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Base-Triggered Oxidative Addition to Gold

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Yago García-Rodeja,^[b] Karinne Miqueu,^[b] and Didier Bourissou^{*[a]}

In memory of François Mathey.

Abstract: The coordination of secondary phosphine oxides (SPO) was shown to efficiently promote the activation of C(sp²)–I bonds by gold, as long as a base is added (NEt₃, K₂CO₃). These transformations stand as a new type of chelation-assisted oxidative addition to gold. The role of the base and the influence of the electronic properties of the P-ligand were analyzed computationally. Accordingly, the oxidative addition was found to be dominated by Au→(Ar–I) backdonation. In this case, gold behaves similarly to palla-

dium, suggesting that the inverse electron flow reported previously (with prevailing (Ar–I)→Au donation, resulting in faster reactions of electron-enriched substrates) is a specific feature of electron-deficient cationic gold(I) complexes. The reaction gives straightforward access to (P=O,C)-cyclometalated Au(III) complexes. The possibility to chemically derivatize the SPO moiety at Au(III) was substantiated by protonation and silylation reactions.

Introduction

The last decade has witnessed major breakthroughs in 2-electron redox chemistry at gold.^[1] Reductive elimination of aryl-aryl bonds from Au(III) turned out to be exceptionally fast and encapsulation within anionic supramolecular cages was shown to accelerate drastically alkyl-alkyl coupling.^[2] Oxidative addition to gold was long considered hardly possible until several approaches relying on strong oxidants/electrophilic substrates, photoredox conditions or chelating/hemilabile ligands were shown to give ready access to organo Au(III) species from Au(I) precursors.^[3] Accordingly, using chelation assistance, we have recently reported the first unambiguous evidence for the oxidative addition of C(sp²)–X bonds to a single gold center, starting from *peri*-halo naphthyl phosphines (Figure 1a).^[4,5] The reaction works for C–I and C–Br bonds, with

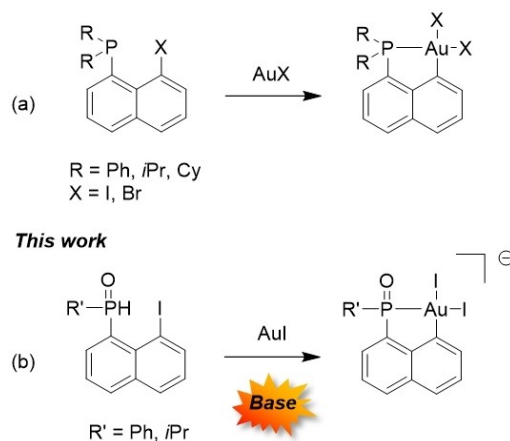


Figure 1. P-chelation assisted oxidative addition of C–X bonds to gold.

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Ph, *i*Pr and Cy substituents at phosphorus. It provides straightforward access to (P,C)-cyclometalated Au(III) complexes which are hardly accessible by the classical C–H activation route due to the propensity of phosphines to be oxidized by Au(III) salts.^[6] The (P,C)Au(III) complexes display rich chemistry, from unprecedented elementary reactivity at gold (migratory insertion, β-H elimination)^[7] to Au(III) catalysis (intermolecular hydroarylation of alkynes).^[8] They also proved efficient and versatile scaffolds to stabilize and authenticate original complexes (C–H agostic, π-arene and π-allyl complexes).^[9]

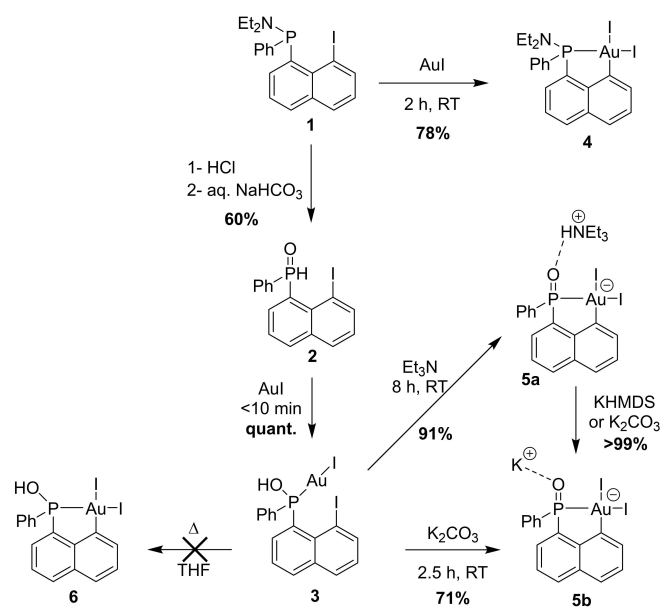
Phosphines, *N*-heterocyclic carbenes and pyridines remain the landmark ligands in gold coordination chemistry,^[10] and it is highly desirable to expand and diversify this landscape. New ligand frameworks are attracting huge interest, as a way to finely tune the structure and properties of gold complexes, as well as to emulate new behaviour.^[11] In this context, we became

