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Facile Oxidative Addition of Aryl Iodides to Gold(I) by Ligand Design: Bending Turns on Reactivity

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Supporting Information

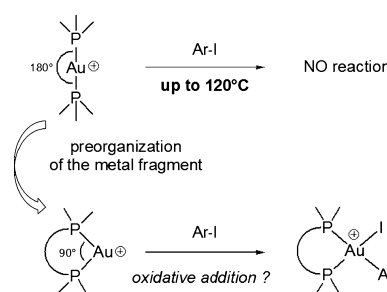
ABSTRACT: Thanks to rational ligand design, the first gold(I) complexes to undergo oxidative addition of aryl iodides were discovered. The reaction proceeds under mild conditions and is general. The ensuing aryl gold(III) complexes have been characterized by spectroscopic and crystallographic means. DFT calculations indicate that the bending induced by the diphosphine ligand plays a key role in this process.

The reactivity of gold complexes is largely dominated by Lewis acid behavior, such as the electrophilic activation of π -CC bonds.¹ Other reaction pathways characteristic of transition metals are very scarce with gold. In particular known gold(I) complexes are reluctant to undergo oxidative addition,² which hampers the realization of classical 2-electron redox catalytic cycles.^{3,4} Most challenging is the activation of $C_{Ar}-X$ bonds with gold(I) complexes,^{5,6} a controversial reactivity that has so far only been unambiguously authenticated intramolecularly using chelating assistance.⁷ Our interest in gold complexes^{2b-e,7,8} prompted us to explore further the oxidative addition of aryl halides with the idea to trigger gold reactivity by ligand design. Contrary to ML_2 complexes of the group 10 metals, linear two-coordinate gold(I) complexes $[LAuX]$ and $[L_2Au^+]$ are highly stable. They are reluctant to achieve higher coordination numbers⁹ and do not undergo oxidative addition.¹⁰ Only monocoordinate cations $[(R_3P)Au^+]$ were shown to react with PhI in the gas phase to give $[R_3PPh^+]$ and AuI via short-lived adducts $[(R_3P)Au(PhI)^+]$.¹¹

A successful approach to enhance the reactivity of late transition metal complexes toward oxidative addition is based on the use of chelating bidentate ligands with small bite angles.¹² Upon bending, the ML_2 fragment is raised in energy and is preorganized to accommodate the square-planar geometry of the ensuing oxidative addition product.¹³ In this context, we envisioned using bidentate ligands and bent two-coordinate $[L_2Au^+]$ fragments to switch on the reactivity of gold complexes toward oxidative addition of aryl iodides (Scheme 1).

It is surprising that this strategy has not been used previously in gold chemistry. This is probably due to the very specific

Scheme 1. Ligand Design Envisioned to Trigger Oxidative Addition of Aryl Iodides to Gold(I) Complexes



coordination chemistry of gold(I) that shows a strong preference for two-coordinate linear geometry.^{1b,9b} In fact, most bidentate ligands form $Au\cdots Au$ dinuclear structures with gold(I).^{14,15} It is difficult to chelate gold(I) with small bite angle bidentate ligands. Noticeable exceptions are carborane diphosphine ligands. Indeed, Laguna and Jones recognized early on the tendency of 1,2-bis(diphenylphosphino)-1,2-dicarba-closo-dodecaborane **1** to form three-coordinate gold(I) complexes.^{16,17}

Carborane diphosphines (DPCb) appeared ideally suited to evaluate our bending strategy, and to do so, we prepared cationic gold(I) complexes thereof. As described hereafter, these complexes undergo oxidative addition of aryl iodides under very mild conditions. The resulting Au(III) species have been characterized by multinuclear NMR spectroscopy, mass spectrometry, and single-crystal X-ray diffraction. The scope of the reaction has been studied, and the effect of bending has been rationalized computationally.

