EDGE ARTICLE

Check for updates

Chelation-assisted C–C bond activation of biphenylene by gold(I) halides†

Hélène Beucher, [ID] ‡[a] Johannes Schörgenhumer, [ID] ‡[a] Estíbaliz Merino [ID] [bc] and Cristina Nevado [ID] *[a]
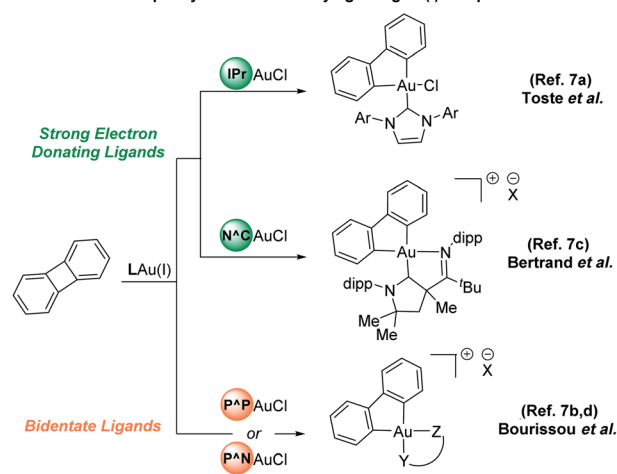
A chelation-assisted oxidative addition of gold(I) into the C–C bond of biphenylene is reported here. The presence of a coordinating group (pyridine, phosphine) in the biphenylene unit enabled the use of readily available gold(I) halide precursors providing a new, straightforward entry towards cyclometalated (N^C^C)- and (P^C)-gold(III) complexes. Our study, combining spectroscopic and crystallographic data with DFT calculations, showcases the importance of neighboring, weakly coordinating groups towards the successful activation of strained C–C bonds by gold.

Activation of C–C bonds by transition metals is challenging given their inertness and ubiquitous presence alongside competing C–H bonds.[1] Both the intrinsic steric hindrance as well as the highly directional character of the p orbitals involved in the σ_{C-C} bond impose a high kinetic barrier for this type of processes.[2,3] Biphenylene, a stable antiaromatic system featuring two benzene rings connected *via* a four-membered cycle, has found widespread application in the study of C–C bond activation. Since the seminal report from Eisch *et al.* on the oxidative addition of a nickel(0) complex into the C–C bond of biphenylene,[4] several other late transition metals have been successfully applied in this context.[5] Interestingly, despite the general reluctance of gold(I) to undergo oxidative addition,[6] its oxidative insertion into the C–C bond of biphenylene was demonstrated in two consecutive reports by the groups of Toste[7a] and Bourissou,[7b] respectively. The high energy barrier associated with the oxidation of gold could be overcome by the utilization of gold(I) precursors bearing ligands that exhibit either a strongly electron-donating character (*e.g.* IPr = [1,3-bis(2,6-diisopropylphenyl)imidazole-2-ylidene])[7a] or small bite angles (*e.g.* DPCb = diphosphino-carborane).[7b,8] In line with these two approaches, more sophisticated bidentate (N^C)- and (P^N)-ligated gold(I) complexes have also been shown to aid the
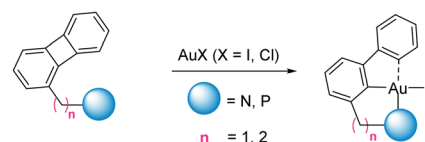
activation of biphenylene at ambient temperature (Scheme 1a).[7c,d]

In this context, we hypothesized that the oxidative insertion of gold(I) into the C–C bond of biphenylene could be facilitated

[a]*Department of Chemistry, University of Zurich, Winterthurerstrasse 190, Zurich, CH 8057, Switzerland. E-mail: cristina.nevado@chem.uzh.ch*

[b]*Universidad de Alcalá, Departamento de Química Orgánica y Química Inorgánica, Instituto de Investigación Andrés M. del Río (IQAR), Facultad de Farmacia, Alcalá de Henares, 28805, Madrid, Spain*

[c]*Instituto Ramón y Cajal de Investigación Sanitaria (IRYCIS), Ctra. de Colmenar Viejo, Km. 9.100, 28034, Madrid, Spain*

‡ Both authors contributed equally to this work.

