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Chemo-selective Stille-type coupling of acyl-chlorides upon phosphine-borane Au(I) catalysis†

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Phosphine-boranes do not promote oxidative addition of acyl chlorides to gold, but the phosphine-borane gold triflimide complex [^{i}Pr$_2$P(*o*-C$_6$H$_4$)BCy$_2$]AuNTf$_2$ was found to catalyze the coupling of acyl chlorides and aryl stannanes. The reaction involves aryl/chloride-bridged dinuclear gold(I) complexes as key intermediates, as substantiated by spectroscopic and crystallographic analyses. Similar to Pd(0)/Pd(II)-catalyzed Stille coupling with phosphine-borane ligands, the gold-catalyzed variant shows complete chemoselectivity for acyl chlorides over aryl iodides and bromides, enabling straightforward access to halogenated aryl ketones.

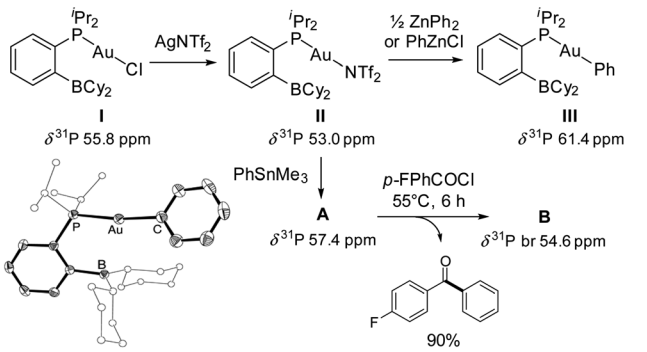
Introduction

Over the past 15 years, phosphine-boranes have emerged as versatile and powerful ligands. The presence of a Lewis moiety in the coordination sphere of transition metals, either directly bonded to the metal or pendant, has been shown to impart peculiar reactivity and to open new catalytic paths.[1] In this context, we have shown that phosphine-boranes enable chemoselective activation and catalytic Stille coupling of acid chlorides at palladium.[2]

Recently, we have started to explore the impact of phosphine-boranes on gold chemistry and discovered some unique features, namely facile organic group transfer between boron and gold(I)[3] and Lewis acid-assisted C(sp^3)–C(sp^3) coupling at gold(III).[4] Here, we investigated the possibility of activating acyl chlorides at gold thanks to the use of phosphine-borane ligands. This work was stimulated by two recent reports. First, Peters *et al.* achieved Stille coupling under gold catalysis for the first and only time so far. Gold nanoparticles supported on active carbon were shown to efficiently promote the coupling of allyl stannanes and alkyl bromides.[5] Second, Gabbaï *et al.* demonstrated the ability of Lewis acids to trigger Au(I) to Au(III) oxidation using a phosphine–xanthylium ambiphilic ligand.[6] As detailed hereafter, we found that phosphine-boranes do not emulate oxidation addition of acyl chlorides to gold, but we discovered that Stille-type coupling is possible under catalytic conditions and with complete chemoselectivity for acyl chlorides over aryl iodides and bromides. Aryl-bridged dinuclear gold(I) complexes with pendant borane moieties have been spectroscopically and structurally authenticated. They are proposed to be key intermediates for acyl chloride activation and aryl transfer.

Results & discussion

The phosphine-borane ^{i}Pr$_2$P(*o*-C$_6$H$_4$)BCy$_2$ (referred to as PBCy$_2$) was chosen for this study. It is easily accessible and rather stable. The Lewis acidity and steric hindrance of the borane moiety are intermediate compared to other phosphine-boranes. The (PBCy$_2$)AuCl complex **I** was prepared following the reported procedure.[7] Treatment with AgNTf$_2$ then readily afforded the



Scheme 1 Synthesis of the (PBCy$_2$) gold complexes **II** and **III**. Molecular structure of **III** (bottom left) with ellipsoids shown at 50% probability and H atoms omitted, and Cy/^{i}Pr substituents at boron/phosphorus simplified. Stoichiometric reactions with *p*F-PhCOCl and PhSnMe$_3$.

