *135*, 13121–13128; c) N. Ishida, W. Ikemoto, M. Murakami, *J. Am. Chem. Soc.* **2014**, *136*, 5912–5915; d) M. V. Pham, N. Cramer, *Angew. Chem. Int. Ed.* **2014**, *53*, 3484–3487; *Angew. Chem.* **2014**, *126*, 3552–3555; e) L. Souillart, E. Parker, N. Cramer, *Angew. Chem. Int. Ed.* **2014**, *53*, 3001–3005; *Angew. Chem.* **2014**, *126*, 3045–3049.

[5] a) P. Gualco, S. Ladeira, K. Miqueu, A. Amgoune, D. Bourissou, *Angew. Chem. Int. Ed.* **2011**, *50*, 8320–8324; *Angew. Chem.* **2011**, *123*, 8470–8474; b) P. Gualco, S. Ladeira, K. Miqueu, A. Amgoune, D. Bourissou, *Organometallics* **2012**, *31*, 6001–6004; c) N. Lassauque, P. Gualco, S. Mallet-Ladeira, K. Miqueu, A. Amgoune, D. Bourissou, *J. Am. Chem. Soc.* **2013**, *135*, 13827–13834; d) J. Guenther, S. Mallet-Ladeira, L. Estevez, K. Miqueu, A. Amgoune, D. Bourissou, *J. Am. Chem. Soc.* **2014**, *136*, 1778–1781.

[6] a) R. E. Bachman, S. A. Bodolosky-Bettis, C. J. Pyle, M. A. Gray, *J. Am. Chem. Soc.* **2008**, *130*, 14303–14310; b) M. Joost, P. Gualco, Y. Coppel, K. Miqueu, C. E. Kefalidis, L. Maron, A. Amgoune, D. Bourissou, *Angew. Chem. Int. Ed.* **2014**, *53*, 747–751; *Angew. Chem.* **2014**, *126*, 766–770; c) M. Joost, Z. Abdallah, L. Estevez, S. Mallet-Ladeira, K. Miqueu, A. Amgoune, D. Bourissou, *J. Am. Chem. Soc.* **2014**, *136*, 14654–14657.

[7] W. Jones, *Top. Curr. Chem.* **2014**, *346*, 1–31.

[8] O. Crespo, M. C. Gimeno, A. Laguna, P. G. Jones, *J. Chem. Soc. Dalton Trans.* **1992**, 1601–1605.

[9] CCDC 1044000 (**3**), 1044001 (**4**), 1044002 (**5**), and 1044003 (**6**) 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.

[10] A CCDC search revealed that P–Au and Au–C bond distances of structurally characterized phosphine organogold(III) complexes span from 2.27–2.42 Å and from 2.013–2.126 Å, respectively.

[11] See the Supporting Information for more details.

[12] After submission of this manuscript, a related contribution from Toste and co-workers appeared. It describes the preparation of gold(III) complexes by oxidative addition of biphenylenes to $[(NHC)Au]^+SbF_6^-$ and their use in Lewis acid catalysis. See: C.-Y. Wu, T. Horibe, C. B. Jacobsen, F. D. Toste, *Nature* **2015**, *517*, 449–453.

[13] P. H. Chen, T. Xu, G. Dong, *Angew. Chem. Int. Ed.* **2014**, *53*, 1674–1678; *Angew. Chem.* **2014**, *126*, 1700–1704.

[14] Only three gold(I) acyl complexes have been crystallographically characterized, see: a) H.-J. Haupt, D. Petters, U. Flörke, *J. Organomet. Chem.* **1998**, *553*, 497–501; b) C. E. Strasser, S. Cronje, H. G. Raubenheimer, *New J. Chem.* **2010**, *34*, 458–469; c) H. G. Raubenheimer, M. W. Esterhuysen, C. Esterhuysen, *Inorg. Chim. Acta* **2005**, *358*, 4217–4228.

[15] S. Komiya, T. Sone, S. Ozaki, M. Ishikawa, N. Kasuga, *J. Organomet. Chem.* **1992**, *428*, 303–313.

[16] a) M. A. Huffman, L. S. Liebeskind, W. T. Pennington, *Organometallics* **1990**, *9*, 2194–2196; b) M. A. Huffman, L. S. Liebeskind, W. T. Pennington, *Organometallics* **1992**, *11*, 255–266.

[17] Y. Masuda, M. Hasegawa, M. Yamashita, K. Nozaki, N. Ishida, M. Murakami, *J. Am. Chem. Soc.* **2013**, *135*, 7142–7145.

[18] a) I. Fernández, F. M. Bickelhaupt, *Chem. Soc. Rev.* **2014**, *43*, 4953 – 4967; b) W. J. van Zeist, F. M. Bickelhaupt, *Org. Biomol. Chem.* **2010**, *8*, 3118 – 3127.
[19] a) J. Vicente, M. Dolores Bermudez, J. Escribano, *Organometallics* **1991**, *10*, 3380 – 3384; b) W. J. Wolf, M. S. Winston, F. D. Toste, *Nat. Chem.* **2014**, *6*, 159 – 164.
[20] The formation of an *exo*-methylene benzocyclobutane by the reductive elimination of a C(aryl)–C(alkyl) bond has been recently reported upon reaction of a tetracoordinate gold(III) bromide complex with a silver salt. See: M. D. Levin, F. D. Toste, *Angew. Chem. Int. Ed.* **2014**, *53*, 6211 – 6215; *Angew. Chem.* **2014**, *126*, 6325 – 6329.
[21] The reductive elimination of a C(alkyl)–C(O) bond from **6** is kinetically and thermodynamically unfavorable, in line with the lower tendency of alkyl over aryl gold(III) complexes to undergo C–C reductive elimination, see: a) S. Komiya, T. A. Albright, R. Hoffmann, J. K. Kochi, *J. Am. Chem. Soc.* **1976**, *98*, 7255 – 7265; b) A. Tamaki, S. A. Magennis, J. K. Kochi, *J. Am. Chem. Soc.* **1974**, *96*, 6140 – 6148; c) A. Nijamudheen, S. Karmakar, A. Datta, *Chem. Eur. J.* **2014**, *20*, 14650 – 14658.
[22] For recent examples of C–C bond cleavage transformations catalyzed by gold, see: a) M. Jiang, L.-P. Liu, M. Shi, Y. Li, *Org. Lett.* **2010**, *12*, 116 – 119; b) M. Gaydou, A. M. Echavarren, *Angew. Chem. Int. Ed.* **2013**, *52*, 13468 – 13471; *Angew. Chem.* **2013**, *125*, 13710 – 13713; c) C. Qin, P. Feng, Y. Ou, T. Shen, T. Wang, N. Jiao, *Angew. Chem. Int. Ed.* **2013**, *52*, 7850 – 7854; *Angew. Chem.* **2013**, *125*, 8004 – 8008.

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