

Activation of Aryl Halides at Gold(I): Practical Synthesis of (P,C) Cyclometalated Gold(III) Complexes

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S Supporting Information

ABSTRACT: Taking advantage of phosphine chelation, direct evidence for oxidative addition of C_{sp}²-X bonds (X = I, Br) to a single gold atom is reported. NMR studies and DFT calculations provide insight into this unprecedented transformation, which gives straightforward access to stable (P,C) cyclometalated gold(III) complexes.

The activation of C_{sp}²-halide bonds (C-X) with transition metals plays a pivotal role in catalytic cross-coupling reactions. This oxidative addition process represents the first step of the catalytic cycles and as such, it is a well-established transformation, especially with late transition metals.¹ In this regard, the coinage metals, and gold in particular, stand as striking exceptions, oxidative addition of C_{sp}²-X bonds to gold being considered highly disfavored, if not impossible.^{2,3}

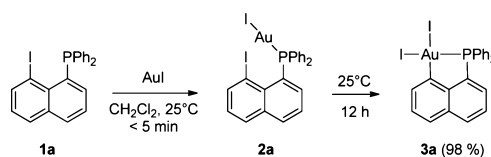
In fact, the seminal work by Corma et al. on gold-catalyzed Sonogashira coupling reactions⁴ has stimulated considerable interest and raised a lively debate⁵ about the ability of gold to undergo oxidative addition of iodoarenes.^{6,7} Due to the supported nature of the involved catalysts, it is hardly possible to identify unequivocally the species that activate the C_{sp}²-X bond and how this proceeds.⁸ Nevertheless, significant progress has been achieved thanks to advanced experimental and theoretical studies, and the ability of multinuclear gold species to activate iodobenzene has been demonstrated for gold nanoparticles^{5c,9} and small gold clusters¹⁰ as well as gold surfaces.¹¹ In parallel, few recent studies have explored the reaction of well-defined mononuclear gold complexes with C_{sp}²-X bonds. No direct evidence for oxidative addition of C_{sp}²-X bonds at a single gold center has been obtained so far,^{12,13} but valuable insights have been gained.^{2c} The reaction of iodobenzene with phosphine gold cations in the gas phase was recently examined using mass spectrometry experiments and DFT calculations.¹⁰ Bisligated complexes such as [(R₃P)₂Au⁺] (R = Me, Ph) were shown not to react with iodobenzene, while under the same conditions, the corresponding monoligated species [(R₃P)Au⁺] form 1:1 adducts that subsequently fragment into the corresponding phosphonium ion [R₃PPh]⁺ and AuI. Reaction of the (IMes)AuPh complex (IMes = N,N'-bis(mesityl)imidazol-2-ylidene) with iodobenzene has also been investigated,

and complete conversion into biphenyl and (IMes)AuI was observed after 50 h at 110 °C in benzene solution.¹⁴ The two latter transformations may involve oxidative addition of iodobenzene to gold, but the putative intermediate Au(III) species have not been characterized.

Our interest for elusive elementary steps at gold^{7,15,16} and phosphine-assisted bond activation with late transition metals¹⁷ prompted us to investigate the reaction of aryl-halides bearing phosphine side arms toward gold. As reported here, this strategy has allowed us to obtain direct evidence for oxidative addition of C_{sp}²-X bonds (X = I, Br). The reactions proceed at a single metal center under relatively mild conditions. The resulting gold(III) complexes have been authenticated crystallographically, and the C_{Ar}-X oxidative addition process has been investigated by spectroscopic and computational means. Such phosphine-directed C_{Ar}-X activation reactions also possess synthetic interest, giving straightforward access to a novel class of thermally robust cyclometalated gold(III) complexes.