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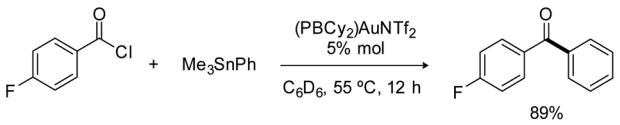
corresponding $(PBCy_2)AuNTf_2$ complex **II** (Scheme 1).[8] For the sake of completeness, the $(PBCy_2)AuPh$ complex **III**, a possible intermediate in Stille coupling, was also targeted. It was synthesized by reacting **I** or **II** with half an equivalent of $ZnPh_2$ (or one equivalent of PhZnCl). All complexes were characterized by multi-nuclear NMR spectroscopy and mass spectrometry. Single crystals of complex **III** were also analyzed by X-ray diffraction. The complex adopts T-shaped geometry with weak Au → B interaction. The Au···B distance (3.086(2) Å, *r* 1.40)[9] and sum of CBC bond angles (Σ(CBC) 358.38°) are similar to those found in **I** (2.903(5) Å, *r* 1.32, 358.6°).[7]

The $PBCy_2$ gold complexes were then reacted with *p*-fluoro benzoyl chloride *p*F-PhCOCl and phenyltrimethyl stannane $PhSnMe_3$ as benchmark substrates. With the acyl chloride alone, no reaction was observed with the chloro and triflimide complexes, as well as the phenyl complex, even upon heating at 65 °C for hours. Apparently, oxidative addition of acyl chloride to gold is not possible whatever the X coligand at gold (Cl, NTf_2 or Ph) and despite the presence of the borane moiety.[10] The $(PBCy_2)AuCl$ complex **I** also proved inert towards the stannane, but the triflimide complex **II** readily reacted with $PhSnMe_3$ over 15 minutes at 25 °C to give a new complex **A** (Scheme 1), as indicated by the appearance of a new ^{31}P NMR signal at δ 57.4 ppm (*versus* 53.0 ppm for **II**). This is not the $(PBCy_2)AuPh$ complex **III** whose ^{31}P NMR signal appears at δ 61.4 ppm. Interestingly, addition of the acyl chloride *p*F-PhCOCl to complex **A** led after 6 hours of heating at 55 °C to the Stille coupling product, *i.e.* the *p*F-PhCO–Ph ketone (in 90% yield, as determined by ^{19}F NMR spectroscopy with C_6F_6 as an internal standard), along with a new $(PBCy_2)Au$ complex **B** (associated with a broad ^{31}P NMR signal at δ 54.6 ppm).

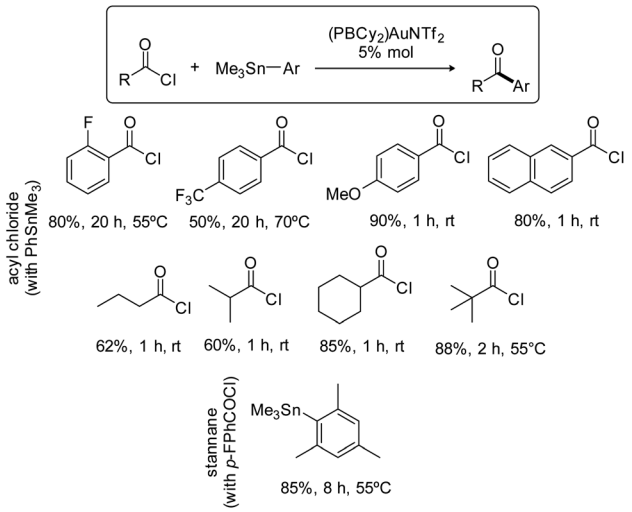
Consistently, reacting the triflimide complex **II** with one equivalent of *p*F-PhCOCl and $PhSnMe_3$ afforded ketone coupling in 78% yield after 5 hours at 55 °C, and gratifyingly, the reaction also works under catalytic conditions (Scheme 2). Using 5 mol% of complex **II**, the *p*F-PhCO–Ph ketone was obtained in 89% yield after 12 hours at 55 °C. No difference was observed when the gold complex was generated *in situ*, from $(PBCy_2)AuCl$ and $AgNTf_2$ (83% yield in ketone after 12 hours at 55 °C with 5 mol% catalyst). Conversely, the chloride complex $(PBCy_2)AuCl$ alone showed no activity, as did the diphosphine-borane $[^iPr_2P(o\text{-}C_6H_4)]_2BPh$ AuCl and $AuNTf_2$ complexes.[11] Of note, a mercury test performed with the $(PBCy_2)AuNTf_2$ catalyst showed no drop in efficiency of the Stille coupling, suggesting that homogeneous not nanoparticle catalysis is operating. A control experiment without gold was also performed and no coupling product was obtained with the phosphine-borane $PBCy_2$ alone.