Scheme 1 (a) Previous reports on oxidative addition of ligated gold(I) precursors onto biphenylene. (b) This work: pyridine- and phosphine-directed C–C bond activation of biphenylene by commercially available gold(I) halides.

by the presence of a neighboring chelating group.[9] This approach would not only circumvent the need for gold(I) precursors featuring strong σ-donor or highly tailored bidentate ligands but also offer a *de novo* entry towards interesting, less explored ligand templates. However, recent work by Breher and co-workers showcased the difficulty of achieving such a transformation.[10]

Herein, we report the oxidative insertion of readily available gold(I) halide precursors into the C–C bond of biphenylene. The appendage of both pyridine and phosphine donors in close proximity to the σ_{C-C} bond bridging the two aromatic rings provides additional stabilization to the metal center and results in a *de novo* entry to cyclometalated (N^C^C)- and (P^C)gold(III) complexes (Scheme 1b).

Our study commenced with the preparation of 5-chloro-1-pyridino-biphenylene system **2** *via* Pd-catalyzed Suzuki cross coupling reaction between 2-bromo-3-methylpyridine and 2-(5-chlorobiphenylen-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **1** (Scheme 2).[11] To our delight, the reaction of **2** with gold(I) iodide in toluene at 130 °C furnished complex κ³-(N^C^C) Au(III)–I **3** in 60% yield.[12,13] Complex **3** was isolated as yellow plate-type crystals from the reaction mixture and its molecular structure was unambiguously assigned by NMR spectroscopy, high-resolution mass spectrometry (HR-MS) and crystallographic analysis. Complex **3** exhibits the expected square-planar geometry around the metal center, with a Au–I bond length of 2.6558(3) Å.[14] The choice of a neutral weakly bound gold(I)-iodide precursor is key for a successful reaction outcome: similar reactions in the presence of [(NHC)AuCl + AgSbF₆] failed to deliver the desired biscyclometalation adducts, as reported by Breher *et al.* in ref. 10. The oxidative insertion of gold(I) iodide into the four-membered ring of pyridino-substituted biphenylene provides a novel and synthetically efficient entry to κ³-(N^C^C)gold(III) halides. These species have recently found widespread application as precursors for the characterization of highly labile, catalytically relevant gold(III) intermediates,[15a–d] as well as for the preparation of highly efficient emitters in OLEDs.[15e–g] Previous synthetic routes towards these attractive biscyclometalated gold(III) systems involved microwave-assisted double C–H functionalization reactions that typically proceed with low to moderate yields.[15a]
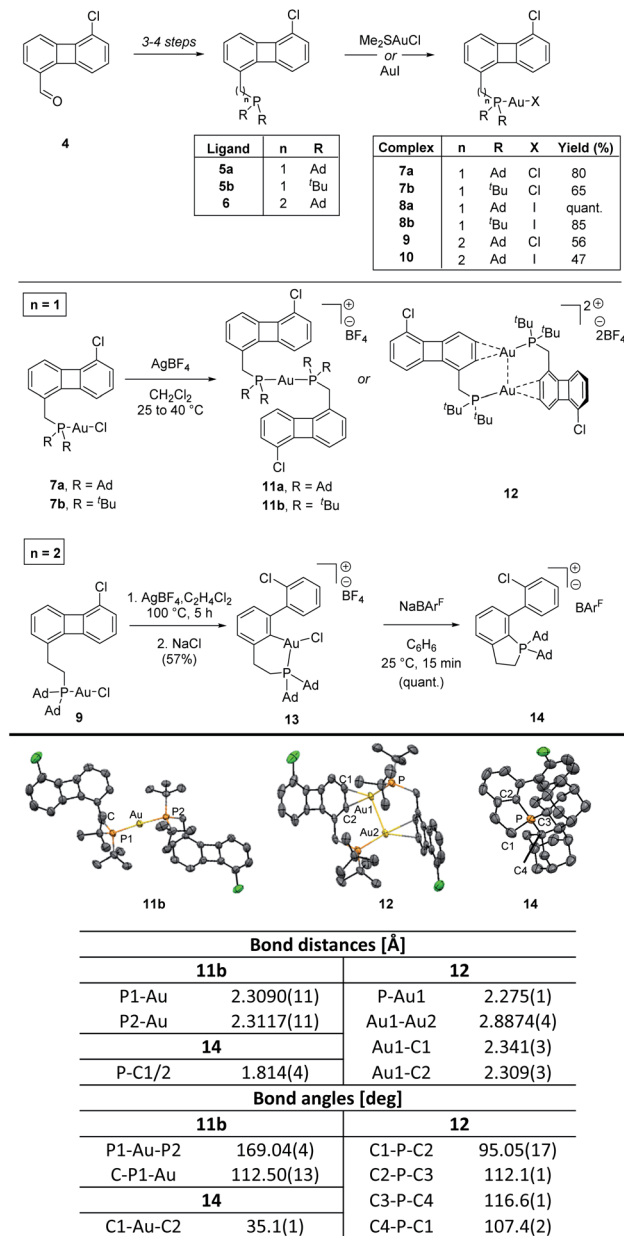
Encouraged by the successful results obtained with the pyridine-substituted biphenylene and considering the prominent use of phosphines in gold chemistry,[6,16] we wondered whether the same reactivity would be observed for a P-containing system. To this end, both adamantyl- and *tert*-butyl-substituted phosphines were appended in C1 position of the biphenylene motif. Starting from 5-chlorobiphenylene-1-carbaldehyde **4**, phosphine-substituted biphenylenes **5a** and **5b** could be accessed in 3 steps (aldehyde reduction to the corresponding alcohol, Appel reaction and nucleophilic displacement of the corresponding benzylic halide) in 64 and 57% overall yields, respectively.[13] The reactions of **5a** and **5b** with commercially available gold(I) halides (Me₂SAuCl and AuI) furnished the corresponding mononuclear complexes **7a–b** and **8a–b**, respectively (Scheme 3).[13] All these complexes were fully characterized and the structures of **7a**, **7b** and **8a** were unambiguously characterized by X-ray diffraction analysis.[13] Interestingly, the nature of the halide has a clear effect on the chemical shift of the phosphine ligand so that a Δδ of *ca.* 5 ppm can be observed in the ³¹P NMR spectra of **7a–b** (Au–Cl) compared to **8a–b** (Au–I), the latter being the more deshielded. The Au–X bond length is also impacted, with a longer Au–I distance (2.5608(1) Å for **8a**) compared to that measured in the Au–Cl analogue (2.2941(7) Å for **7a**) (Δd = 0.27 Å).[13]