The study of phosphine-chelated C_{Ar}-X bond activation at gold was initiated with 8-halo naphthyl phosphines **1**.¹⁸ The naphthyl backbone was envisioned to place the metal center and C_{Ar}-X bond in close proximity.¹⁹ To start with, the 8-iodo naphthyl phosphine **1a** was reacted with AuI in dichloromethane at room temperature (Scheme 1). Surprisingly, oxidative addition of the C_{Ar}-I bond proceeds readily under these conditions to give the cyclometalated gold(III) complex **3a**. ³¹P NMR monitoring revealed that the coordination of the phosphorus atom to gold occurs instantaneously to give the phosphine gold(I) complex **2a** (³¹P NMR, δ = 35.4 ppm). Then,

Scheme 1. Coordination of the 8-Iodo Naphthyl Phosphine 1a: Spontaneous Oxidative Addition of the C_{Ar}-I Bond to Gold



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complex **2a** is gradually and cleanly converted into **3a** (^{31}P NMR, $\delta = 51.8$ ppm). The formation of the gold(III) complex is complete within 24 h at 25 °C and follows first-order kinetics (Figure 1, left), in agreement with an intramolecular

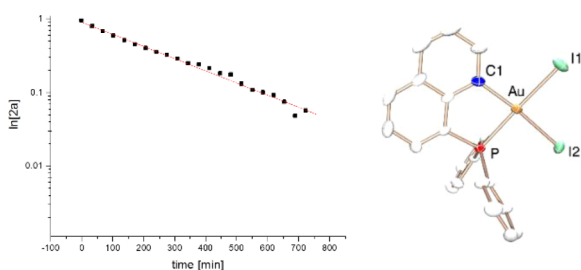


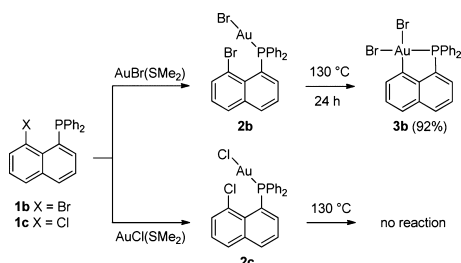
Figure 1. Plot of $\ln[2a]$ vs time at 40 °C, indicating first-order behavior (left). Molecular structure of complex **3a** in the solid state (right). Ellipsoids set at 50% probability; hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: Au–C1 2.070(4); Au–P 2.284(1); Au–I1 2.6288(3); Au–I2 2.6621(3); C1–Au–P 84.4(1); C1–Au–I1 96.1(1); C1–Au–I2 172.2(1); P–Au–I1 175.06(3); P–Au–I2 89.72(2); I1–Au–I2 90.23(1).

unimolecular process.²⁰ Upon heating, the transformation of **2a** into **3a** is significantly accelerated (complete conversion within 2–3 h at 55 °C). The first-order rate constant k_{obs} value was determined at different temperatures, and the activation parameters for the oxidative addition of the $\text{C}_{\text{Ar}}\text{--I}$ bond were derived from an Eyring plot: $\Delta H^\ddagger = 25 \pm 4$ kcal/mol and $\Delta S^\ddagger = 12 \pm 10$ cal/K·mol (Figure S3).

Both complexes **2a** and **3a** have been characterized by multinuclear NMR spectroscopy. Most indicative of the oxidative addition is the disappearance of the ^{13}C NMR resonance signal corresponding to the C–I atom at δ 92.6 ppm in **2a** ($d, J_{\text{PC}} = 5.9$ Hz) and the appearance of a new signal at δ 153.8 ppm ($d, J_{\text{PC}} = 7.2$ Hz) for the *peri*-carbon atom bond to gold in **3a**. The molecular structure of **3a** was confirmed by single crystal X-ray diffraction analysis (Figure 1, right). The gold atom is tetracoordinated with the two iodine atoms, and the five-membered (P,C) chelate organized in a quasi-ideal square-planar arrangement (bond angles deviate by $<8^\circ$). The most noticeable distortion is the 5–6° tilt of the C–P bond toward Au in order to accommodate a relatively short PAu distance [2.284(1) Å].²¹