Scheme 2 Stille coupling catalyzed by the $PBCy_2$ triflimide gold complex **II**.

The scope of the Stille coupling catalyzed by the $(PBCy_2)AuNTf_2$ complex **II** was then investigated. Besides *p*F-PhCOCl, four benzoyl chlorides were selected to test the compatibility of electron-donating and withdrawing groups and of substitution in *ortho*, *meta* and *para* positions (Scheme 3). In all cases, upon reaction with $PhSnMe_3$, the ketone coupling product was obtained in good to high yield. The best result was obtained with *p*MeO-PhCOCl, 90% yield within 1 hour at room temperature, while *p*F_3C-PhCOCl required prolonged heating at 70 °C and afforded only 50% of the ketone. Aliphatic acid chlorides are also efficiently coupled, including those featuring sterically demanding isopropyl, cyclohexyl and *tert*-butyl substituents. As for the stannane partner, the coupling of $MesSnMe_3$ with *p*F-PhCOCl worked nicely, showing again good tolerance to steric hindrance.

Having shown that phosphine-borane ligands impart complete chemoselectivity for acyl chlorides in the Pd-catalyzed Stille coupling,[2] we then investigated the functional group compatibility of the phosphine-borane gold catalyzed transformation towards common aryl electrophiles (Scheme 4). First, competitive experiments were carried out using 1 equivalent of *p*F-PhCOCl acyl chloride and 1 equivalent of *p*-tolyl bromide, iodide or triflate. In all cases, the ArX (X = Br, I, OTf) additive remained intact and the yield of the ketone coupling product was not significantly compromised. Then, the coupling of bifunctional substrates was attempted. The *p*Br-PhCOCl and *p*I-PhCOCl acyl chlorides reacted selectively with $PhSnMe_3$ to afford the corresponding *p*-halogenated dibenzophenones in 75–85% yield. In the same way, the coupling of the *p*I-$PhSnMe_3$ stannane with *p*F-PhCOCl proceeded cleanly and efficiently to give the corresponding *p*-dihalogenated benzophenone (80% yield). Thus, the phosphine-borane gold complex **II** displays high selectivity for acyl chlorides and tolerates $C(sp^2)$–X bonds in both partners of the transformation, enabling straightforward access to functionalized ketones.



Scheme 3 Scope of the Stille coupling catalyzed by the $PBCy_2$ triflimide gold complex **II**. Yields in ketone, as determined by ^{19}F or ^1H NMR spectroscopy with internal standard, C_6F_6 or $ClCH_2CH_2Cl$.

