

Communication

Subscriber access provided by Brought to you by ST ANDREWS UNIVERSITY LIBRARY

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

Johannes Guenther, Sonia Mallet-Ladeira, Laura Estévez, Karinne Miqueu, Abderrahmane Amgoune, and Didier Bourissou

J. Am. Chem. Soc., Just Accepted Manuscript • DOI: 10.1021/ja412432k • Publication Date (Web): 16 Jan 2014 Downloaded from http://pubs.acs.org on January 17, 2014

Just Accepted

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a free service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are accessible to all readers and citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.



Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036 Published by American Chemical Society. Copyright © American Chemical Society. However, no copyright claim is made to original U.S. Government works, or works produced by employees of any Commonwealth realm Crown government in the course of their duties.

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

Johannes Guenther,[‡] Sonia Mallet–Ladeira,[†] Laura Estevez,[#] Karinne Miqueu,[#] Abderrahmane Amgoune,[‡]* and Didier Bourissou[‡]*

[‡]Laboratoire Hétérochimie Fondamentale et Appliquée, Université Paul Sabatier / CNRS UMR 5069, 118 Route de Narbonne, 31062 Toulouse Cedex 09, France.

[†]Institut de Chimie de Toulouse (FR 2599), 118 Route de Narbonne, 31062 Toulouse Cedex 09, France

[#]Institut Pluridisciplinaire de Recherche sur l'Environnement et les Matériaux, Equipe Chimie Physique. Université de Pau et des Pays de l'Adour / CNRS UMR 5254, Hélioparc, 2 Avenue du Président Angot, 64053 Pau cedex 09, France

Supporting Information Placeholder

ABSTRACT: Taking advantage of phosphine chelation, direct evidence for oxidative addition of C_{sp2} -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) cyclometallated gold(III) complexes.

The activation of C_{sp2} -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_{sp2} –X bonds to gold being considered highly disfavoured, 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 Csp2-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 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_{sp2} -X bonds. No direct evidence for oxidative addition of C_{sp2}-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 $[(R_3P)_2Au^+]$ (R = Me, Ph) were shown not to react with iodobenzene, while under the same conditions, the corresponding monoligated species $[(R_3P)Au^+]$ 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-2vlidene) with iodobenzene has also been investigated and complete conversion into biphenyl and (IMes)AuI was observed after 50 hours 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 sidearms towards gold. As reported here, this strategy has allowed us to obtain direct evidence for oxidative addition of C_{sp2} –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 cyclometallated gold(III) complexes.

The study of phosphine-chelated CAr-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 CAr-X bond in close proximity.¹⁹ To start with, the 8-iodo naphthyl phosphine 1a was reacted with AuI in dichloromethane at room temperature. Surprisingly, oxidative addition of the $C_{\mbox{\scriptsize Ar}}\mbox{-I}$ bond proceeds readily under these conditions to give the cyclometallated 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 $({}^{31}P$ NMR, $\delta = 35.4$ ppm). Then, complex **2a** is gradually and cleanly converted into **3a** (³¹P 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 unimolecular process.20 Upon heating, the transformation of 2a into 3a is significantly accelerated (complete conversion within 2-3 hours 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 CAr-I bond were derived from an Eyring plot: $\Delta H^{\neq} = 25 \pm 4$ kcal/mol and ΔS^{\neq} = 12 ± 10 cal/K.mol (Figure S3).



Scheme 1. Coordination of the 8–iodo naphthyl phosphine 1a: spontaneous oxidative addition of the C_{Ar} –I bond to gold.

Both complexes **2a** and **3a** have been characterized by multinuclear NMR spectroscopy. Most indicative of the oxidative addition are the disappearance of the ¹³C NMR resonance signal corresponding to the *C*–I atom at δ 92.6 ppm in **2a** (d, $J_{PC} = 5.9$ Hz) and the appearance of a new signal at δ 153.8 ppm (d, $J_{PC} =$ 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 less than 8°). The most noticeable distortion is the 5–6° tilt of the C–P bond towards Au in order to accommodate a relatively short PAu distance [2.284(1) Å].²¹



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).