Despite numerous attempts to promote the C–C activation in these complexes,[10,13] all reactions resulted in the formation of highly stable cationic species **11a–b** and **12**, which could be easily isolated from the reaction media. In the case of cationic mononuclear-gold(I) complexes **11**, a ligand scrambling reaction in which the chloride ligand is replaced by a phosphine in the absence of a scavenger, a process previously described for gold(I) species, can be used to justify the reaction outcome.[17] The formation of dinuclear gold complex **12** can be ascribed to the combination of a strong aurophilic interaction between the two gold centers (Au–Au = 2.8874(4) Å) and the stabilizing η²-coordination of the metal center to the aromatic ring of biphenylene. Similar η²-coordinated gold(I) complexes have been reported but, to the best of our knowledge, only as mononuclear species.[18]

Taking into consideration the observed geometry of complexes **7a–b** in the solid state,[13] the facile formation of stable cationic species **11** and **12** and the lack of reactivity of the gold(I) iodides **8a–b**, we hypothesized that the free rotation around the C–P bond was probably restricted, placing the gold(I) center away from the biphenylene system and thus preventing the desired oxidative insertion reaction. To overcome this problem, we set out to elongate the arm bearing the phosphine unit with an additional methylene group, introduced *via* a Wittig reaction from compound **4** to yield ligand **6**, prepared in 4 steps in 27% overall yield. Coordination with Me₂SAuCl and AuI resulted in gold(I) complexes **9** and **10**, respectively (Scheme 3). The structure of **9** was unambiguously assigned by X-ray diffraction analysis and a similar environment around the metal center to that determined for complex **7a** was observed for this complex.[13]

With complexes **9** and **10** in hand, we explored their reactivity towards C–C activation of the four-membered ring of

Scheme 2 Synthesis of complex **3** *via* oxidative addition of Au(I) into the C–C bond of pyridine-substituted biphenylene. X-ray structures of complex **3** with atoms drawn using 50% probability ellipsoids. Hydrogen atoms have been omitted for clarity. Additional selected bond distances [Å]: N–Au = 2.126(2), C1–Au = 1.973(2), C2–Au = 2.025(2), Au–I = 2.6558(3) and bond angles [deg]: N–Au–I = 99.25(6), N–Au–C1 = 79.82(9), C1–Au–C2 = 81.2(1), C2–Au–I = 99.73(8). For experimental details, see ESI.†

Ligand	n	R
5a	1	Ad
5b	1	^{t}Bu
6	2	Ad

Complex	n	R	X	Yield (%)
7a	1	Ad	Cl	80
7b	1	^{t}Bu	Cl	65
8a	1	Ad	I	quant.
8b	1	^{t}Bu	I	85
9	2	Ad	Cl	56
10	2	Ad	I	47