First, the gold(I) chloride complex **2**¹⁶ was reacted with $GaCl_3$ with the aim to generate the bent two-coordinate $[(DPCb)Au^+]$ fragment. ³¹P NMR monitoring at $-30^\circ C$ indicated instantaneous formation of a single compound (δ shifts from 36 to 58 ppm). However, this species decomposes within a few hours to give metallic gold and the previously reported four-coordinate complex $[(DPCb)_2Au^+]$ ($\delta^{31P} = 42$ ppm).¹⁶

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Scheme 2. Oxidative Addition of PhI to the Carborane Bisphosphine Gold(I) Complex 2

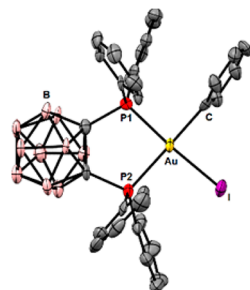
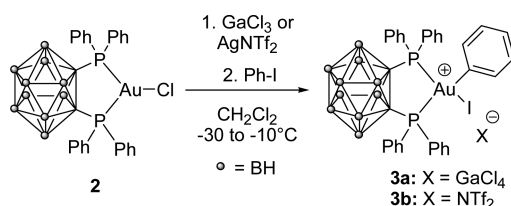


Figure 1. Molecular structure of complex **3b**. The triflimide counteranion, solvent molecules, and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): P1Au 2.329(4), P2Au 2.395(4), AuC 2.14(2), AuI 2.596(1), and P1AuP2 91.7(1).

Therefore, an excess of iodobenzene (30 equiv) was added right after chloride abstraction, and the reaction was left to proceed at -10°C for 10 h (Scheme 2). Strikingly, the oxidative addition of the $\text{C}_{\text{Ar}}\text{--I}$ bond proceeded readily and quantitatively under these mild conditions. The resulting complex **3a** is too unstable to be isolated (it rapidly decomposes above -10°C), but its structure was unambiguously assigned by multinuclear NMR spectroscopy at -80°C . The ^{31}P NMR spectrum displays two resonances signals at $\delta = 61.8$ and 44.6 ppm ($J_{\text{PP}} = 29.1$ Hz) in agreement with the dissymmetry of the complex. Also diagnostic of the oxidative addition of the $\text{C}_{\text{Ar}}\text{--I}$ bond is the ^{13}C NMR signal of the C_{ipso} atom bound to gold at $\delta = 144.8$ ppm with a large C–P coupling constant ($J_{\text{CP}} = 122.0$ Hz).⁷

Similar results were obtained using AgNTf_2 as the chloride scavenger, but in the case of **3b**, crystals could be obtained by slow diffusion of pentane in a concentrated CH_2Cl_2 solution at -60°C . X-ray diffraction analysis confirmed the oxidative addition of PhI to gold leading to a cationic gold(III) species (Figure 1). Complex **3b** adopts a discrete ion pair structure. The gold atom is four-coordinate with the phenyl, the iodide, and the diphosphine ligand organized in a quasi-perfect square-planar arrangement (torsion angle of 2.6° between the PAuP and CAuI planes, bond angles of $90 \pm 2^\circ$).

At this stage, the Ph substituents at phosphorus were replaced for amino groups in order to increase the electron-donating character of the carborane diphosphine and hopefully to increase the stability of the ensuing cationic gold complexes.¹⁸ Gratifyingly, reaction of the DPCb gold(I) chloride complex **4** with AgNTf_2 yielded a stable gold(I) triflimide complex **5**, which can be isolated and handled conveniently at room temperature (Figure 2). The ^{31}P NMR spectrum of **5** displays a single ^{31}P NMR resonance at $\delta = 138.3$ ppm (vs 116.6 ppm for **4**), in line with symmetric coordination of the two P atoms. X-ray crystallography confirmed the molecular structure of **5**. The DPCb ligand chelates the gold center, and the PAuP fragment is strongly bent ($100.73(2)^\circ$). The coordination sphere is completed by the triflimide ion, resulting in a three-coordinate

