

Spontaneous Oxidative Addition of σ -Si–Si Bonds at Gold**

Pauline Gualco, Sonia Ladeira, Karinne Miqueu,* Abderrahmane Amgoune,* and Didier Bourissou*

The past decade has witnessed tremendous development in homogeneous gold catalysis.^[1] Thanks to unique soft and tunable Lewis acidity, gold(I) and gold(III) complexes have been shown to efficiently activate most types of π -bonded substrates. Besides these synthetic achievements, mechanistic issues have attracted considerable attention, and much progress has been accomplished recently thanks to the characterization of several key intermediates.^[2]

With the aim of further extending the scope of gold catalysis, major interest has been devoted over the last few years to gold-mediated processes involving two-electron redox cycles. The isolobal analogy between Au(I/III) and Pd(0/II) complexes is stimulating the search for “gold versions” of palladium-catalyzed transformations, and in particular cross-couplings.^[3] Accordingly, a variety of intra- and intermolecular coupling reactions have been shown to be efficiently catalyzed by gold complexes in the presence of strong exogenous oxidants.^[4] A few studies have also suggested the ability of gold complexes to promote cross-couplings in a similar way to palladium catalysts,^[5] but possible palladium contamination has recently cast doubt on the involvement of gold complexes in these transformations.^[6] These recent contributions as a whole open a new facet of gold catalysis, and at the same time, raise fundamental

questions about the properties and behavior of gold complexes. In particular, better knowledge on the basic elementary steps involved in redox cycles (oxidative addition, transmetalation, migratory insertion, β elimination, reductive elimination) is highly desirable to help further developments into this emerging area of gold catalysis.^[7–9] In this regard, it is striking to note that, despite the stability and availability of both Au^I and Au^{III} complexes,^[10] oxidative addition reactions at gold remain very elusive. In fact, the reluctance of gold to undergo oxidative addition is presumed to be an intrinsic limitation to achieve Au^I/Au^{III} redox cycles akin to those typically operating with Pd.^[4i,11] Rare evidence for oxidative addition at gold dates back to the pioneering contribution of Kochi on the reaction of highly polarized sp^3 C–X bonds with alkyl gold(I) complexes.^[12] Furthermore, Bachman et al. reported in 2008 the first and to date only example of activation of an apolar σ bond with gold.^[13] Fluorinated disulfides were shown to oxidatively add and reductively eliminate at gold in a reversible fashion.

Seeking to gain more insight into σ -bond activation and oxidative addition at gold, we became interested in extrapolating the strategy we have been developing for some years to study unusual metal–ligand interactions. Our approach consists in the use of anchoring phosphine sites, and this has been applied to support the coordination of Lewis acids^[14] and most recently σ -Si–Si bonds.^[15] Accordingly, the coordination of the diphosphine–disilane ligand **1** to copper and silver has been explored (Scheme 1), leading to the first structural characterization of a σ complex with a coinage metal. As a further extension of this work, we were intrigued by the coordination of **1** to gold, considering three possible scenarios: 1) Formation of a σ -complex upon side-on coordination of the disilane moiety, as observed with copper;^[16] 2) no participation of the σ -Si–Si bond to the coordination, as observed with silver; or 3) oxidative addition of the σ -Si–Si bond to give a bis(silyl)gold(III) complex. Oxidative addition

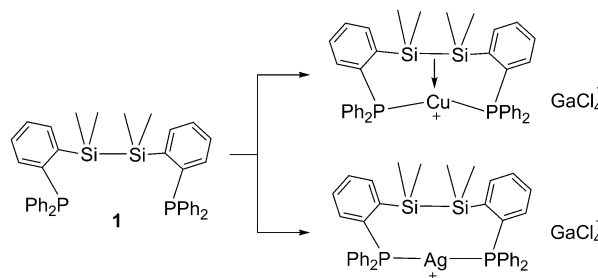
[*] P. Gualco, Dr. A. Amgoune, Dr. D. Bourissou
Laboratoire Hétérochimie Fondamentale et Appliquée
du Université Paul Sabatier, UPS, LHFA
118 Route de Narbonne, 31062 Toulouse Cedex 09 (France)
and
CNRS, LHFA UMR 5069
31062 Toulouse (France)
E-mail: amgoune@chimie.ups-tlse.fr
dbouriss@chimie.ups-tlse.fr