Bond distances [Å]			
11b		**12**	
P1-Au	2.3090(11)	P-Au1	2.275(1)
P2-Au	2.3117(11)	Au1-Au2	2.8874(4)
14		Au1-C1	2.341(3)
P-C1/2	1.814(4)	Au1-C2	2.309(3)
Bond angles [deg]			
11b		**12**	
P1-Au-P2	169.04(4)	C1-P-C2	95.05(17)
C-P1-Au	112.50(13)	C2-P-C3	112.1(1)
14		C3-P-C4	116.6(1)
C1-Au-C2	35.1(1)	C4-P-C1	107.4(2)

Scheme 3 Synthesis and reactivity of complexes **7a–b**, **8a–b**, **9** and **10**. X-ray structure of complexes **11b**, **12** and **14** with atoms drawn using 50% probability ellipsoids. Hydrogen atoms have been omitted for clarity. For experimental details and X-ray structures see ESI.†

biphenylene.[19] After chloride abstraction and upon heating at 100 °C for 5 hours, ring opening of the biphenylene system was observed for complex **9**. Interestingly, formation of mono-cyclometalated adduct **13** was exclusively observed (the structure of **13** was confirmed by ^{1}H, ^{13}C, ^{31}P, ^{19}F, ^{11}B and 2D NMR spectroscopy and HR-MS).[13] The solvent appears to play a major role in this process, as performing the reaction in non-chlorinated solvents resulted in stable cationic complexes similar to **11**.[13,20,21] The presence of adventitious water is likely responsible for the formation of the monocyclometalated (P^C) gold(III) complex **13** as when the reaction was carried out in

$C_2H_4Cl_2$ previously treated with D_2O, the corresponding deuterated adduct **13-d** could be detected in the reaction media. These results showcase the difficulties associated with the bis-cyclometalation for P-based complexes as well as the labile nature of the expected biscyclometalated adducts. Interestingly though, these processes can be seen as a *de novo* entry towards relatively underexplored (P^C)gold(III) species.[22]

The C–C activation was further confirmed by X-ray diffraction analysis of the phosphonium salt **14**, which arise from the reductive elimination at the gold(III) center in **13** upon exchange of the BF_4^- counter-anion with the weakly coordinating sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaBAr^F).[13,23] The phosphorus atom is four-coordinate, with weak bonding observed to the distant counter-anion and a distorted tetrahedral geometry (C1–P–C2 = 95.05(17), C2–P–C3 = 112.1(1), C3–P–C4 = 116.6(1), C4–P–C1 = 107.4(2) deg). These results represent the third example in which the C(sp^2)–P bond reductive elimination at gold(III) has been reported.[24]

Further, it is important to note that, in contrast to the reactivity observed for the pyridine-substituted biphenylene, neither P-coordinated gold(I) iodo complexes **8a**, **8b** nor **10** reacted to give cyclometalated products despite prolonged heating, which highlights the need for highly reactive cationized gold(I) species to undergo oxidative addition when phosphine ligands are flanking the C–C bond.[13]