interested in integrating secondary phosphine oxide moieties (SPO). Although much less developed than simple phosphines, SPOs possess versatile and interesting coordination properties thanks to the $>P^V(=O)-H/ >P^{III}-OH$ tautomerism. Additional valuable attributes of SPO are the possibility for P-centered chirality as well as chemical derivatization / non-innocence of the O atom.^[12] It is striking to note that there is very little precedents for SPO in gold chemistry: a few $>P(OH)AuX$ and $>P(=O)AuL$ complexes were prepared and characterized in the 1980–2000's,^[13] and some $>P(OH)AuCl$ complexes were applied in Au(I) π -activation catalysis, i.e. the prototypical cyclization/functionalization of 1,6-enynes, in 2014.^[14] In addition, SPOs have been applied as functional ligands for Au clusters and nanoparticles in (photoelectro)catalytic hydrogenation reactions.^[15] However, to the best of our knowledge, nothing is known about SPO in Au(III) chemistry.^[16]

In this work, we interrogated the ability of SPO to promote oxidative addition to gold by chelation. Starting from *peri*-iodo naphthyl SPO, we discovered that the C–I bond can indeed add to gold, but the reaction requires a base to proceed and cleanly give the corresponding (P=O,C)-cyclometalated complex (Figure 1b). DFT calculations shed light into the role of the base and unveil the key factors influencing oxidative addition of C(sp²)–I bonds to gold. Subsequent reactivity of the P=O group bonded to gold was exemplified.

Results and Discussions

The *peri*-iodo naphthyl SPO **2** was prepared in two steps from diiodo-naphthalene (Scheme 1).^[17] First, lithiation followed by electrophilic trapping with the chloro-amino-phosphine ClPPh(NEt₂) afforded the *peri*-iodo naphthyl phosphine **1** (80%



Scheme 1. Synthesis of the *peri*-iodo naphthyl SPO **2**, P-chelation assisted and base-triggered oxidative addition of the C–I bond.

isolated yield). Treatment with HCl and quenching with aqueous NaHCO₃ then gave the SPO **2** isolated in 60% overall yield as a yellow solid after column chromatography over silica gel.

Coordination to gold and oxidative addition of the C–I bond was then investigated. The SPO **2** reacts rapidly with AuI (within 10 min at room temperature) to give complex **3**. P(=O)H to P(OH) tautomerization is clearly apparent from the respective ¹H NMR signal at about 9.7 ppm, from a doublet with large ¹J_{HP} coupling for **2** (521.0 Hz) to a broad singlet for **3**.^[17] In the meantime, the ³¹P NMR signal shifts from δ 15.76 ppm (d, ¹J_{HP} = 521.0 Hz) for **2**, to δ 89.44 ppm (s) for **3**, indicating the coordination of the P atom to gold. A spectroscopic signature for oxidative addition of *peri*-iodo naphthyl phosphines to gold is typically the appearance of a deshielded ¹H NMR signal for the CH(naphthyl) next to gold, at δ 9.0–9.5 ppm.^[17] Such a feature is not observed for **3** (the most deshielded aromatic CH signal appears at δ < 8.5 ppm, suggesting the C–I bond is intact). X-ray diffraction (XRD) analysis of the related chloro complex **3'** (Figure 2a) unambiguously confirmed the coordination of the P(OH)Ph moiety to gold without oxidative addition of the C–I bond.^[18] Its structural features will be discussed in more detail in the following section.

Attempts to promote oxidative addition of the C–I bond of complex **3** resulted only in complex mixtures or degradation. No trace of the corresponding Au(III) complex was detected (Table S1).^[17] This behavior is in marked contrast with that of the amino-phosphine **1**. Following spontaneous coordination to gold (as apparent from the shift of the ³¹P NMR signal from δ 57.0 ppm to 79.6 ppm), oxidative addition proceeds slowly at room temperature and is essentially complete after 2 h at 60 °C. The corresponding (P,C)-cyclometalated Au(III)I₂ complex **4** is thereby obtained cleanly (δ ³¹P 85.3 ppm).^[17] In this case, the diagnostic ¹H NMR signal for the CH(naphthyl) next to Au is

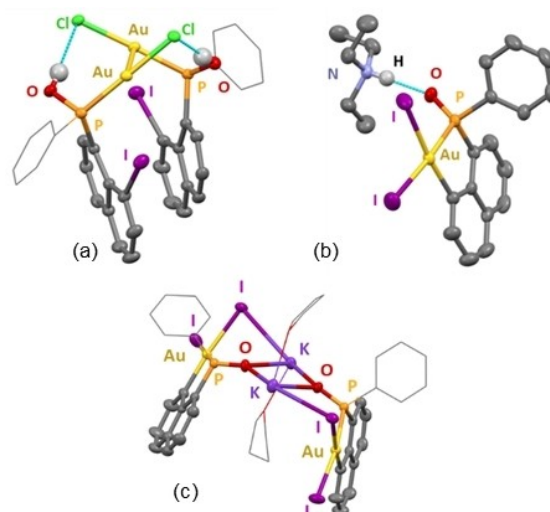


Figure 2. Molecular structures of the *peri*-iodo naphthyl SPO AuCl complex **3'** (a), (P=O,C)-cyclometalated Au(III)I₂ complex as its ammonium and potassium salts **5a** (b) and **5b** (c), respectively. The phenyl group of **3'**, **5b** and the THF molecule of **5b** are simplified, for clarity.