The formation of **3a** clearly benefits from phosphine chelation, but the oxidative addition of the C_{Ar} –I bond of **1a** is unexpectedly easy. This prompted us to explore the behavior of the related ligands **1b** and **1c** featuring C_{Ar} –Br and C_{Ar} –Cl bonds. The corresponding gold(I) complexes **2b** and **2c** were readily prepared upon reaction with [AuX(SMe₂)] (X = Br, Cl) at room temperature (Scheme 2).²² Complex **2c** (X = Cl) was heated in xylene but oxidative addition of the C_{Ar} –Cl bond did not occur even after several hours at 130 °C. In contrast, the C_{Ar} –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. Cyclometallation of the naphthyl phosphine is unambiguously supported by the diagnostic NMR signals found at $\delta^{31}P = 66.9$ ppm and $\delta^{13}C = 152.6$ ppm (d, $J_{PC} = 6.4$ Hz, *C*–Au).



Scheme 2. Coordination of the 8–bromo/chloro naphthyl phosphines 1b/1c to gold: oxidative addition of the C_{Ar} -Br bond to gold.

The computed values of $\Delta G^{\neq} = 21.9$ kcal/mol and $\Delta H^{\neq} = 21.6$ kcal/mol for C_{Ar} –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 Å, *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°). 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, $\Sigma r_{cov} = 2.75$ 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 C_{Ar} -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 ($\Delta G^{\neq} =$ 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 C_{Ar} -Cl bond ($2c^* \rightarrow 3c^*$) is slightly endergonic ($\Delta G = 0.5$ kcal/mol at 25 °C) and involves a prohibitively high activation barrier ($\Delta G^{\neq} = 39.7$ kcal/mol). The formation of complexes 3a and 3b provide the first direct evidence for C_{Ar} -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. Cyclometallation 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 interest,²⁴ on their own²⁵ as well as for therapeutic,²⁶ luminescent²⁷ 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 multi-step process involving transmetallation from

1

2

3

4

5

6

7

8

9

10

11

12

13

14 15 16

17

18

19

20

21 22

23

24

25

26

27

28

29

30

31

32

33

34

35

36

37

38

39

40

41

42

43

44

45

46

47

48

49

50

51

52

53

54

55 56

57

58

59 60

organomercury salts.^{24,32} Alternative routes to cyclometallated gold(III) complexes are thus highly desirable and phosphinedirected CAr-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) cyclometallated 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(SMe₂)] in toluene at 60 °C resulted in the coordination of the two phosphines and oxidative addition of the CAr-Br bond (Scheme 3).³⁴ The ensuing Au(III) complex **5** was 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).



Scheme 3. Synthesis of the (PCP) gold(III) pincer complex 5 by C_{Ar} -Br oxidative addition to gold.

In addition, single crystals of 5 were grown by slow evaporation of a CH₃CN solution at room temperature and an X-ray diffraction study was performed (Figure 3). The gold 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 (AuBr2 = 2.9946 Å).³⁷ Intrigued by the influence that the two phosphine sidearms may have on the CAr-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 ($\Delta G^{\neq} = 16.3 \text{ kcal/mol}$) (Figure 4). An alternative mechanism involving chelation by only one of the phosphine sidearm 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 ($\Delta G^{\neq} = 39.2$ kcal/mol). These calculations substantiate the beneficial effect of the second phosphine sidearm 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 ([$(R_3P)_nAu^+$] 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) cyclometallated 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.



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–Br1 171.9(1); C1–Au–Br2 92.7(1); C1–Au–Br2 87.93(3); P2–Au–Br1 98.98(3); P2–Au–Br2 105.48(3); Br1–Au–Br2 94.14(2).



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.