Dr. S. Ladeira
Institut de Chimie de Toulouse, Université Paul Sabatier
FR2599 Toulouse (France)

Dr. K. Miqueu
Institut Pluridisciplinaire de Recherche sur l'Environnement et
les Matériaux (UMR 5254), Equipe Chimie Physique
Université de Pau et des Pays de l'Adour Hélio Parc
2 Avenue du Président Angot, 64053 Pau cedex 09 (France)
E-mail: karinne.miqueu@univ-pau.fr

[**] Financial support from the Centre National de la Recherche Scientifique, the Pôle de Recherche et d'Enseignement Supérieur de l'Université de Toulouse (fellowship to P.G.), and the Agence Nationale de la Recherche (ANR-10-BLAN-070901) is gratefully acknowledged. The theoretical work was granted access to HPC resources of Idris under allocation 2011 (i2011080045) made by GENCI (Grand Equipement National de Calcul Intensif).

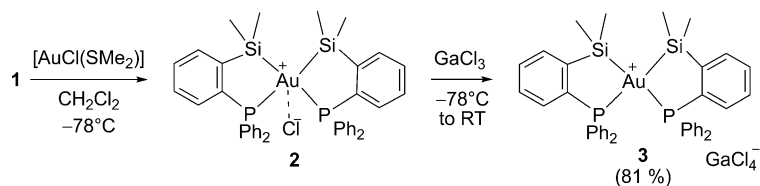
Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201103719>.



Scheme 1. Coordination of the diphosphine–disilane **1** to copper and silver.

of disilanes at transition metals, especially palladium and platinum, is a well-known process of great synthetic value.^[17] Comparatively, such an elementary step is unprecedented at gold, although it has been suggested recently by Klinkhamer et al. to account for an unusual σ bond metathesis process observed within hypersilyl gold clusters.^[18] Upon coordination of phosphine–disilanes to gold, we gained evidence for the spontaneous oxidative addition of σ -Si–Si bonds at gold to form hitherto unknown bis(silyl) gold(III) complexes.^[19,20] These experimental results are reported herein, along with some theoretical insights.

The reaction of the diphosphine–disilane **1** with [AuCl(SMe₂)] in dichloromethane at –78°C resulted in the formation of the bis(silyl) gold(III) complex **2** (Scheme 2). In marked contrast with that observed with copper and silver,



Scheme 2. Synthesis of complexes **2** and **3** by oxidative addition of the σ -Si–Si bond of the diphosphine–disilane **1** at gold.

the σ -Si–Si bond is not retained but oxidatively adds to gold. Complex **2** is not stable above –60°C, but its structure was unambiguously ascertained by multinuclear NMR spectroscopy at low temperature. The ²⁹Si NMR resonance signal is shifted downfield (33.7 ppm for **2** versus –21.2 ppm for **1**), indicating the cleavage of the σ -Si–Si bond. The associated coupling pattern (two Si–P coupling constants of 121.1 and 9.4 Hz) is very similar to that typically encountered in diphosphine bis(silyl)palladium and platinum complexes,^[21] suggesting a *cis* arrangement of the bis(silyl) complex **2**. It is worth noting that NMR monitoring indicated the spontaneous formation of the bis(silyl)gold(III) complex **2** at –80°C, with no intermediate being detected along the oxidative addition process. With the aim of improving thermal stability and obtaining crystals suitable for X-ray diffraction analysis, complex **2** was reacted with one equivalent of GaCl₃ as a chloride abstractor. Gratifyingly, the ensuing cationic bis(silyl)gold(III) complex **3** was isolated in 81% yield as a stable white powder (no sign of decomposition within days at room temperature). The ³¹P and ²⁹Si NMR data for complex **3** (³¹P: δ = 62.9 ppm and ²⁹Si: δ = 34.4 ppm, dd, $J_{\text{Si-P}}$ = 121.0 and 9.2 Hz) are very close to those of **2**, suggesting in both cases strong ionic character and only a weak interaction, if any, between the gold center and the counteranion.^[22]