To get a deeper understanding on the observed differences in reactivity for the N- *vs.* P-based directing groups, ground- and transition-state structures for the oxidative insertion of gold(I) halides in C1-substituted biphenylenes were computed by DFT calculations. The reactions of Py-substituted **2** with AuI to give **3** (**I**) and those of P-substituted **7a** (**II**) and **9** (**III**) featuring the cationization of the gold(I) species were chosen as models for comparative purposes with the experimental conditions (Fig. 1 and S1–S10 in the ESI†).[25–27] The computed activation energies for the three processes are in good agreement with the experimental data. The pyridine-substituted biphenylene **I** exhibits the lowest activation barrier for the oxidative insertion process ($\Delta G^\ddagger = 34.4$ kcal mol^{-1}). The reaction on the phosphine-substituted derivatives **II** and **III** proved to be, after cationization of the corresponding gold(I) halide complexes (**II**-BF$_4$, **III**-BF$_4$) higher in energy ($\Delta G^\ddagger = 39.6$ and 46.3 kcal mol^{-1} respectively), although the obtained values do not rule out the feasibility of the C–C activation process. The transition state between **I** and **I'** exhibits several interesting geometrical features: (a) the biphenylene is significantly bent, (b) the cleavage of the C–C bond is well advanced ($d_{C-C} = 1.898$ Å in **TS$_I$** *vs.* $d_{C-C} = 1.504$ Å in **I**), and (c) the two C and the I atoms form a Y-shape around gold with minimal coordination from the pyridine ($d_{N-Au} = 2.742$ Å in **TS$_I$** *vs.* $d_{N-Au} = 2.093$ Å in **I** and 2.157 Å in **I'**, respectively). The transition-state structures found for the P-based ligands (**TS$_{II}$** and **TS$_{III}$**) also show an elongation of the C–C bond and display a bent biphenylene. However, much shorter P–Au distances ($d_{P-Au} = 2.330$ Å for **TS$_{II}$** and 2.314 Å for **TS$_{III}$**) can be observed compared to the pyridine-based system, as expected due to the steric and electronic differences between these two coordinating groups. Analogously, longer C–Au distances were also found for the P-based systems ($d_{C1-Au} = 2.152$ Å for **TS$_I$** *vs.*
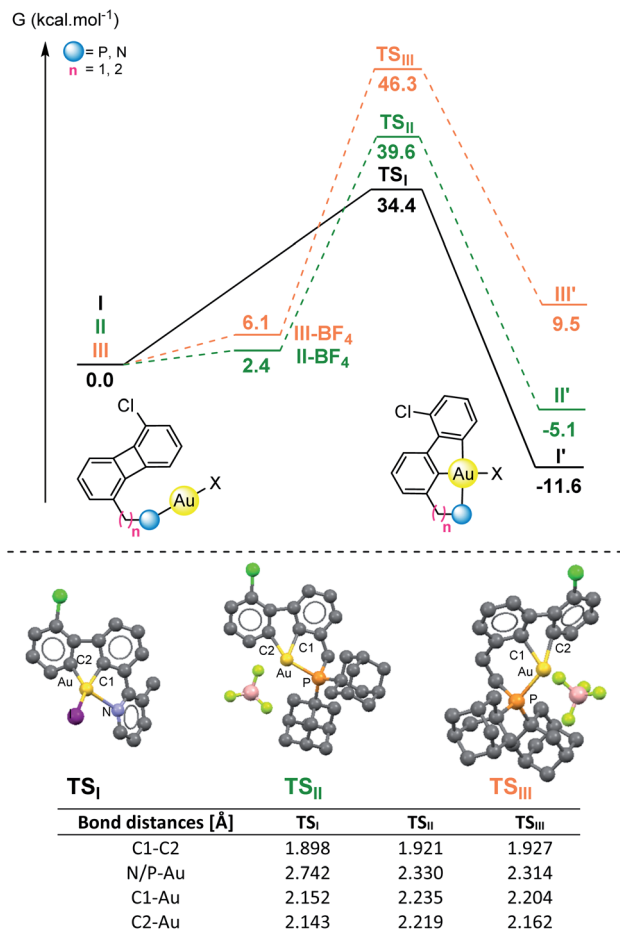
Fig. 1 Energy profile (ΔG and $\Delta G^{\ddagger}$ in kcal mol^{-1}), optimized structures, transition states computed at the IEFPCM (toluene/1,2-dichloro-ethane)-B3PW91/DEF2QZVPP(Au,I)/6-31++G(d,p)(other atoms) level of theory for the C–C activation of biphenylene with gold(I) iodide from **I** and gold(I) cationic from **II** and **III**. Computed structures of the transition states (**TS$_I$**, **TS$_{II}$** and **TS$_{III}$**) and table summarizing relevant distances.

2.235 Å and 2.204 Å for **TS$_{II}$** and **TS$_{III}$**; $d_{C2–Au} = 2.143$ Å for **TS$_I$** *vs.* 2.219 Å and 2.162 Å for **TS$_{II}$** and **TS$_{III}$**), with a larger deviation of square planarity for Au in **TS$_{III}$** compared to **TS$_{II}$**.[28,29] These results suggest that, provided the appropriate distance to the C–C bond is in place, the strong coordination of phosphorous to the gold(I) center does not prevent the C–C activation of biphenylene but other reactions (*i.e.* formation of diphosphine gold(I) cationic species, protodemetalation) can outcompete the expected biscyclometalation process. In contrast, a weaker donor such as pyridine offers a suitable balance bringing the gold in close proximity to the C–C bond and enables both the oxidative cleavage as well as the formation of the double metalation product.

Conclusions

In conclusion, biphenylene derivatives featuring both pyridine and phosphine coordinating groups at C2 position have been synthesized enabling the facile activation of the neighboring

$\sigma_{C–C}$ bond *via* oxidative cyclometalation from readily available gold(I) halide precursors. The reactions provide a new entry towards cyclometalated (N^C^C)- and (P^C)-gold(III) species. Aided by DFT calculations, we demonstrate the importance of the neighboring chelating group, as its coordination properties strongly influence the outcome of the reaction towards the formation of bis- or monocyclometalated complexes.