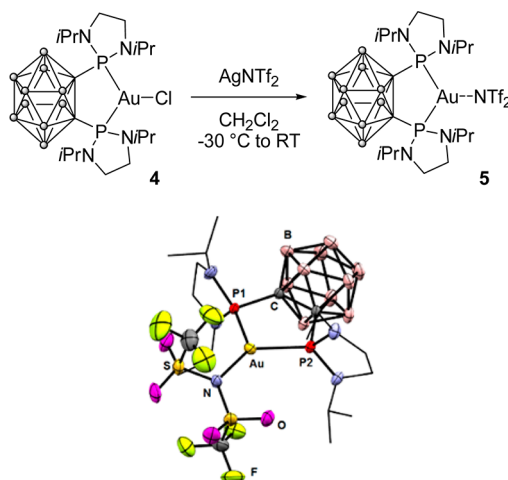
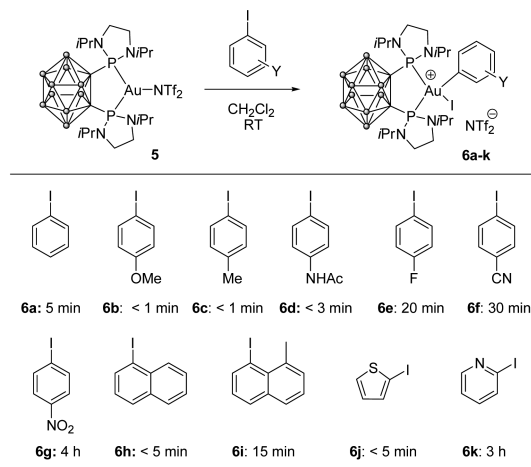


Figure 2. Synthesis and molecular structure of complex **5**. Solvent molecules and hydrogen atoms are omitted, isopropyl groups are simplified for clarity. Selected bond lengths (Å) and angles (deg): P1Au 2.3215(5), P2Au 2.3172(5), AuN 2.221(2), P1AuP2 100.73(2), P1AuN 129.52(4), and P2AuN 129.74(4).

gold complex. The Au–N bond distance ($\text{AuN} = 2.221(1)$ Å) is longer than that of Gagosz's complex [$(\text{Ph}_3\text{P})\text{AuNTf}_2$, $2.102(3)$ Å],¹⁹ suggesting that dissociation of the NTf_2 counteranion may easily occur in solution.

Complex **5** reacts spontaneously and rapidly with iodobenzene at room temperature. Complete conversion is achieved within less than 5 min, and the resulting gold(III) complex **6a** is significantly more stable than **3b**. The reaction is general and a variety of aryl iodides were found to undergo oxidative addition under these mild conditions (Scheme 3). The reaction shows good functional group compatibility (*p*-OMe, NHAc, F, CN, and NO_2 substituted iodobenzenes).

It works with 1-iodonaphthalenes as well as 2-iodoheterocycles, as exemplified with 2-iodothiophene and 2-iodopyridine. Complexes **6i** and **6k** were characterized by X-ray crystallography.²⁰ Compound **6i** (Figure 3) resulting from the oxidative addition of 1-iodo-8-methyl naphthalene was isolated in 93% yield as a red powder. It is remarkably stable: no sign of

Scheme 3. Oxidative Addition of Aryl Iodides to the Carborane Bis(phosphine) Gold Complex 5^a

^aTimes to reach complete conversion of complex **5** using 5 equiv of ArI.

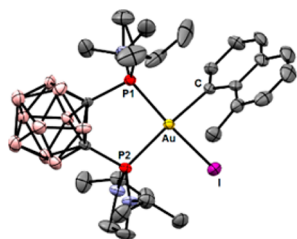


Figure 3. Molecular structure of complex **6i**. The triflimide counteranion, solvent molecules, and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): P1Au 2.327(2), P2Au 2.381(1), AuC 2.092(5), AuI 2.6218(5), AuC_{methyl} 3.153(7), and P1AuP2 93.67(5).

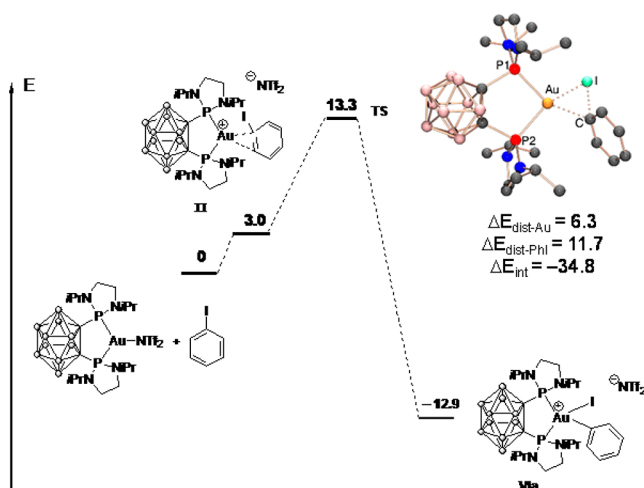


Figure 4. Energy profile (electronic energy including ZPE correction, in kcal/mol) computed at the B97D/SDD+f(Au),SDD(I),6-31+G** (other atoms)/B97D/SDD+f(Au),SDD(I),6-31G** (other atoms) level of theory for the oxidative addition of PhI to gold, taking into account solvent effect (SMD model, dichloromethane). Distortion/interaction analysis of the associated transition state.