The molecular structure of **3** was analyzed by X-ray diffraction (Figure 1). The ionic nature of complex **3** is apparent from the absence of significant interaction between the metal center and the GaCl₄[–] counteranion (shortest Cl...Au distance 3.9759(8) Å). The gold center is surrounded by the two phosphorus and the two silicon atoms, and adopts square-planar geometry, as expected for a gold(III) center.^[23] Consistent with the spectroscopic data, the two phosphine–

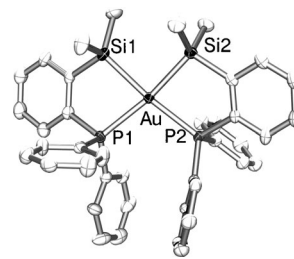


Figure 1. View of complex **3** in the solid state (ellipsoids set at 50% probability; hydrogen atoms, counteranion, and solvate molecules omitted for clarity). Selected bond lengths [Å] and angles [°]: Au–P1 2.4135(6), Au–P2 2.4176(6), Au–Si1 2.4128(6), Au–Si2 2.4213(6); P1–Au–P2 103.63(2), Si1–Au–Si2 89.95(2), P1–Au–Si1 84.67(2), P2–Au–Si2 82.16(2).

silyl skeletons are positioned tail-to-tail. The Au–Si bonds (2.4128(6) and 2.4213(6) Å) are slightly longer than those observed in the few structurally authenticated gold(I) silyl complexes (2.365 Å),^[24] but still shorter than the sum of the covalent radii (2.47 Å).^[25] Furthermore, the absence of residual contact between the two silicon atoms is shown by the long Si–Si distance (3.4167(9) Å).

The coordination of the diphosphine–disilane **1** to gold thus proceeds with oxidative addition of the σ -Si–Si bond. Such a behavior has been well-documented with palladium and platinum,^[17] but is unprecedented with gold.^[26] The ensuing bis(silyl)gold(III) complexes **2** and **3** expand the variety of silyl complexes of gold, that, to the best of our knowledge, was limited to date to mono-(silyl)gold(I) species.^[24]

At this stage, the paucity of such oxidative additions at gold prompted us to assess computationally the activation of the σ -Si–Si bond by exploring the potential energy surface (PES) of the model complex **3*** featuring methyl instead of phenyl substituents at the phosphorus atoms (Figure 2).^[27]

The optimized geometry for the bis(silyl)gold(III) complex **3*(III)** nicely reproduces that determined crystallographically (with deviations of less than 0.05 Å in the key P–Au, Au–Si, and Si–Si distances). Another minimum was located on the PES for the corresponding Au^I isomer **3*(I)**. It is less stable in energy by 11.3 kcal mol^{–1} and has a two-coordinate linear structure without coordination of the disilane moiety (Si–Si and Au–Si distances of 2.404 and 3.360 Å, respectively). A transition state **3*-TS** associated with oxidative addition of the σ -Si–Si bond of **3*(I)** leading to **3*(III)** was also located. The geometric features indicate a rather late transition state with advanced cleavage of the σ -Si–Si bond (2.855 Å), well-developed Au–Si bonds (2.554 Å), and pronounced bending of the P–Au–P skeleton (144°). The associated activation barrier is remarkably low (10.4 kcal mol^{–1}) and accounts well for the spontaneous oxidative addition of the σ -Si–Si bond at low temperature, as observed experimentally.

We then sought to determine how general the unusual σ -Si–Si bond activation might be that is observed upon coordination of **1** to gold and to which degree chelating assistance facilitates the oxidative addition process. On one