Data availability

Deposition Numbers 2065053 (for **3**), 2065060 (for **7a**), 2065062 (for **7b**), 2065061 (for **8a**), 2065065 (for **9**), 2065063 (for **11b**), 2065064 (for **12**) and 2065066 (for **14**) contain the supplementary crystallographic data for this paper.

Author contributions

Conceptualisation, supervision and writing – C. N.; investigation and methodology – H. B., J. S., E. M., C. N.; all authors have given approval to the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Notes and references

1 (*a*) M. Murakami and N. Ishida, in *Cleavage of Carbon-Carbon Single Bonds by Transition Metals*, ed. M. Murakami and N. Chatani, Wiley-Hoboken, 2015; (*b*) P. H. Chen, B. Billett, T. Tsukamoto and G. Dong, *ACS Catal.*, 2017, **7**, 1340.

2 (*a*) C. Perthuisot, B. L. Edelbach, D. L. Zubris, N. Simhai, C. N. Iverson, C. Müller, T. Satoh and W. D. Jones, *J. Mol. Catal. A: Chem.*, 2002, **189**, 157; (*b*) K. Ruhland, *Eur. J. Org. Chem.*, 2012, 2683; (*c*) W. Jones, *Top. Curr. Chem.*, 2014, **346**, 1; (*d*) L. Souillart and N. Cramer, *Chem. Rev.*, 2015, **115**, 9410.

3 E. M. Siegbahn and M. R. A. Blomberg, *J. Am. Chem. Soc.*, 1992, **114**, 10548.

4 J. J. Eisch, A. M. Plotrotrowski, K. I. Han, C. Krüger and Y. H. Tsay, *Organometallics*, 1985, **4**, 224.

5 For selected references, see: (*a*) C. Perthuisot and W. D. Jones, *J. Am. Chem. Soc.*, 1994, **116**, 3647; (*b*) Z. Lu,

C.-H. Jun, S. R. de Gala, M. Sigalas, O. Eisenstein and R. H. Crabtree, *Organometallics*, 1995, **14**, 1168; (*c*) C. Perthuisot, B. L. Edelbach, D. L. Zubris and W. D. Jones, *Organometallics*, 1997, **16**, 2016; (*d*) W.-Y. Yeh, S. C. N. Hsu, S.-M. Peng and G.-H. Lee, *Organometallics*, 1998, **17**, 2477; (*e*) B. L. Edelbach, R. J. Lachicotte and W. D. Jones, *J. Am. Chem. Soc.*, 1998, **120**, 2843; (*f*) C. N. Iverson and W. D. Jones, *Organometallics*, 2001, **20**, 5745; (*g*) C. Müller, R. J. Lachicotte and W. D. Jones, *Organometallics*, 2002, **21**, 1975; (*h*) S. Kumaraswamy, S. S. Jalisatgi, A. J. Matzger, O. S. Milijanic and K. P. C. Vollhardt, *Angew. Chem., Int. Ed.*, 2004, **43**, 3711; (*i*) T. Schaub and U. Radius, *Chem.– Eur. J.*, 2005, **11**, 5024; (*j*) D. D. Wick and W. D. Jones, *Inorg. Chim. Acta*, 2009, **362**, 4416; (*k*) A. B Chaplin, R. Tonner and A. S. Weller, *Organometallics*, 2010, **29**, 2710; (*l*) R. Beck and S. A. Johnson, *Chem. Commun.*, 2011, **47**, 9233; (*m*) J. M. Darmon, S. C. E. Stieber, K. T. Sylvester, I. Fernández, E. Lobkovsky, S. P. Semproni, E. Bill, K. Wieghardt, S. DeBeer and P. J. Chirik, *J. Am. Chem. Soc.*, 2012, **134**, 17125; (*n*) D. A. Laviska, C. Guan, T. J. Ernge, M. Wiklow-Marnell, W. W. Brennessel, W. D. Jones, K. Krogh-Jespersen and A. S. Goldman, *Dalton Trans.*, 2014, **43**, 16354.