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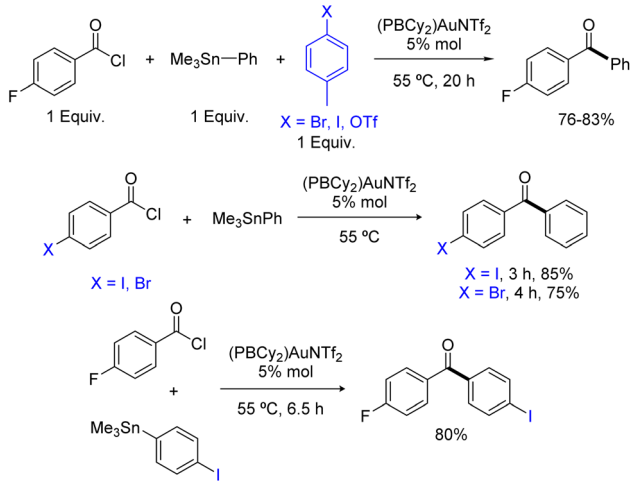
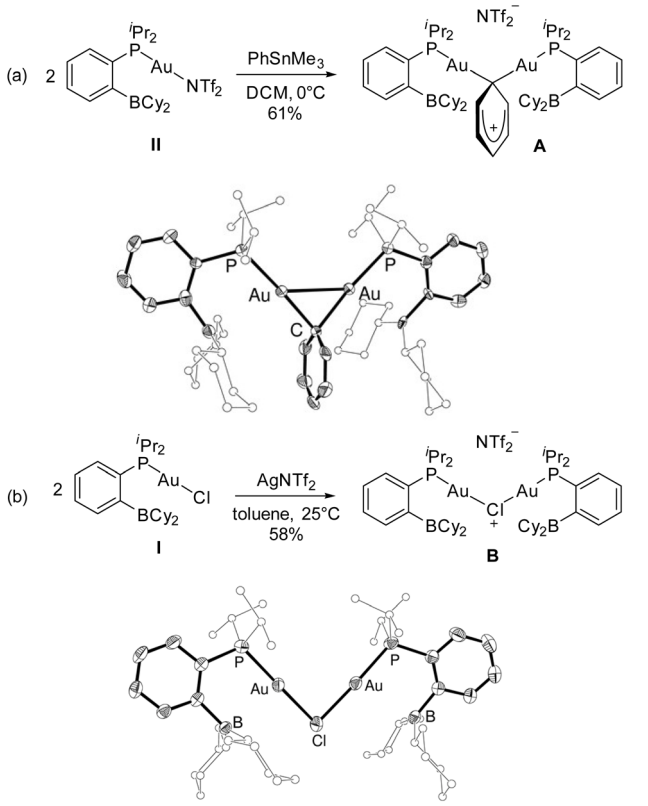


Scheme 4 Chemoselectivity of the Stille coupling catalyzed by the $PBCy_2$ triflimide gold complex **II**. Yields in ketone, as determined by ^{19}F or ^{1}H NMR spectroscopy with internal standard, C_6F_6 or $ClCH_2CH_2Cl$.



Scheme 5 Synthesis and molecular structures of the PB-ligated dinuclear Au(I) complexes **A** (a) and **B** (b). Ellipsoids are drawn at 50% probability. For clarity, the counter-anion and hydrogen atoms are omitted, the ^{i}Pr and Cy substituents are simplified, and only one molecule of the unit cell is shown for **A**.

Efforts were then made to decipher how the catalytic transformation works. To this end, we first aimed at isolating and characterizing the complexes **A** and **B** formed in our initial stoichiometric studies and supposed to be key intermediates. Complex **A** was most efficiently prepared by reacting the triflimide complex **II** with half an equivalent of $PhSnMe_3$ in dichloromethane. It was isolated in 61% yield and unambiguously authenticated as the geminal digold(I) aryl complex (μ-Ph)$[Au(PBCy_2)]_2NTf_2$ by single-crystal X-ray diffraction analysis (Scheme 5a). Since the seminal contribution of Schmidbaur *et al.* in 2003,[12] such aryl-bridged dinuclear gold complexes have attracted considerable attention[13] and been identified as off-cycle resting states in some catalytic transformations.[14] The solid-state structure of complex **A** shows a W-shape conformation with an eclipsed arrangement of the $PBCy_2$ ligands, which probably minimizes steric constraints. The Au···Au distance (2.795(1) Å) and Au–C–Au bond angle (79.9(3)°) fall in the middle range of those found in related complexes (2.70–2.88 Å and 76.6–85.7°),[15] indicating strong aurophilic interaction. The Au···B distances (3.17(1) and 3.18(1) Å) are slightly elongated compared to that found in the $(PBCy_2)$AuPh complex **III** (3.086(2) Å). Complex **A** was also characterized by multi-nuclear NMR spectroscopy and mass spectrometry. Worthy of note is the ^{13}C NMR signal for the carbon atom of the phenyl ring bridging the two gold centers. While this signal has proved so far undetectable,[12,16] it could be easily observed and authenticated for complex **A**. It appears as a triplet at δ 145.7 ppm ($^{2}J_{CP}$ 49 Hz), shielded by about 33 ppm compared with the monometallic $(PBCy_2)$AuPh complex **III** (δ 178.9 ppm, $^{2}J_{CP}$ 113 Hz), in line with a Wheland-type structure.[17] The stability and catalytic activity of complex **A** were then investigated. It proved thermally robust (no sign of decomposition was detected by NMR spectroscopy after 2 days at 55 °C), gave the same results as complex **II** in the catalytic coupling of *p*F-PhCOCl or *t*BuCOCl and Me_3-SnPh (87% yield after 20 h at 55 °C and 70% yield after 1 h 30 at 55 °C, respectively) and did not interfere with C(sp^2)–I bonds (as substantiated by the coupling of *p*F-PhCOCl and $PhSnMe_3$ in the presence of *p*-tol-I as well as the coupling of *p*F-PhCOCl and *p*-$IPhSnMe_3$).[18]