decomposition after weeks in the solid state (mp = 126–129 °C), and only little decomposition in solution after several days. Interestingly, oxidative addition of *p*-substituted iodobenzenes proceeds faster with electron-donating than with electron-withdrawing substituents. For instance, 4-iodoanisole reacts immediately (<1 min), while oxidative addition of 1-iodo-4-nitrobenzene requires 4 h to reach completion. The reactivity trend observed with gold is opposite to that encountered upon oxidative addition of aryl halides to L₂Pd(0) complexes.²¹ This points to some specific behavior of gold.²²

To gain more insight into the mechanism of oxidative addition of aryl iodides to gold(I), DFT calculations were carried out with [(DPCb)AuNTf₂] and PhI (Figure 4). The starting point of the reaction is the displacement of the weakly coordinating NTf₂ anion by the aryl iodide substrate to give a π -complex **II**, which is slightly uphill in energy (ΔE = 3.0 kcal/mol and ΔG = 12.5 kcal/mol). The aryl iodide is coordinated in η^2 fashion to the cationic gold center ($d(\text{AuC}_{\text{ipso}})$ = 2.876 Å and $d(\text{AuC}_{\text{ortho}})$ = 2.612 Å).^{23–25} Oxidative addition of PhI then proceeds via a 3-center transition state **TS**. The associated activation barrier is remarkably low (ΔE^\ddagger = 10.3 kcal/mol and ΔG^\ddagger = 10.7 kcal/mol from complex **II**), in line with the mild conditions in which the reaction occurs experimentally. The most noticeable structural data of **TS** are (i) the short C_{ipso} to gold distance ($d(\text{AuC}_{\text{ipso}})$ down to 2.34 Å) and (ii) the elongated C–I bond

(by 0.26 Å) and its bending out of the Ph plane (by 35.6°). **TS** collapses into the square-planar cationic gold(III) complex **VIa**. Calculations were carried out with the linear model complex [(Me₃P)₂Au⁺] for comparison.^{11,20} In this case, oxidative addition of PhI requires a larger activation barrier (ΔE^\ddagger = 14.4 kcal/mol and ΔG^\ddagger = 27.6 kcal/mol) and is less favorable energetically (ΔE = −1.8 kcal/mol and ΔG = 12.7 kcal/mol). These results are consistent with experimental observations, i.e., the absence of reaction between linear bis(phosphine) gold complexes and PhI. They also emphasize the major role played by the bent geometry induced by the DPCb ligand. It preorganizes the coordination sphere of gold and thereby turns on the reactivity toward the oxidative addition of aryl iodides.²⁶ To precisely assess the influence of bending, the transition state **TS** was analyzed using the activation strain model.^{27,28} Accordingly, the activation energy ΔE^\ddagger is divided in different components, the strain energy ($\Delta E^\ddagger_{\text{strain}} = \Delta E^\ddagger_{\text{dist-Au}} + \Delta E^\ddagger_{\text{dist-PhI}}$) and the interaction energy ($\Delta E^\ddagger_{\text{int}}$). Most of the strain energy associated with **TS** comes from PhI (11.7 kcal/mol), while distortion of the [(DPCb)Au⁺] fragment requires only 6.3 kcal/mol thanks to preorganization. The interaction energy between the distorted fragments is fairly large (−34.8 kcal/mol), resulting overall in a small activation barrier. A higher $\Delta E^\ddagger_{\text{dist-PhI}}$ and a relatively lower $\Delta E^\ddagger_{\text{int}}$ components (18.5 and −28.6 kcal/mol, respectively) are found for the reaction of PhI with the linear complex [(Me₃P)₂Au⁺], but the most important difference comes from the $\Delta E^\ddagger_{\text{dist-Au}}$ term (24.4 kcal/mol), which is much higher than for [(DPCb)Au⁺], in agreement with the large distortion required to achieve the **TS** geometry. These data confirm that the large difference between the activation barriers of the two systems originates essentially from the bent vs linear geometry of the [bis(phosphine)Au⁺] fragment.