6 M. Joost, A. Amgoune and D. Bourissou, *Angew. Chem., Int. Ed.*, 2015, **54**, 15022.

7 (*a*) C.-Y. Wu, T. Horibe, C. B. Jacobsen and F. D. Toste, *Nature*, 2015, **517**, 449; (*b*) M. Joost, L. Estévez, K. Miqueu, A. Amgoune and D. Bourissou, *Angew. Chem., Int. Ed.*, 2015, **54**, 5236; (*c*) J. Chu, D. Munz, R. Jazzar, M. Melaimi and G. Bertrand, *J. Am. Chem. Soc.*, 2016, **138**, 7884; (*d*) A. Zeineddine, L. Estévez, S. Mallet-Ladeira, K. Miqueu, A. Amgoune and D. Bourissou, *Nat. Commun.*, 2017, **8**, 565.

8 M. Joost, A. Zeineddine, L. Estévez, S. Mallet-Ladeira, K. Miqueu, A. Amgoune and D. Bourissou, *J. Am. Chem. Soc.*, 2014, **136**, 14654.

9 For precedents on directed activation of biphenylene, see: (*a*) Y. Koga, M. Kamo, Y. Yamada, T. Matsumoto and K. Matsubara, *Eur. J. Inorg. Chem.*, 2011, 2869; (*b*) H. Takano, T. Ito, K. S. Kanyiva and T. Shibata, *Chem.–Eur. J.*, 2018, **24**, 15173; (*c*) D. Frejka, J. Ulč, E. Assen, B. Kantchev, I. Císařová and M. Kotora, *ACS Catal.*, 2018, **8**, 10290. For a directed activation of strained systems with Au(III), see also:; (*d*) J. A. González, F. Verdugo, J. L. Mascareñas, F. López and C. Nevado, *Angew. Chem., Int. Ed.*, 2020, **59**, 20049.

10 W. Feuerstein and F. Breher, *Dalton Trans.*, 2021, **50**, 9754.

11 S.-L. Wang, M.-L. Pan, W.-S. Su and Y.-T. Wu, *Angew. Chem., Int. Ed.*, 2017, **56**, 14694.

12 The introduction of a Me-substituent in *meta* position of the pyridine ring aimed to improve the solubility of the ligand. The corresponding pyridine-coordinated gold(I) halide intermediate was observed in solution but could not be isolated due to its labile character.

13 See ESI† for further details.

14 The analogous reaction with AuCl did not furnish the desired cyclometalated adduct, in line with the work reported in ref. 10, and with previous reports showcasing the high energy demand associated to the oxidative addition for AuCl and AuBr species, see: J. Guenther, S. Mallet-Ladeira, L. Estevez, K. Miqueu, A. Amgoune and D. Bourissou, *J. Am. Chem. Soc.*, 2014, **136**, 1778.

15 (*a*) R. Kumar, A. Linden and C. Nevado, *Angew. Chem., Int. Ed.*, 2015, **54**, 14287; (*b*) R. Kumar, J.-P. Krieger, E. Gómez-Bengoa, T. Fox, A. Linden and C. Nevado, *Angew. Chem., Int. Ed.*, 2017, **56**, 12862; (*c*) L. Rocchigiani, J. Fernandez-Cestau, I. Chambrier, P. Hrobárik and M. Bochmann, *J. Am. Chem. Soc.*, 2018, **140**, 8287; (*d*) H. Beucher, E. Merino, A. Genoux, T. Fox and C. Nevado, *Angew. Chem., Int. Ed.*, 2019, **58**, 9064; (*e*) L.-K. Li, M.-C. Tang, S.-L. Lai, M. Ng, W.-K. Kwok, M.-Y. Chan and V. W.-W. Yam, *Nat. Photonics*, 2019, **13**, 185; (*f*) H. Beucher, S. Kumar, E. Merino, W.-H. Hu, G. Stemmler, S. Cuesta-Galisteo, J. A. González, J. Jagielski, C.-J. Shih and C. Nevado, *Chem. Mater.*, 2020, **32**, 1605; (*g*) H. Beucher, S. Kumar, R. Kumar, E. Merino, W.-H. Hu, G. Stemmler, S. Cuesta-Galisteo, J. A. González, L. Bezinge, J. Jagielski, C.-J. Shih and C. Nevado, *Chem.– Eur. J.*, 2020, **26**, 17604.

16 (*a*) R. Dorel and A. M. Echavarren, *Chem. Rev.*, 2015, **115**, 9028; (*b*) D. Pflästerer and A. S. K. Hashmi, *Chem. Soc. Rev.*, 2016, **45**, 1331.