The formation of **3a** clearly benefits from phosphine chelation, but the oxidative addition of the $\text{C}_{\text{Ar}}\text{--I}$ bond of **1a** is unexpectedly easy. This prompted us to explore the behavior of the related ligands **1b** and **1c** featuring $\text{C}_{\text{Ar}}\text{--Br}$ and $\text{C}_{\text{Ar}}\text{--Cl}$ bonds. The corresponding gold(I) complexes **2b** and **2c** were readily prepared upon reaction with $[\text{AuX}(\text{SMe}_2)]$ (X = Br, Cl) at room temperature (Scheme 2).²² Complex **2c** (X = Cl) was

Scheme 2. Coordination of the 8-Bromo/Chloro Naphthyl Phosphines **1b/1c** to Gold: Oxidative Addition of the $\text{C}_{\text{Ar}}\text{--Br}$ Bond to Gold



heated in xylene, but oxidative addition of the $\text{C}_{\text{Ar}}\text{--Cl}$ bond did not occur even after several hours at 130 °C. In contrast, the $\text{C}_{\text{Ar}}\text{--Br}$ bond of complex **2b** is activated under the same conditions, and the thermally stable gold(III) dibromide complex **3b** is obtained in quantitative yield. Cyclometalation of the naphthyl phosphine is unambiguously supported by the diagnostic NMR signals found at δ $^{31}\text{P} = 66.9$ ppm and δ $^{13}\text{C} = 152.6$ ppm ($d, J_{\text{PC}} = 6.4$ Hz, C–Au).

The computed values of $\Delta G^\ddagger = 21.9$ kcal/mol and $\Delta H^\ddagger = 21.6$ kcal/mol for $\text{C}_{\text{Ar}}\text{--I}$ activation are in good agreement with the activation parameters determined by NMR.²⁰ The geometric features of the transition state connecting **2a*** and **3a*** deserve comment: the cleavage of the C–I1 bond is advanced (2.58 vs 2.12 Å in **2a***), the Au–C1 bond formation is well-developed (2.154 Å), and the P–Au–I2 fragment is noticeably bent (138.7°), see Figure 2. The P, C, and I2 atoms are organized in a Y-shape arrangement around gold, and I1 stands above this trigonal plane, rather far away from gold (AuI1 = 3.041 Å, $\Sigma r_{\text{cov}} = 2.75$ Å).²³

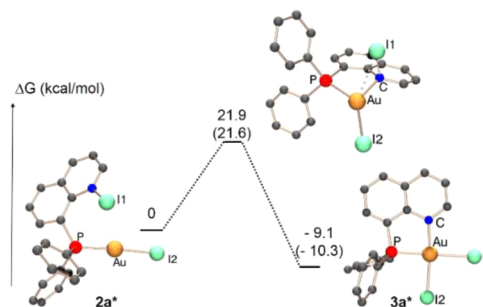
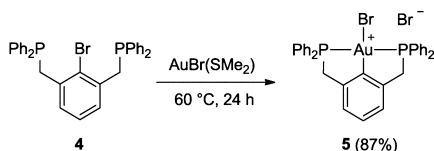


Figure 2. Energy profile computed at the B3PW91/SDD+pol(Au,I),6-31G** (other atoms) level of theory for the oxidative addition of the $\text{C}_{\text{Ar}}\text{--I}$ bond to gold. Free energy ΔG at 25 °C including ZPE correction (kcal/mol). Enthalpy values are given in brackets.