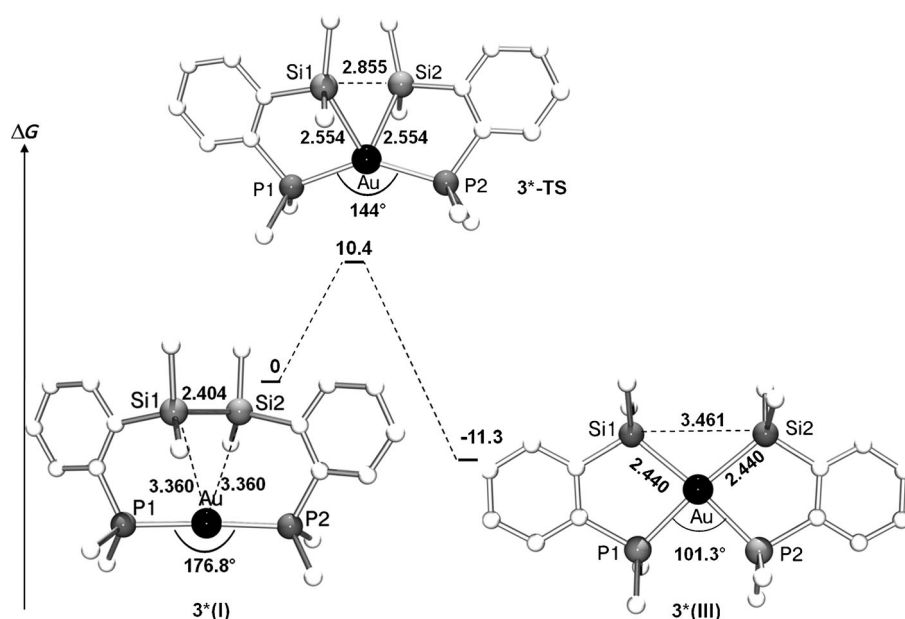
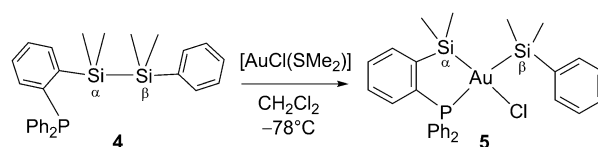


Figure 2. Energy profile computed at the B3PW91/SDD + f(Au),6-31G** (Si,P,C,H) level for the oxidative addition of the σ -Si-Si bond in complex **3***. Free energy ΔG at 25 °C including ZPE correction [kcal mol⁻¹], interatomic distances [Å], angles [°].

hand, it is clear that the coordination of the two phosphorus buttresses ideally presents the disilane moiety to the metal center, but on the other, the structures of the related copper and silver complexes^[15] show that oxidative addition is not imposed geometrically and strongly depends on the intrinsic properties of the metal center. To impart higher flexibility to the disilane moiety, the monophosphine-disilane **4** was prepared^[27] and its coordination to gold was investigated. Upon reaction with [AuCl(SMe₂)], the neutral bis(silyl)gold(III) complex **5** was formed quantitatively (Scheme 3), substantiating that oxidative addition of the σ -Si-Si bond occurs readily even when supported by a single phosphine buttress. Again, NMR spectroscopic monitoring at low temperature revealed that the reaction proceeds instantaneously at -80 °C with no detectable intermediate. The resulting complex is not stable above -30 °C, but its structure was unambiguously authenticated by NMR spectroscopy. The two ²⁹Si NMR resonance signals are diagnostically shifted downfield upon oxidative addition (δ from -22.2 and -20.1 ppm for the free ligand **4** to 15.0 and 23.8 ppm for complex **5**). Another characteristic feature is the large Si-P coupling constant observed for the silicon atom Si _{β}

bound to gold in *trans* position to the phosphorus atom ($J_{\text{Si-P}}$ from 4.2 Hz in **4** to 149.2 Hz in **5**).

DFT calculations were also performed on the model complex **5*** to gain more insight into the mechanism of σ -Si-Si bond activation. Overall, the reaction path for the oxidative addition at gold (Figure 3) is very similar to that computed for **3***. The square-planar bis(silyl)gold(III) complex **5*(III)** is more stable than the linear gold(I) isomer **5*(I)** (in which the disilane moiety remains pendant) by 13.1 kcal mol⁻¹. The oxidative addition proceeds via a rather late transition state **5*-TS** with advanced cleavage of the σ -Si-Si bond (2.666 Å), well-developed AuSi bonds (2.529/2.636 Å), and pronounced bending of the PAuCl



Scheme 3. Synthesis of complex **5** by oxidative addition of the σ -Si-Si bond of the monophosphine-disilane **4** at gold.