17 (*a*) G. D. Frey, R. D. Dewhurst, S. Kousar, B. Donnadieu and G. Betrand, *J. Organomet. Chem.*, 2008, **693**, 1674; (*b*) U. Monkowius, M. Zabel and H. Yersin, *Inorg. Chem. Commun.*, 2008, **11**, 409; (*c*) E. W. Ainscough, G. A. Bowmaker, A. M. Brodie, G. H. Freeman, J. V. Hanna, P. C. Healy, W. T. Robinson, B. W. Skelton, M. E. Smith, A. N. Sobolev and A. H. White, *Eur. J. Inorg. Chem.*, 2010, 2044; (*d*) H. Sivaram, R. Jothibasu and H. V. Huynh, *Organometallics*, 2012, **31**, 1195; (*e*) S. K. Goetzfried, C. M. Gallati, M. Cziferszky, R. A. Talmazan, K. Wurst, K. R. Liedl, M. Podewitz and R. Gust, *Inorg. Chem.*, 2020, **59**, 15312.

18 (*a*) E. Herrero-Gómez, C. Nieto-Oberhuber, S. López, J. Benet-Buchholz and A. M. Echavarren, *Angew. Chem., Int. Ed.*, 2006, **45**, 5455; (*b*) Q.-S. Li, C.-Q. Wan, R.-Y. Zou, F.-B. Xu, H.-B. Song, X.-J. Wan and Z.-Z. Zhang, *Inorg. Chem.*, 2006, **45**, 1888; (*c*) V. Lavallo, G. D. Frey, S. Kousar, B. Donnadieu and G. Betrand, *PNAS*, 2007, **104**, 13569; (*d*) P. Pérez-Galán, N. Delpont, E. Herrero-Gómez, F. Maseras and A. M. Echavarren, *Chem.–Eur. J.*, 2010, **16**, 5324.

19 Even at elevated temperatures, **10** did not show any reactivity, in line with our observations for complexes **8a– b** (Section 3 in the ESI†).

20 When the reaction was carried out in $C_2D_2Cl_4$, adduct **13** was also obtained according to HR-MS analysis.

21 The influence of the solvent on the activation of biphenylene with cationic gold(I) complexes has been computed and the results can be found in Table S3 in the ESI.†

22 For previous reports on the synthesis of (P^C)gold(III) complexes, see: (*a*) M. A. Bennett, K. Hoskins, W. R. Kneen, R. S. Nyholm, P. B. Hitchcock, R. Mason, G. B. Robertson and A. D. C. Towl, *J. Am. Chem. Soc.*, 1971, **93**, 4591; (*b*) L. C. Wilkins, Y. Kim, E. D. Litle and

F. P. Gabbai, *Angew. Chem., Int. Ed.*, 2019, **58**, 18266, and ref. 14.

23 BF$_4$ was also exchanged for other anions, such as triflate, tetraphenylborane and bistriflimide, but no C–P bond reductive elimination was observed in these cases.

24 (*a*) H. Kawai, W. J. Wolf, A. G. DiPasquale, M. S. Winston and F. D. Toste, *J. Am. Chem. Soc.*, 2016, **138**, 587; (*b*) R. Bonsignore, S. R. Thomas, W. T. Klooster, S. J. Coles, R. L. Jenkins, D. Bourissou, G. Barone and A. Casini, *Chem.–Eur. J.*, 2020, **26**, 4226.

25 The oxidative insertion of gold(I) complexes (iodide, chloride and cationic) in C1-substituted biphenylenes **2**, **7** and **9** has been computed and the results can be found in the ESI.†

26 For previous DFT calculations on the oxidative addition of other metals to biphenylene, see: (*a*) Z. Gu,

G. B. Boursalian, V. Gandon, R. Padilla, H. Shen, T. V. Timofeeva, P. Tongwa, K. P. C. Vollhardt and A. A. Yakovenko, *Angew. Chem., Int. Ed.*, 2011, **50**, 9413; (*b*) R. Y. Kong and M. R. Crimmin, *Angew. Chem., Int. Ed.*, 2020, **60**, 2619, and ref. 7c.

27 The involvement of a Wheland intermediate in the mechanism was also considered, yet no stable structures were found for this pathway.

28 For a previous comparison between pyridine and phosphine coordination on the reactivity of gold(III) complexes, see: J. Serra, P. Font, E. D. Sosa Carrizo, S. Mallet Ladeira, S. Massou, T. Parella, K. Miqueu, A. Amgoune, X. Ribas and D. Bourissou, *Chem. Sci.*, 2018, **9**, 3832.

29 The NBOs for the transition state structures have been calculated and can be found in the ESI (Fig. S12–S14†).