Calculations predict a similar pathway for the oxidative addition of the C–Br and C–Cl bonds of **2b,c***, but the corresponding energy maps differ significantly from one halogen to the other (Figure S30 and S31). Oxidative addition of the C–Br is endergonic by 7.2 kcal/mol, and the associated activation barrier ($\Delta G^\ddagger = 32.1$ kcal/mol) is substantially higher than that of C–I bond activation but remains accessible upon heating. In accordance with experimental results, activation of the $\text{C}_{\text{Ar}}\text{--Cl}$ bond (**2c*** → **3c***) is slightly endergonic ($\Delta G = 0.5$ kcal/mol at 25 °C) and involves a prohibitively high activation barrier ($\Delta G^\ddagger = 39.7$ kcal/mol). The formation of complexes **3a** and **3b** provides the first direct evidence for $\text{C}_{\text{Ar}}\text{--X}$ (X = I, Br) oxidative addition at a single gold center. Besides its fundamental relevance, this transformation is interesting synthetically as it gives direct access to well-defined stable (P,C) gold(III) complexes. Cyclometalation is known to impart high thermal stability to gold(III) complexes by preventing undesirable reductions. Gold(III) complexes deriving from (C,N) ligands have recently attracted much interest²⁴ on their own²⁵ as well as for therapeutic,²⁶ luminescent,²⁷ and catalytic applications.²⁸ However, synthetic issues hamper further development in this area. Direct cyclometalation of N-ligands may be achieved by C–H activation with gold(III) precursors.^{29–31} But this route is far from general and most (C,N) gold(III) complexes are in fact prepared by a multistep process involving transmetalation from organomercury salts.^{24,32} Alternative routes to cyclometalated gold(III) complexes are thus highly desirable, and phosphine-

directed $C_{Ar}-X$ oxidative addition appears attractive to this end. With the aim to illustrate further the synthetic potential of this approach, we became interested in reacting diphosphine ligands of type **4** with gold(I) precursors. The scarcity of (P,C) cyclometalated Au(III) species^{33,34} combined with the interest for Au(III) pincer complexes make (P,C,P)-chelated Au(III) complexes particularly appealing targets. Gratifyingly, reaction of **4** with $[AuBr(SMe_2)]$ in toluene at 60 °C resulted in the coordination of the two phosphines and oxidative addition of the $C_{Ar}-Br$ bond (Scheme 3).³⁴ The ensuing Au(III) complex **5** was

Scheme 3. Synthesis of the (P,C,P) Gold(III) Pincer Complex **5** by $C_{Ar}-Br$ Oxidative Addition to Gold



isolated in 87% yield. It is stable to air (no sign of decomposition detected after several days). Its (P,C,P) pincer structure is clearly apparent from the NMR signals at $\delta^{31}P = 49.8$ ppm and $\delta^{13}C$ 160.8 ppm ($C-Au$, t , $J_{PC} = 4.7$ Hz).

In addition, single crystals of **5** were grown by slow evaporation of a CH_3CN solution at room temperature, and an X-ray diffraction study was performed (Figure 3). The gold

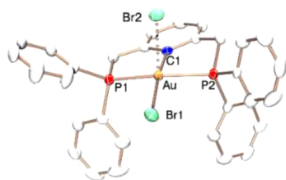


Figure 3. Molecular view of complex **5** in the solid state. Ellipsoids set at 50% probability; hydrogen atoms and solvate molecules omitted for clarity. Selected bond lengths [Å] and angles [°]: Au–C1 2.060(4); Au–P1 2.329(1); Au–P2 2.329(1); Au–Br1 2.5179(5); Au–Br2 2.9945(5); P1–Au–P2 160.43(4); C1–Au–Br1 171.9(1); C1–Au–Br2 92.7(1); C1–Au–P1 81.7(1); C1–Au–P2 83.5(1); P1–Au–Br1 94.08(3); P1–Au–Br2 87.93(3); P2–Au–Br1 98.98(3); P2–Au–Br2 105.48(3); Br1–Au–Br2 94.14(2).