Complex **B** was formed along with the Stille coupling product upon the reaction of complex **A** with *p*F-PhCOCl (Scheme 1). Given the structure of **A**, we surmised the related chloro-bridged digold(I) structure for complex **B**. Independent synthesis upon reacting the chloro complex **I** with half-an-equivalent of $AgNTf_2$ confirmed this hypothesis. The resulting complex showed spectroscopic features identical to those of **B** and it was unequivocally identified as (μ-Cl)$[Au(PBCy_2)]_2$,NTf_2 by single-crystal X-ray diffraction (Scheme 5b). Like **A**, complex **B** adopts a W-shape eclipsed conformation in the solid state, but the Au···Au distance (3.2846(7) Å) and bridging Au–Cl–Au bond angle (88.39(3)°) are substantially larger. The Au···B distances (2.946(4)/2.988(4) Å) are similar to that found in the $(PBCy_2)$AuCl complex **I** (2.903(5) Å). Chloro-bridged dinuclear Au(I) complexes are well-known.[13] Their propensity to further aggregate and form clusters sustained by Au···Au aurophilic interactions has been recognized early on.[19] They are also common by-products in the activation of LAuCl precatalysts with silver salts, often displaying reduced activity if not completely inert.[20] To assess the possibility of catalytic turnover from complex **B**, it was reacted with Me_3-SnPh and pleasingly, the phenyl-bridged complex **A** was quantitatively reformed within 20 minutes at 25 °C.

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To gain further mechanistic insights, kinetic investigations were performed on the coupling reaction between *p*F-PhCOCl and Me_3SnPh with different concentrations of $(PBCy_2)AuNTf_2$ **II**.[18] Using the initial rate method, the partial order in the mononuclear gold(I) complex was found to be 0.5, in line with a dinuclear mechanism (see below). In addition, two catalytic reactions were monitored by ^{31}P NMR spectroscopy.[18] In both cases, the aryl-bridged digold(I) complex **A** was found to be very major species, with a minor (and increasing over the course of the reaction) amount of chloro-bridged digold(I) complex **B**. Complex **A** thus stands as the resting state of the catalytic cycle.

Based on all these experimental observations, we propose the catalytic cycle displayed in Fig. 1 to account for the chemoselective Stille coupling with the phosphine-borane gold(I) complex **II**. It does not proceed by oxidative addition of the acyl chloride to gold and Au(I)/Au(III) redox cycling,[21,22] but rather operates at a constant Au(I) redox state with aryl-bridged dinuclear complexes such as **A** as key intermediates.