In conclusion, the first gold complexes to undergo oxidative addition of aryl iodides have been discovered thanks to rational design. The reactivity of gold(I) is turned on by carborane diphosphines, which form bent chelate complexes. On the basis of this approach, the new diphosphine cationic gold complex [(DPCb)AuNTf₂] **4** was prepared. It is stable at room temperature and readily activates C_{Ar}–I bonds under mild conditions. Oxidative addition proceeds with a variety of aryl iodides and follows a rather unusual trend, electron-rich substrates reacting faster. Bent two-coordinate gold(I) complexes open the way to σ -bond activation processes, and future work will seek to explore further the potential of this bending strategy.

■ ASSOCIATED CONTENT

● Supporting Information

Detailed experimental conditions and procedures, theoretical details, analytical data, and crystallographic data for compounds **3b**, **5**, **6i**, and **6k**. 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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■ REFERENCES

- (1) (a) Hashmi, A. S. K.; Toste, F. D., Eds. *Modern Gold Catalyzed Synthesis*; Wiley-VCH: Weinheim, Germany, 2012. (b) Fürstner, A.; Davies, P. *Angew. Chem., Int. Ed.* **2007**, *46*, 3410.
- (2) For oxidative addition of S–S, Si–Si, and Sn–Sn bonds, see: (a) Bachman, R. E.; Bodolosky-Bettis, S. A.; Pyle, C. J.; Gray, M. A. *J. Am. Chem. Soc.* **2008**, *130*, 14303. (b) Gualco, P.; Ladeira, S.; Miqueu, K.; Amgoune, A.; Bourissou, D. *Angew. Chem., Int. Ed.* **2011**, *50*, 8320. (c) Gualco, P.; Ladeira, S.; Miqueu, K.; Amgoune, A.; Bourissou, D. *Organometallics* **2012**, *31*, 6001. (d) Lassauque, N.; Gualco, P.; Mallet-Ladeira, S.; Miqueu, K.; Amgoune, A.; Bourissou, D. *J. Am. Chem. Soc.* **2013**, *135*, 13827. (e) Joost, M.; Gualco, P.; Coppel, Y.; Miqueu, K.; Kefalidis, C. E.; Maron, L.; Amgoune, A.; Bourissou, D. *Angew. Chem., Int. Ed.* **2014**, *53*, 747.
- (3) To date, only few catalytic cross-coupling reactions have been reported with gold complexes, and exogenous oxidants are usually employed to generate the Au(III) species: (a) Hopkinson, M. N.; Gee, A. D.; Gouverneur, V. *Chem.—Eur. J.* **2011**, *17*, 8248. (b) Ball, L. T.; Lloyd-Jones, G. C.; Russell, C. A. *Science* **2012**, *337*, 1644. (c) Ball, L. T.; Lloyd-Jones, G. C.; Russell, C. A. *J. Am. Chem. Soc.* **2014**, *136*, 254.
- (4) Levin, M. D.; Toste, F. D. *Angew. Chem., Int. Ed.* **2014**, *53*, 6211.
- (5) (a) Plenio, H. *Angew. Chem., Int. Ed.* **2008**, *47*, 6954. (b) Lauterbach, T.; Livendahl, M.; Rosellón, A.; Espinet, P.; Echavarren, A. M. *Org. Lett.* **2010**, *12*, 3006. (c) Corma, A.; Juárez, R.; Boronat, M.; Sanchez, F.; Iglesias, M.; Garcia, H. *Chem. Commun.* **2011**, *47*, 1446. (d) 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. (e) Hansmann, M. M.; Pernpointner, M.; Döpp, R.; Hashmi, A. S. K. *Chem.—Eur. J.* **2013**, *19*, 15290. (f) Livendahl, M.; Goehry, C.; Maseras, F.; Echavarren, A. M. *Chem. Commun.* **2014**, *50*, 1533.