ASSOCIATED CONTENT

Supporting Information

Detailed experimental conditions and procedures, theoretical details, and analytical data and crystallographic data (CIF) for compounds 3_a and 5. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

amgoune@chimie.ups-tlse.fr; dbouriss@chimie.ups-tlse.fr Notes

The authors declare no competing financial interests.

ACKNOWLEDGMENT

Financial support from the Centre National de la Recherche Scientifique, the Université de Toulouse, and the Agence Nationale de la Recherche (ANR-10-BLAN-070901) is acknowledged. The theoretical work was granted access to HPC resources of Idris under Allocation 2013 (i2013080045) made by Grand Equipement National de Calcul Intensif (GENCI). IPREM from the Université de Pau is also acknowledged for calculation facilities

REFERENCES

 (a) Crabtree R. H. *The Organometallic Chemistry of the Transition Metals*, 4th ed. Wiley Interscience: New York, **2005**. (b) Hartwig, J. F. *Organotransition Metal Chemistry: From Bonding to Catalysis*. University Science Books. **2009**. Sausalito, CA. (2) (a) Hopkinson, M. N.; Gee, A. D.; Gouverneur, V. Chem. Eur. J. 2011, 17, 8248. (b) Boorman, T. C.; Larrosa, I. Chem. Soc. Rev. 2011, 40, 1910. (c) Hashmi, A. S. K.; Lothschütz, C.; Döpp, R.; Ackermann, M.; De Buck Becker, J.; Rudolph, M.; Scholz, C.; Rominger, F. Adv. Synth. Catal. 2012, 354, 133. (d) Hansmann, M. M.; Pernpointner, M.; Döpp, R.; Hashmi, A. S. K. Chem. Eur. J. 2013, 19, 15290. (e) Hashmi, A. S. K.; Lothschütz, C.; Döp, R.; Rudolph, M.; Ramamurthi, T. D.; Rominger, F. Angew. Chem. Int. Ed. 2009, 48, 8243. (f) Hashmi, A. S. K.; Döp, R.; Rudolph, M.; Riedel, D.; Rominger, F. Adv. Synth. Catal. 2010, 352, 1307.

(3) In the context of Ullman cross–coupling reactions, using triazamacrocylic ligands, Ribas *et al.* have recently reported direct evidence for C_{sp2} –Br reductive elimination from aryl Cu(III) complexes and oxidative addition of C_{sp2} –X bonds to Cu(I). See: Casitas, A.; Ribas, X. *Chem. Sci.* **2013**, *4*, 2301. and references therein.

(4) (a) Gonzalez-Arellano, C.; Abad, A.; Corma, A.; Garcia, H.;
Iglesias, M.; Sanchez, F. Angew. Chem. Int. Ed. 2007, 46, 1536. (b) Boronat, M.; Combita, D.; Concepción, P.; Corma, A.; Garcia, H.; Juarez, R.;
Laursen, S.; de Dios Lopez-Castro, J. J. Phys. Chem. C 2012, 116, 24855.
(c) Wang et al. reported Sonogoshira reactions catalyzed by Au(I) iodide complexes, see: Li, P.; Wang,L.; Wang, M.; Feng, Y. Eur. J. Org. Chem. 2008, 5946.

(5) (a) Plenio H. Angew. Chem. Int. Ed. 2008, 47, 6954. (b) Lauterbach, T.; Livendahl, M.; Rosellon, A.; Espinet, P.; Echavarren, A. M. Org. Lett. 2010, 12, 3006. (c) Corma, A.; Juarez, R.; Boronat, M.; Sanchez, F.; Iglesias, M.; Garcia, H. Chem. Commun. 2011, 47, 1446.

(6) For oxidative addition of a disulfide to gold, see: Bachman, R. E.; Bodolosky-Bettis, S. A.; Pyle, C. J.; Gray, M. A. *J. Am. Chem. Soc.* **2008**, *130*, 14303.