To assess the role of the borane moiety, Gagosz's complex $(Ph_3P)AuNTf_2$[23] was tested in the catalytic coupling of *p*F-PhCOCl and $PhSnMe_3$ under similar conditions. The coupling product was obtained in only 3% yield. The C–C bond formation is likely to occur *via* a Friedel–Crafts-type mechanism, although it is difficult to ascertain precisely in the absence of detectable intermediates besides the dinuclear gold(I) complexes **A** and **B**. At this stage, we surmise that the pendant borane moieties of complex **A** activate the acyl chloride while gold transfers the μ-aryl bridged group. It is worth mentioning that Friedel–Crafts coupling of acyl chlorides and aryl stannanes is known with strong Lewis acids such as $AlCl_3$.[24] Of note, no coupling was observed combining the aryl-bridged dinuclear gold complex $(\mu\text{-MeOPh})[Au(PPh_3)]_2NTf_2$[16a] with exogeneous boranes (BPh_3 or $BMes_3$),[18] demonstrating the critical role of the phosphine-borane ligand. To further support the contribution of the borane moiety, the accessibility and Lewis acidity of boron were reduced. The cationic gold complexes $(PB)AuNTf_2$ deriving from $PBMes_2$ and PBpin phosphine-boranes[25] showed significantly lower activity in the catalytic coupling of *p*F-PhCOCl and $PhSnMe_3$ than that derived from $PBCy_2$. The coupling product was obtained in only 62 and 23% yields after 20 hours at 55 °C with $PBMes_2$ and PBpin, compared to 89% within 12 h with $PBCy_2$.

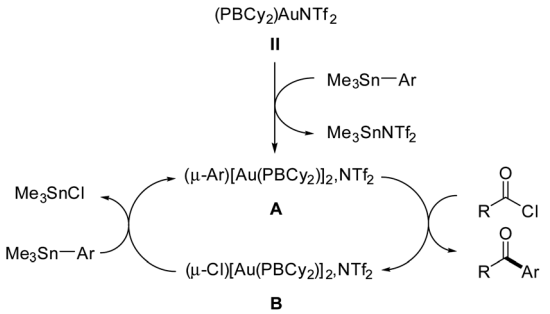

Fig. 1 Catalytic cycle proposed to account for the Stille coupling of acyl chlorides with organostannanes with phosphine-borane gold(I) complexes.

Conclusion

In summary, the phosphine-borane gold triflimide complex **II** was found to efficiently promote the Stille coupling of acyl chlorides and aryl stannanes with complete chemoselectivity over aryl iodides and bromides. The reaction involves an aryl-bridged dinuclear gold(I) complex as the key intermediate, as supported by NMR spectroscopy and X-ray diffraction.

Over the past 5 years, ligand design has been shown to dramatically impact the reactivity profile of gold complexes, emulating new reactivity paths and enabling new catalytic transformations. Chelating P^P and hemilabile P^N ligands has in particular opened the way to a variety of Au(I)/Au(III) redox cross-coupling. The results reported here demonstrate that phosphine-boranes, prototype ambiphilic ligands, may also trigger unusual reactivity at gold and expand the scope of gold-catalyzed transformations. Future studies are planned to explore further the impact of Lewis acid moieties on the reactivity and catalytic activity of gold complexes. Special interest will also be devoted to the ability of ambiphilic ligands to drive chemoselectivity upon C–X bond activation at transition metals.

Data availability

All experimental and characterization data in this manuscript are available in the ESI.† Crystallographic data for complexes **II**, **A** and **B** have been deposited at the CCDC and assigned the numbers 2298251, 2298252 and 2298253, respectively.

Author contributions

N. Hidalgo and A. Le Gac performed the experimental work and spectroscopic analyses. S. M.-L. carried out the X-ray diffraction analyses. All authors analyzed the data and contributed to the manuscript preparation. G. B. and D. B. conceived and supervised the project.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Notes and references

1 For selected reviews, see: (*a*) A. Amgoune and D. Bourissou, *Chem. Commun.*, 2011, **47**, 859; (*b*) H. Kameo and H. Nakazawa, *Chem.–Asian J.*, 2013, **8**, 1720; (*c*) G. Bouhadir

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and D. Bourissou, *Chem. Soc. Rev.*, 2016, **45**, 1065; (*d*) D. You and F. P. Gabbaï, *Trends Chem.*, 2019, **1**, 485; (*e*) B. Chatterjee, W.-C. Chang, S. Jena and C. Werlé, *ACS Catal.*, 2020, **10**, 14024; (*f*) T. Komuro, Y. Nakajima, J. Takaya and H. Hashimoto, *Coord. Chem. Rev.*, 2022, **473**, 214837; (*g*) J. A. Zurakowski, B. J. H. Austen and M. W. Drover, *Trends Chem.*, 2022, **4**, 331.