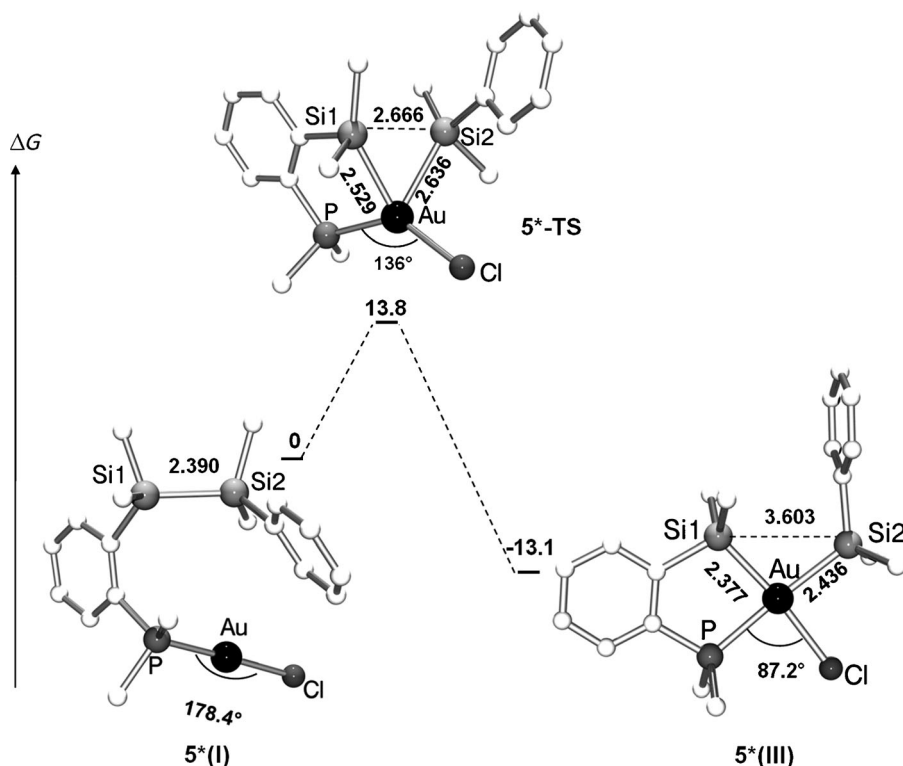


Figure 3. Energy profile computed at the B3PW91/SDD + f(Au),6-31G** (Si,P,C,H) level for the oxidative addition of the σ -Si-Si bond in complex **5***. Free energy ΔG at 25 °C including ZPE correction [kcal mol⁻¹], interatomic distances [Å], angles [°].

skeleton (136°). Most remarkably, the associated activation barrier is only slightly higher for the monophosphine–disilane (13.8 kcal mol⁻¹) than with the diphosphine–disilane, indicating that the oxidative addition of the σ -Si–Si bond is an intrinsically favorable process.

In conclusion, the spontaneous formation of complexes **3** and **5** upon coordination of diphosphine and monophosphine disilanes **1** and **4** provides direct evidence for oxidative addition of σ -Si–Si bonds at gold. Such a behavior markedly contrasts with that observed with copper and silver, and remarkably, the activation of the disilane at gold proceeds readily at low temperature even when supported by a single phosphorus buttress. These results indicate that gold is not as reluctant as assumed to undergo oxidative addition and shows some unexpected similarity with the other late transition metals, typically palladium and platinum, towards σ bond activation. The straightforward formation of bis(silyl)gold(III) complexes lends credence to the redox pathway invoked recently by Klinkhammer et al. to account for Si–Si bond metathesis around gold,^[18] and opens new synthetic avenues. For example, is catalytic bis(silylation) achievable with gold? Future work will seek to investigate the reactivity of the new bis(silyl)gold(III) complexes and to compare further the behavior of gold (and other coinage-metal) complexes with those of palladium and platinum in the key elementary steps typically involved in redox cycles.

Received: May 31, 2011

Published online: July 19, 2011

Keywords: density functional calculations · gold · oxidative addition · silicon · X-ray diffraction