(7) For oxidative addition of disilanes and distannanes to gold, see:
(a) Gualco, P.; Ladeira, S.; Miqueu, K.; Amgoune, A.; Bourissou, D. Angew. Chem. Int. Ed. 2011, 50, 8320. (b) Lassauque, N.; Gualco, P.; Mallet-Ladeira, S.; Miqueu, K.; Amgoune, A.; Bourissou, D. J. Am. Chem. Soc. 2013, 135, 13827. (c) Joost, M.; Gualco, P.; Coppel, Y.; Miqueu, K.; Kefalidis, C. E.; Maron, L.; Amgoune, A.; Bourissou, D. Angew. Chem. Int. Ed. 2014, 53, 747–751.

(8) Crabtree, R. H. Chem. Rev. 2011, 112, 1536.

(9) (a) Beaumont, S. K.; Kyriakou, G.; Lambert, R. M. J. Am. Chem. Soc. **2010**, *132*, 12246. (b) Kyriakou, G.; Beaumont, S. K.; Humphrey, S. M.; Antonetti, C.; Lambert, R. M. ChemCatChem **2010**, *2*, 1444.

(10) Robinson, P. S. D.; Khairallah, G. N.; da Silva, G.; Lioe, H.; O'Hair, R. A. J. *Angew. Chem. Int. Ed.* **2012**, *51*, 3812.

(11) Kanuru, V. K.; Kyriakou, G.; Beaumont, S. K.; Papageorgiou,
A. C.; Watson, D. J.; Lambert, R. M. *J. Am. Chem. Soc.* 2010, *132*, 8081.
(12) For recent studies on C–N, C–F and C–Cl reductive elimina-

(12) For fectent studies on C=N, C=P and C=C feductive eminination from gold(III) aryl complexes, see: a) 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. b) Mankad, N. P.; Toste, F. D. Chem. Sci. 2012, 3, 72. c) Ghidiu, M. J.; Pistner, A. J.; Yap, G. P. A.; Lutterman, D. A.; Rosenthal, J. Organometallics 2013, 32, 5026.

(13) For a computational study of C_{sp2} -F bond activation at gold, see: Lv, H.; Zhan, J. H.; Cai, Y. B.; Yu, Y.; Wang, B.; Zhang, J. L. *J. Am. Chem. Soc.* **2012**, *134*, 16216.

(14) Johnson, M. T.; Marthinus Janse van Rensburg, J.; Axelsson,M.; Ahlquist, M. S. G.; Wendt, O. F. *Chem. Sci.* 2011, *2*, 2373.

(15) Joost, M.; Gualco, P.; Mallet-Ladeira, S.; Amgoune, A.; Bourissou, D. *Angew. Chem. Int. Ed.* **2013**, *52*, 7160.

(16) Bertrand *et al.* have reported the first examples of α - and β hydride abstractions in gold alkyl complexes, see: Ung, G.; Bertrand, G. *Angew. Chem. Int. Ed.* **2013**, *52*, 11388.

(17) (a) Derrah, E. J.; Ladeira, S.; Bouhadir, G.; Miqueu, K.; Bourissou, D. *Chem. Commun.* **2011**, *47*, 8611. (b) Derrah, E. J.; Martin, C.; Mallet-Ladeira, S.; Miqueu, K.; Bouhadir, G.; Bourissou, D. *Organometallics* **2013**, *32*, 1121.

(18) The coordination of 8-fluoro naphthyl phosphines to gold has been recently studied by Togni *et al.* in the context of remote C-F···Au

interactions: Stanek, K.; Czarniecki, B.; Aardoom, R.; Rüegger, H.; Togni, A. Organometallics **2010**, *29*, 2540.

(19) For the coordination of *peri*-substituted naphthyl phosphines, see the following review: Kilian, P.; Knight, F. R.; Woollins, J. D. *Coord. Chem. Rev.* **2011**, 255, 1387.

(20) See Supporting Information.