2 M. Boudjelel, O. Sadek, S. Mallet-Ladeira, Y. García-Rodeja, E. D. Sosa Carrizo, K. Miqueu, G. Bouhadir and D. Bourissou, *ACS Catal.*, 2021, **11**, 3822.

3 (*a*) C. A. Theulier, Y. García-Rodeja, N. Saffon-Merceron, K. Miqueu, G. Bouhadir and D. Bourissou, *Chem. Commun.*, 2021, **57**, 347; (*b*) C. A. Theulier, Y. García-Rodeja, S. Mallet-Ladeira, K. Miqueu, G. Bouhadir and D. Bourissou, *Organometallics*, 2021, **40**, 2409.

4 C. A. Theulier, Y. García-Rodeja, K. Miqueu, G. Bouhadir and D. Bourissou, *J. Am. Chem. Soc.*, 2023, **145**, 10800.

5 J. Holz, C. Pfeffer, H. Zuo, D. Beierlein, G. Richter, E. Klemm and R. Peters, *Angew. Chem., Int. Ed.*, 2019, **58**, 10330.

6 L. C. Wilkins, Y. Kim, E. D. Litle and F. P. Gabbaï, *Angew. Chem., Int. Ed.*, 2019, **58**, 18266.

7 S. Bontemps, G. Bouhadir, K. Miqueu and D. Bourissou, *J. Am. Chem. Soc.*, 2006, **128**, 12056.

8 For gold(I) triflimide complexes deriving from vicinal phosphine-boranes, see: A. Ueno, K. Watanabe, C. G. Daniliuc, G. Kehr and G. Erker, *Chem. Commun.*, 2019, **55**, 4367.

9 To compare M → Z complexes, taking into account the size of the involved atoms, we commonly refer to the ratio r between the MZ distance and the sum of the covalent radii of M and Z. See ref. 1*a*.

10 For a recent example of Au(I) to Au(III) oxidation assisted by the Lewis acid moiety of an ambiphilic ligand, see ref. 6.

11 (*a*) M. Sircoglou, S. Bontemps, M. Mercy, N. Saffon, M. Takahashi, G. Bouhadir, L. Maron and D. Bourissou, *Angew. Chem., Int. Ed.*, 2007, **56**, 8583; (*b*) F. Inagaki, C. Matsumoto, Y. Okada, N. Maruyama and C. Mukai, *Angew. Chem., Int. Ed.*, 2015, **54**, 818.

12 R.-Y. Liau, A. Schier and H. Schmidbaur, *Organometallics*, 2003, **22**, 4922.

13 T. A. C. A. Bayrakdar, T. Scattolin, X. Ma and S. P. Nolan, *Chem. Soc. Rev.*, 2020, **49**, 7044.

14 (*a*) J. Preindl, K. Jouvin, D. Laurich, G. Seidel and A. Fürstner, *Chem.–Eur. J.*, 2016, **22**, 237; (*b*) Y. Tang, J. Li, Y. Zhu, Y. Li and B. Yu, *J. Am. Chem. Soc.*, 2013, **135**, 18396; (*c*) M. Hansmann, M. Rudolph, F. Rominger and A. S. Hashmi, *Angew. Chem., Int. Ed.*, 2013, **52**, 2593.

15 According to a Cambridge database search, slightly over 30 related (hetero)aryl-bridged dinuclear gold(I) complexes have been characterized by X-ray diffraction analysis. The mean values of Au···Au distances and Au–C–Au bond angles are 2.775 Å and 80.73°, respectively.

16 (*a*) D. Weber, T. D. Jones, L. L. Adduci and M. R. Gagné, *Angew. Chem., Int. Ed.*, 2012, **51**, 2452; (*b*) J. E. Heckler, M. Zeller, A. D. Hunter and T. G. Gray, *Angew. Chem., Int. Ed.*, 2012, **51**, 5924; (*c*) M. Hansmann, F. Rominger, M. P. Boone, D. W. Stephan and A. S. Hashmi, *Organometallics*, 2014, **33**, 4461.