- (6) For C_{sp^3} –X bond activation, see: (a) Tamaki, A.; Kochi, J. K. *J. Organomet. Chem.* **1972**, *40*, C81. (b) Tamaki, A.; Kochi, J. K. *J. Chem. Soc., Dalton Trans.* **1973**, 2620. (c) Tamaki, A.; Kochi, J. K. *J. Organomet. Chem.* **1974**, *64*, 411. (d) Winston, M. S.; Wolf, W. J.; Toste, D. J. *Am. Chem. Soc.* **2014**, *136*, 7777.
- (7) Guenther, J.; Mallet-Ladeira, S.; Estevez, L.; Miqueu, K.; Amgoune, A.; Bourissou, D. *J. Am. Chem. Soc.* **2014**, *136*, 1778.
- (8) (a) Joost, M.; Gualco, P.; Mallet-Ladeira, S.; Amgoune, A.; Bourissou, D. *Angew. Chem., Int. Ed.* **2013**, *52*, 7160. (b) Joost, M.; Estevez, L.; Mallet-Ladeira, S.; Miqueu, K.; Amgoune, A.; Bourissou, D. *J. Am. Chem. Soc.* **2014**, *136*, 10373.
- (9) (a) Schwerdtfeger, P.; Hermann, H. L.; Schmidbaur, H. *Inorg. Chem.* **2003**, *42*, 1334. (b) Carvajal, M. A.; Novoa, J. J.; Alvarez, S. *J. Am. Chem. Soc.* **2004**, *126*, 1465.
- (10) The reaction of (NHC)AuPh complexes with iodobenzene has been investigated. Complete conversion to biphenyl and (NHC)Au(I) was observed after 50 h at 110 °C, but no evidence for oxidative addition was reported; see: Johnson, M. T.; Marthinus Janse van Rensburg, J.; Axelsson, M.; Ahlquist, M. S. G.; Wendt, O. F. *Chem. Sci.* **2011**, *2*, 2373.
- (11) Robinson, P. S. D.; Khairallah, G. N.; da Silva, G.; Lioe, H.; O'Hair, R. A. J. *Angew. Chem., Int. Ed.* **2012**, *51*, 3812.
- (12) Van Leeuwen, P. W. N. M.; Kamer, P. C. J.; Reek, J. N. H.; Dierkes, P. *Chem. Rev.* **2000**, *100*, 2741.
- (13) Hofmann, P.; Heis, P.; Müller, G. Z. *Naturforsch. B* **1987**, *42*, 395.
- (14) (a) Gimeno, M. C.; Laguna, A. *Chem. Rev.* **1997**, *97*, 511. (b) Schmidbaur, H.; Schier, A. *Chem. Soc. Rev.* **2012**, *41*, 370.
- (15) For example, the coordination of dppbz [$Ph_2P(o-C_6H_4)PPh_2$] to gold(I) has been reported to afford either dinuclear complexes [(dppbz)AuCl]₂ or tetracoordinated gold complexes [(dppbz)₂Au⁺]; see: (a) Mohamed, A. A.; Krause Bauer, J. A.; Bruce, A. E.; Bruce, M. R. *Acta Crystallogr.* **2003**, *59*, m84. (b) Yoshinari, N.; Kitani, N.; Tsukuda, T.; Konno, T. *Acta Crystallogr.* **2011**, *67*, m121. (c) Kaeser, A.; Moudam, O.; Accorsi, G.; Séguy, I.; Navarro, J.; Belbakra, A.; Duhayon, C.; Armaroli, N.; Delavaux-Nicot, B.; Nierengarten, J.-F. *Eur. J. Inorg. Chem.* **2014**, *2014*, 1345.
- (16) Crespo, O.; Gimeno, M. C.; Laguna, A.; Jones, P. G. *J. Chem. Soc., Dalton. Trans.* **1992**, 1601.
- (17) For recent contributions on ligands incorporating carborane cages, see: (a) Weller, A. *Nat. Chem.* **2011**, *3*, 577. (b) Spokoyny, A. M.; Machan, C. W.; Clingerman, D. J.; Rosen, M. S.; Wiester, M. J.; Kennedy, R. D.; Stern, C. L.; Sarjeant, A. A.; Mirkin, C. A. *Nat. Chem.* **2011**, *3*, 590. (c) Spokoyny, A. M.; Lewis, C. D.; Teverovskiy, G.; Buchwald, S. L. *Organometallics* **2012**, *31*, 8478. (d) Lavallo, V.; Wright, J. H.; Tham, F. S.; Quinlivan, S. *Angew. Chem., Int. Ed.* **2013**, *52*, 3172. (e) Visbal, R.; Ospino, I.; López-de-Luzuriaga, J. M.; Laguna, A.; Gimeno, M. C. *J. Am. Chem. Soc.* **2013**, *135*, 4712.