center is organized in a slightly distorted square-planar geometry [$P1-Au-P2$ 160.43(4)° and $C1-Au-Br1$ 171.9(1)°], and the two phosphines are tightly bound to gold [$Au-P1$ and $Au-P2$ 2.329(1) Å]. The bromide counter-anion sits in apical position and only weakly interacts with the metal ($Au-Br2 = 2.9946$ Å).³⁷ Intrigued by the influence that the two phosphine side arms may have on the $C_{Ar}-Br$ oxidative addition, we examined the formation of complex **5** by DFT.²¹ Accordingly, bidentate coordination of the two phosphorus atoms of **4** (complex $4^{**}-AuBr$) was found to precede facile $C_{Ar}-Br$ oxidative addition to gold ($\Delta G^\ddagger = 16.3$ kcal/mol) (Figure 4). An alternative mechanism involving chelation by only one of the phosphine side arm was also considered. The corresponding complex $4^{*}-AuBr$ is slightly more stable than the chelate structure (3.5 kcal/mol), but the activation barrier for the $C_{Ar}-Br$ bond activation is much larger ($\Delta G^\ddagger = 39.2$ kcal/mol). These calculations substantiate the beneficial effect of the second phosphine side arm whose coordination facilitates the oxidative addition process leading to complex **5**. The chelate system is quite unique in that respect, since so far, increasing the coordination number of gold

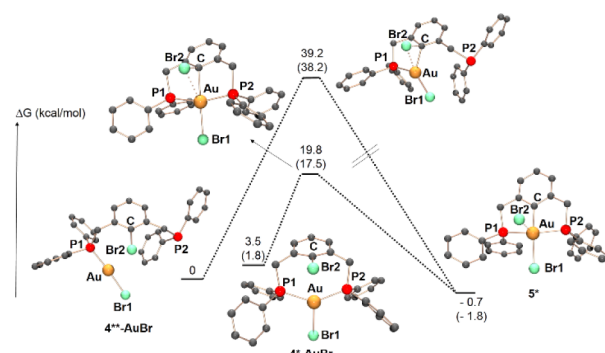


Figure 4. Energy profile computed at the B3PW91/SDD+pol(Au,I),6-31G** (other atoms) level of theory for the oxidative addition of the $C_{Ar}-Br$ bond to gold upon coordination of **4** to gold. Free energy ΔG at 25 °C including ZPE correction (kcal/mol). Enthalpy values are given in brackets.

($[(R_3P)_nAu^+]$ with $n > 1$) has been predicted to disfavor oxidative addition.¹⁰

In conclusion, the results described herein demonstrate that mononuclear gold complexes can undergo oxidative addition of aryl-iodides and -bromides. Such phosphine-directed $C_{Ar}-X$ bond activations provide straightforward access to hitherto unknown (P,C) and (P,C,P) cyclometalated Au(III) complexes. The properties and reactivity of the latter species are under active investigation in our group. Future work will also seek to determine if oxidative addition of $C_{Ar}-X$ bonds can be achieved intermolecularly at gold.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures and characterization data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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(33) Halogenation of *ortho*-vinyl phenylphosphine gold(I) complexes was reported to give six-membered cyclometallated gold(III) complexes, see: Bennett, M. A.; Hoskins, K.; Kneen, W. R.; Nyholm, R. S.; Hitchcock, P. B.; Mason, R.; Robertson, G. B.; Towl, A. D. C. *J. Am. Chem. Soc.* **1971**, *93*, 4591.

(34) For (P,C) cyclometallated polynuclear complexes, see: Bennett, M. A.; Hockless, D. C. R.; Rae, A. D.; Welling, I. L.; Willis, A. C. *Organometallics* **2001**, *20*, 79.

(35) In contrast, the reaction of the arylchloride analogue of **4** with $[AuCl(SMe_2)]$ resulted in the formation of the corresponding three-coordinate diphosphine–AuCl complex without activation of the C_{Ar} -Cl bond.²⁰

(36) The geometry of **5** is similar to that of $[AuPhCl_2(PPh_3)_2]$, that was prepared in two steps, C–H activation of benzene with $[AuCl_3]_2$ followed by PPh_3 coordination, see: Lavy, S.; Miller, J. J.; Pazicky, M.; Rodrigues, A. S.; Rominger, F.; Jäkel, C.; Serra, D.; Vinokurov, N.; Limbach, M. *Adv. Synth. Catal.* **2010**, *352*, 2993.