17 A mono-metallic Wheland-type complex has been recently authenticated spectroscopically, see: M. S. M. Holmsen, C. Blons, A. Amgoune, M. Regnacq, D. Lesage, E. D. Sosa Carrizo, P. Lavedan, Y. Gimbert, K. Miqueu and D. Bourissou, *J. Am. Chem. Soc.*, 2022, **144**, 22722.

18 See the ESI.†

19 (*a*) A. Hamel, N. W. Mitzel and H. Schmidbaur, *J. Am. Chem. Soc.*, 2001, **123**, 5106; (*b*) H. Schmidbaur, A. Hamel, N. W. Mitzel, A. Schier and S. Nogai, *Proc. Natl. Acad. Sci. U.S.A.*, 2002, **99**(8), 4916.

20 (*a*) A. Homms, I. Escofet and A. M. Echavarren, *Org. Lett.*, 2013, **15**, 5782; (*b*) A. Grirrane, E. Álvarez, H. García and A. Corma, *Angew. Chem., Int. Ed.*, 2014, **53**, 7253; (*c*) Z. Lu, J. Han, G. B. Hammond and B. Xu, *Org. Lett.*, 2015, **17**, 4534.

21 For recent reviews dealing with Au(I)/Au(III) (photo)catalysis, see: (*a*) M. N. Hopkinson, A. Tlahuext-Aca and F. Glorius, *Acc. Chem. Res.*, 2016, **49**, 2261; (*b*) M. O. Akram, S. Banerjee, S. S. Saswade, V. Bedi and N. T. Patil, *Chem. Commun.*, 2018, **54**, 11069; (*c*) S. Banerjee, V. W. Bhoyare and N. T. Patil, *Chem. Commun.*, 2020, **56**, 2677; (*d*) A. Nijamudheen and A. Datta, *Chem.–Eur. J.*, 2020, **26**, 1442; (*e*) B. Huang, M. Hu and F. D. Toste, *Trends Chem.*, 2020, **2**, 707; (*f*) S. Witzel, A. S. K. Hashmi and J. Xie, *Chem. Rev.*, 2021, **121**, 8868; (*g*) V. W. Bhoyare, A. G. Tathe, A. Das, C. C. Chintawar and N. T. Patil, *Chem. Soc. Rev.*, 2021, **50**, 10422; (*h*) P. Font and X. Ribas, *Eur. J. Inorg. Chem.*, 2021, 2556; (*i*) S. B. Ambegave and N. T. Patil, *Synlett*, 2023, **34**, 698.

22 We believe that this scenario is very unlikely for several reasons: (i) none of the features we found crucial to enable oxidative addition to gold are present in complexes **II** and **A**, (ii) the ensuing Au(III) species is likely to lie very high in energy (the phosphine-borane ligand cannot provide stabilization by chelation), and (iii) activation of the acyl chloride by the borane moiety (*via* O → B interaction) is not expected to enable oxidative addition to gold by itself.

23 N. Mézailles, L. Ricard and F. Gagosz, *Org. Lett.*, 2005, **7**, 4133.

24 (*a*) M. J. L. Feigo, G. F. Silbestri, A. B. Chopa and M. T. Lockhart, *J. Org. Chem.*, 2011, **76**, 1707; (*b*) M. Roemer, S. T. Keaveney and N. Proschogo, *J. Org. Chem.*, 2021, **86**, 9007.

25 (*a*) M. W. P. Bebbington, S. Bontemps, G. Bouhadir and D. Bourissou, *Angew. Chem., Int. Ed.*, 2007, **46**, 3333; (*b*) S. Porcel, G. Bouhadir, N. Saffon, L. Maron and D. Bourissou, *Angew. Chem., Int. Ed.*, 2010, **49**, 6186; (*c*) O. Baslé, S. Porcel, S. Ladeira, G. Bouhadir and D. Bourissou, *Chem. Commun.*, 2012, **48**, 4495; (*d*) R. Declercq, G. Bouhadir, D. Bourissou, M.-A. Légaré, M.-A. Courtemanche, K. Syrine Nahi, N. Bouchard, F.-G. Fontaine and L. Maron, *ACS Catal.*, 2015, **5**, 2513.