- [1] For recent reviews, see: a) A. S. K. Hashmi, G. J. Hutchings, *Angew. Chem.* **2006**, *118*, 8064–8105; *Angew. Chem. Int. Ed.* **2006**, *45*, 7896–7936; b) A. S. K. Hashmi, *Chem. Rev.* **2007**, *107*, 3180–3211; c) A. Fürstner, P. W. Davies, *Angew. Chem.* **2007**, *119*, 3478–3519; *Angew. Chem. Int. Ed.* **2007**, *46*, 3410–3449; d) Z. Li, C. Brouwer, C. He, *Chem. Rev.* **2008**, *108*, 3239–3265; e) A. Arcadi, *Chem. Rev.* **2008**, *108*, 3266–3325; f) E. Jimenez-Nunez, A. M. Echavarren, *Chem. Rev.* **2008**, *108*, 3326–3350; g) D. J. Gorin, B. D. Sherry, F. D. Toste, *Chem. Rev.* **2008**, *108*, 3351–3378; h) A. Fürstner, *Chem. Soc. Rev.* **2009**, *38*, 3208–3221.
- [2] A. S. K. Hashmi, *Angew. Chem.* **2010**, *122*, 5360–5369; *Angew. Chem. Int. Ed.* **2010**, *49*, 5232–5241.
- [3] a) P. Garcia, M. Malacria, C. Aubert, V. Gandon, L. Fensterbank, *ChemCatChem* **2010**, *2*, 493–497; b) M. Hopkinson, A. D. Gee, V. Gouverneur, *Chem. Eur. J.* **2011**, DOI: 10.1002/chem.201100736.
- [4] For selected references, see: a) A. S. K. Hashmi, T. D. Ramamurthi, F. Rominger, *J. Organomet. Chem.* **2009**, *694*, 592–597; b) G. Zhang, Y. Peng, L. Cui, L. Zhang, *Angew. Chem.* **2009**, *121*, 3158–3161; *Angew. Chem. Int. Ed.* **2009**, *48*, 3112–3115; c) A. Iglesias, K. Muniz, *Chem. Eur. J.* **2009**, *15*, 10563–10569; d) G. Zhang, L. Cui, Y. Wang, L. Zhang, *J. Am. Chem. Soc.* **2010**, *132*, 1474–1475; e) N. P. Mankad, F. D. Toste, *J. Am. Chem. Soc.* **2010**, *132*, 12859–12861; f) A. D. Melhado, W. E. Brenzovich, A. D. Lackner, F. D. Toste, *J. Am. Chem. Soc.* **2010**, *132*, 8885–8887; g) W. E. Brenzovich, D. Benitez, A. D. Lackner, H. P. Shunatona, E. Tkatchouk, W. A. Goddard, F. D. Toste, *Angew. Chem.* **2010**, *122*, 5651–5654; *Angew. Chem. Int. Ed.* **2010**, *49*, 5519–5522; h) T. de Haro, C. Nevado, *J. Am. Chem. Soc.* **2010**, *132*, 1512–1513; i) L. T. Ball, M. Green, G. C. Lloyd-Jones, C. A. Russell, *Org. Lett.* **2010**, *12*, 4724–4727; j) W. B. Wang, J. Jasinski, G. B. Hammond, B. Xu, *Angew. Chem.* **2010**, *122*, 7405–7410; *Angew. Chem. Int. Ed.* **2010**, *49*, 7247–7252.
- [5] a) C. Gonzalez-Arellano, A. Corma, M. Iglesias, F. Sanchez, *J. Catal.* **2006**, *238*, 497–501; b) C. González-Arellano, A. Abad, A. Corma, H. Garcia, M. Iglesias, F. Sanchez, *Angew. Chem.* **2007**, *119*, 1558–1560; *Angew. Chem. Int. Ed.* **2007**, *46*, 1536–1538; c) P. Li, L. Wang, M. Wang, F. You, *Eur. J. Org. Chem.* **2008**, 5946–5951.
- [6] a) T. Lauterbach, M. Livendahl, A. Rosellon, P. Espinet, A. M. Echavarren, *Org. Lett.* **2010**, *12*, 3006–3009; b) A. S. K. Hashmi, C. Lothschütz, R. Döpp, M. Rudolph, T. D. Ramamurthi, F. Rominger, *Angew. Chem.* **2009**, *121*, 8392–8395; *Angew. Chem. Int. Ed.* **2009**, *48*, — 8243–8246; c) A. S. K. Hashmi, R. Döpp, C. Lothschütz, M. Rudolph, D. Riedel, F. Rominger, *Adv. Synth. Catal.* **2010**, *352*, 1307–1314.