(21) A CCDC search revealed that PAu bond distances of structurally characterized phosphine organo gold(III) complexes span from 2.27 to 2.42 Å.

(22) The reactions were carried out with the same halide on the naphthyl ligand and gold precursor (C_{Ar} –Br/AuBr and C_{Ar} –Cl/AuCl), because halide scrambling was observed when two different halides were used.

(23) Cordero, B.; Gomez, V.; Platero-Prats, A. E.; Reves, M.; Echeverria, J.; Cremades, E.; Barragan, F.; Alvarez, S. *Dalton Trans.* **2008**, 2832.

(24) Henderson, W. Adv. Organomet. Chem. 2006, 54, 207.

Using (C,N,C) pincer ligands, Bochmann *et al.* have obtained stable gold(III) hydride, alkene and peroxide complexes, see: (a) Rosa, D. A.; Smith, D. A.; Hughes, D. L.; Bochmann, M. *Angew. Chem. Int. Ed.* **2012**, *51*, 10643. (b) highlight: Hashmi, A. S. K. *Angew. Chem. Int. Ed.* **2012**, *51*, 12935. (c) Savjani, N.; Rosca, D.; Schormann, M.; Bochmann, M. *Angew. Chem. Int. Ed.* **2013**, *52*, 874. (d) Rosca, D. A.; Wright, J. A.; Hughes, D. L.; Bochmann, M. *Nat. Commun.* **2013**, *4*, doi:10.1038/ncomms3167.

(26) Zou, T.; Lum, C. T.; Chui, S. S.-Y.; Che, C. M. Angew. Chem. Int. Ed. **2013**, *52*, 2930.

(27) (a) Yam, V. W.-W.; Cheng, E. C.-C. *Chem. Soc. Rev.* 2008, *37*, 1806. (b) Bronner, C.; Wenger, O. S. *Dalton Trans.* 2011, *40*, 12409. (c) To, W. P.; Tong, G. S.-M.; Lu, W.; Ma, C.; Liu, J.; Chow, A. L.-F.; Che, C. M. *Angew. Chem. Int. Ed.* 2012, *51*, 2654. (d) To, W. P.; Chan, K. T.; Tong, G. S. M.; Ma, C.; Kwok, W. M.; Guan, X.; Low, K. H.; Che, C. M. *Angew. Chem. Int. Ed.* 2013, *52*, 6648.

(28) (a) Schmidbaur, H.; Schier, A. Arab. J. Sci. Eng. 2012, 37, 1187. (b) Kung, K. K.-Y.; Lo, V. K.-Y.; Ko, H. M.; Li, G. L.; Chan, P. Y.; Leung, K. C.; Zhou, Z.; Wang, M. Z.; Che, C. M.; Wong, M. K. Adv. Synth. Catal. 2013, 355, 2055. (c) Ko, H. M.; Kung, K. K.-Y.; Cui, J. F.; Wong, M. K. Chem. Commun. 2013, 49, 8869.

(29) (a) Albrecht, M. *Chem. Rev.* **2009**, *110*, 576. (b) Lu, W.; Chan, K. T.; Wu, S. X.; Chen, Y.; Che, C. M. *Chem. Sci.* **2012**, *3*, 752.

(30) Tilset et *al.* have reported high yield synthesis of (C,N) cyclometallated Au(III) complexes using microwave techniques, see: (a) Shaw, A. P.; Tilset, M.; Heyn, R. H.; Jakobsen, S. *J. Coord. Chem.* **2010**, *64*, 38. (b) Langseth, E.; Görbitz, C. H.; Heyn, R. H.; Tilset, M. Organo-metallics **2012**, *31*, 6567.

(31) This strategy is not applicable to the cyclometallation of phosphines since gold(III) salts oxidize phosphines.

(32) Wong, K. H.; Cheung, K. K.; Chan, M. C.-W.; Che, C. M. Organometallics **1998**, *17*, 3505.

(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.

(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 PPh₃ 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.