- (18) The introduction of bis-diamino substituents at P is a common way to stabilize electrodefinient species. For recent examples, see: (a) Krysiak, J.; Lyon, C.; Baceiredo, A.; Gornitzka, H.; Mikolajczyk, M.; Bertrand, G. *Chem.—Eur. J.* **2004**, *10*, 1982. (b) Rodriguez, R.; Gau, D.; Kato, T.; Saffon-Merceron, N.; De Cózar, A.; Cossio, F. P.; Baceiredo, A. *Angew. Chem., Int. Ed.* **2011**, *50*, 10414.
- (19) Mézailles, N.; Ricard, L.; Gagosz, F. *Org. Lett.* **2005**, *7*, 4133.
- (20) See Supporting Informations for details.
- (21) (a) Lewis, A. K.; Caddick, S.; Cloke, F. G.; Billingham, N. C.; Hitchcock, P. B.; Leonard, J. *J. Am. Chem. Soc.* **2003**, *125*, 10066. (b) Lam, K. C.; Marder, T. B.; Lin, Z. *Organometallics* **2007**, *26*, 758.
- (22) It is possible that the rate-enhancement effect of electron-donating substituents is related to the transient formation of π -intermediates (see mechanistic discussions). However, the key factors controlling reactivity cannot be unequivocally delineated at this stage.
- (23) The authors acknowledge one of the referees for a helpful suggestion concerning the involvement of η^2 -arene gold intermediates.
- (24) For π -arene complexes of gold(I), see, for example: (a) Herrero-Gómez, E.; Nieto-Oberhuber, C.; López, S.; Benet-Buchholz, J.; Echavarren, A. M. *Angew. Chem., Int. Ed.* **2006**, *118*, 5581. (b) Lavallo, V.; Frey, G. D.; Kousar, S.; Donnadiou, B.; Bertrand, G. *Proc. Natl. Acad. Sci.* **2007**, *104*, 13569.
- (25) Another minimum corresponding to an iodine adduct **I** ($d(AuI) = 2.800 \text{ \AA}$) was located on the PES ($d(AuI) = 2.800 \text{ \AA}$). It is located only 2.3 kcal/mol higher in energy than the π -complex **II** and may also be involved in the process.
- (26) The bent geometry will also influence the nature and the energy level of the frontier molecular orbitals. For a detailed discussion, see: (a) Nakanishi, W.; Yamanaka, M.; Nakamura, E. *J. Am. Chem. Soc.* **2005**, *127*, 1466. (b) Yoshikai, N.; Nakamura, E. *Chem. Rev.* **2012**, *112*, 2339.
- (27) (a) Fernandez, I.; Bickelhaupt, F. M. *Chem. Soc. Rev.* **2014**, *43*, 4953. (b) van Zeist, W. J.; Bickelhaupt, F. M. *Org. Biomol. Chem.* **2010**, *8*, 3118.
- (28) For comparison, calculations (reaction profile and strain model analyses) have been carried out on the putative [(dmpbz)Au⁺] complex [dmpbz = $Me_2P(o-C_6H_4)PMe_2$]. A very low activation barrier ($\Delta G^\ddagger = 10.4 \text{ kcal/mol}$) was found, confirming the key influence of bending on the oxidative addition process (see Supporting Information).

■ NOTE ADDED IN PROOF

During manuscript revision, a computational study assessing the key role of the bending of gold(I) complexes on the oxidative addition of aryl halides has appeared, see: I. Fernández, L. P. Wolters, F. M. Bickelhaupt, *J. Comp. Chem.* **2014**, *35*, 2140–2145.