- [7] In the gold(I)-catalyzed annulations of salicylaldehydes and alkynes, Li proposed oxidative addition of the aldehyde C–H bond assisted by the coordination of the adjacent phenol moiety: R. Skouta, C. J. Li, *Angew. Chem.* **2007**, *119*, 1135–1137; *Angew. Chem. Int. Ed.* **2007**, *46*, 1117–1119.
- [8] Oxidative addition of sp^2 C–H bonds at gold have been considered as an alternative pathway to concerted metalation deprotonation to account for gold(I)-mediated C–H activation of arenes: P. Lu, T. C. Boorman, A. M. Z. Slawin, I. Larrosa, *J. Am. Chem. Soc.* **2010**, *132*, 5580–5581.
- [9] Using triazamacrocyclic ligands, direct observation of oxidative addition of aryl halides at copper has been recently achieved: A. Casitas, A. E. King, T. Parella, M. Costas, S. S. Stahl, X. Ribas, *Chem. Sci.* **2010**, *1*, 326–330.
- [10] Relativistic effects are known to impart higher stability to gold(III) species over complexes of the other coinage metals: a) P. Schwerdtfeger, *J. Am. Chem. Soc.* **1989**, *111*, 7261–7262; b) P. Schwerdtfeger, P. D. W. Boyd, S. Brienne, A. K. Burell, *Inorg. Chem.* **1992**, *31*, 3411–3422; c) W. Nakanishi, M. Yamana, E. Nakamura, *J. Am. Chem. Soc.* **2005**, *127*, 1446–1453.
- [11] a) D. J. Gorin, F. D. Toste, *Nature* **2007**, *446*, 395–403; b) T. C. Boorman, I. Larrosa, *Chem. Soc. Rev.* **2011**, *40*, 1910–1925; c) D. Weber, M. R. Gagné, *Chem. Commun.* **2011**, 47, 5172–5174.
- [12] a) A. Tamaki, J. K. Kochi, *J. Organomet. Chem.* **1972**, *40*, C81–C84; b) A. Tamaki, J. K. Kochi, *J. Chem. Soc. Dalton Trans.* **1973**, 2620–2626; c) A. Tamaki, J. K. Kochi, *J. Organomet. Chem.* **1974**, *64*, 411–425.
- [13] R. E. Bachman, S. A. Bodolosky-Bettis, C. J. Pyle, M. A. Gray, *J. Am. Chem. Soc.* **2008**, *130*, 14303–14310.
- [14] a) S. Bontemps, H. Gornitzka, G. Bouhadir, K. Miqueu, D. Bourissou, *Angew. Chem.* **2006**, *118*, 1641–1644; *Angew. Chem. Int. Ed.* **2006**, *45*, 1611–1614; b) S. Bontemps, G. Bouhadir, K. Miqueu, D. Bourissou, *J. Am. Chem. Soc.* **2006**, *128*, 12056–12057; c) M. Sircoglou, S. Bontemps, M. Mercy, N. Saffon, M. Takahashi, G. Bouhadir, L. Maron, D. Bourissou, *Angew. Chem.* **2007**, *119*, 8737–8740; *Angew. Chem. Int. Ed.* **2007**, *46*, 8583–8586; d) S. Bontemps, M. Sircoglou, G. Bouhadir, H. Puschmann, J. A. K. Howard, P. W. Dyer, K. Miqueu, D. Bourissou, *Chem. Eur. J.* **2008**, *14*, 731–740; e) S. Bontemps, G. Bouhadir, W. Gu, M. Mercy, C.-H. Chen, B. M. Foxman, L. Maron, O. V. Ozerov, D. Bourissou, *Angew. Chem.* **2008**, *120*, 1503–1506; *Angew. Chem. Int. Ed.* **2008**, *47*, 1481–1484; f) M. Sircoglou, S. Bontemps, G. Bouhadir, N. Saffon, K. Miqueu, W. Gu, M. Mercy, C.-H. Chen, B. M. Foxman, L. Maron, O. V. Ozerov, D. Bourissou, *J. Am. Chem. Soc.* **2008**, *130*, 16729–16738; g) M. Sircoglou, M. Mercy, N. Saffon, Y. Coppel, G. Bouhadir, L. Maron, D. Bourissou, *Angew. Chem.* **2009**, *121*, 3506–3509; *Angew. Chem. Int. Ed.* **2009**, *48*, 3454–3457; h) P. Gualco, T. P. Lin, M. Sircoglou, M. Mercy, S. Ladeira, G. Bouhadir, L. M.

- Perez, A. Amgoune, L. Maron, F. P. Gabbaï, D. Bourissou, *Angew. Chem.* **2009**, *121*, 10076–10079; *Angew. Chem. Int. Ed.* **2009**, *48*, 9892–9895; i) A. Amgoune, D. Bourissou, *Chem. Commun.* **2011**, *47*, 859–871.
- [15] P. Gualco, A. Amgoune, K. Miqueu, S. Ladeira, D. Bourissou, *J. Am. Chem. Soc.* **2011**, *133*, 4257–4259.
- [16] The coordination of σ -Si–Si bonds has been rarely observed: a) W. Chen, S. Shimada, M. Tanaka, *Science* **2002**, *295*, 308–310; b) E. C. Sherer, C. R. Kinsinger, B. L. Kormos, J. D. Thompson, C. J. Cramer, *Angew. Chem.* **2002**, *114*, 2033–2036; *Angew. Chem. Int. Ed.* **2002**, *41*, 1953–1956; c) G. Aullón, A. Lledos, S. Alvarez, *Angew. Chem.* **2002**, *114*, 2036–2039; *Angew. Chem. Int. Ed.* **2002**, *41*, 1956–1959; d) R. C. Boyle, D. Pool, H. Jacobsen, M. J. Fink, *J. Am. Chem. Soc.* **2006**, *128*, 9054–9055.
- [17] a) M. Sugimoto, Y. Ito, *J. Chem. Soc. Dalton Trans.* **1998**, 1925–1934; b) M. Sugimoto, Y. Ito, *Chem. Rev.* **2000**, *100*, 3221–3256; c) I. Beletskaya, C. Moberg, *Chem. Rev.* **2006**, *106*, 2320–2354.
- [18] a) M. Wilfling, K. Klinkhammer, *Angew. Chem.* **2010**, *122*, 3287–3291; *Angew. Chem. Int. Ed.* **2010**, *49*, 3219–3223.
- [19] For recent examples of oxidative addition involving chelating assistance by phosphine side arms, see: a) K. Ruhland, A. Obenhuber, S. D. Hoffmann, *Organometallics* **2008**, *27*, 3482–3495; b) A. Obenhuber, K. Ruhland, *Organometallics* **2011**, *30*, 171–186.
- [20] Following the same strategy, we recently observed an original C–P(O) bond cleavage upon coordination of a diphosphine–phosphine oxide to palladium(0): E. J. Derrah, S. Ladeira, G. Bouhadir, K. Miqueu, D. Bourissou, *Chem. Commun.* **2011**, DOI: 10.1039/C1CC12477C.
- [21] a) H. Gilges, G. Kickelbick, U. Schubert, *J. Organomet. Chem.* **1997**, *548*, 57–63; b) M. Murakami, T. Yoshida, Y. Ito, *Organometallics* **1994**, *13*, 2900–2902.
- [22] Consistently, the DFT-optimized geometry of the model complex **2*** exhibits a long Au–Cl distance (2.824 Å) as to compared with the model complex **5*** (2.467 Å).
- [23] For unique examples of square-planar gold(I) complexes, see references [14c] and [14h].
- [24] a) J. Meyer, J. Willnecker, U. Schubert, *Chem. Ber.* **1989**, *122*, 223–230; b) H. Piana, H. Wagner, U. Schubert, *Chem. Ber.* **1991**, *124*, 63–67; c) J. Meyer, H. Piana, H. Wagner, U. Schubert, *Chem. Ber.* **1990**, *123*, 791–793; d) M. Theil, P. Jutzi, B. Neumann, A. Stammler, H.-G. Stammler, *J. Organomet. Chem.* **2002**, *662*, 34–42.
- [25] B. Cordero, V. Gomez, A. E. Platero-Prats, M. Reves, J. Echeverria, E. Cremades, F. Barragan, S. Alvarez, *Dalton Trans.* **2008**, 2832–2838.
- [26] Note that for tin, the reverse step, a gold-catalyzed Sn–Sn bond formation, has been reported: H. Ito, T. Yajima, J.-I. Tateiwa, A. Hosimi, *Tetrahedron Lett.* **1999**, *40*, 7807–7810.
- [27] See the Supporting Information.