observed at δ 9.3 ppm. The acidic proton of the SPO moiety and the less electron-rich nature of the P atom in the hydroxy phosphine (vs the amino phosphine) may be the blocking factors for the oxidative addition to occur from **3**. To probe this hypothesis, we decided to react complex **3** with a base. Gratifyingly, adding triethylamine (3 equiv.) induced clean conversion into **5a** within 8 h at room temperature. The Au(III)₂ complex **5a** was isolated in 91 % yield as a yellow solid and fully characterized.^[17] First evidence for oxidative addition of the C–I bond was given by the deshielded CH(naphthyl) ¹H NMR signal found at δ 9.23 ppm. X-ray diffraction analysis (Figure 2b) of crystals grown by pentane diffusion into a THF solution then unambiguously authenticated **5a** as a H-bonded ion-pair between the anionic (P=O,C)AuI₂ complex and the HNEt₃ ammonium (see the following section for detailed discussion of the molecular structure). The possibility to exchange the ammonium counter-cation was then investigated. Complexes **5a** cleanly and quickly react with the potassium salts KHMDs and K₂CO₃ to give **5b**. Alternatively, **5b** can be prepared directly from the SPO Au(I) complex **3**, using K₂CO₃ (1.2 equiv.) as a base to trigger the oxidative addition.^[17] Crystallographic analysis revealed that **5b** adopts a dinuclear structure with the P=O group and the potassium ion bridging two motifs (Figure 2c).

To assess the generality of the SPO-chelated oxidative addition to gold and the need for a base, the substituent at phosphorus was changed from phenyl to isopropyl (Scheme 2). The corresponding *peri*-iodo naphthyl SPO **2'** was found to behave exactly as **2**. Upon treatment with AuI, only tautomerization/P-coordination was observed, but the addition of triethylamine (3 equiv.) triggered oxidative addition and induced complete conversion into the (P=O,C)Au(III)₂ complex **4'a** within 4 h at room temperature.^[17]

Structural features of the SPO-derived Au(I) and Au(III) complexes

Besides the P-coordination to gold and retention of the C–I bond, the crystallographic analysis of the *peri*-iodo naphthyl SPO AuCl complex **3'** (Figure 2a) revealed some interesting features.^[17,18] The complex adopts a dinuclear structure held by intermolecular O–H...Cl hydrogen bonding (H...Cl 2.24(3) Å, O...Cl 3.068(1) Å, O–H...Cl 176(3)°) and Au...Au auriphilic (3.1512(5) Å) interactions.^[19] In addition, the SPO group and the iodine atom in *peri* positions of the naphthyl group experience

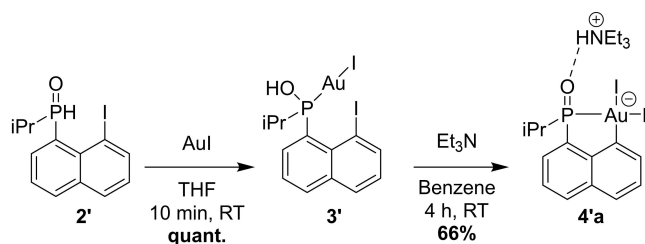
strong distortions to accommodate the steric congestion. The P–C and C–I bay angles significantly exceed the nominal value (120°) at 127.9(1)° and 124.6(1)°, respectively.^[20] In addition, the phosphorus and iodine atoms sit on opposite sides of the naphthyl plane, resulting in noticeable out-of-plane distortion (P–C...C–I 25.1(1)°).

Oxidative addition of the C–I bond to gold results in square-planar Au(III) complexes, as apparent from the XRD structures of **5a** and **5b** (Figures 2b and 2c).^[17] (P=O,C)-Cyclometalation relieves the strain induced by the *peri* substitution in the Au(I) precursor. The phosphorus and gold atoms only marginally deviate from the naphthyl plane (P–C...C–Au 5.0(1)° for **5a** and 5.5(1)° for **5b**). The P–O bond acquires significant double bond character, as indicated by its shortening from 1.608(1) Å in **3'**, to 1.502(2) Å in **5a** and 1.498(2) Å in **5b**. The Et₃NH salt **5a** adopts an H-bonded ion-pair structure, with the proton initially at O transferred to N: O...H–N 1.82(4) Å, O...N 2.656(4) Å, O...H–N 167(4)°. The potassium salt **5b** forms 1D chains in the solid state. The potassium ion is engaged in weak intra and intermolecular K...I contacts. It is also bonded to the P=O group, forming a (OK)₂ bridge.

Theoretical investigation of the SPO-chelated and base-triggered oxidative addition of the C–I bond to gold

In order to gain further insight into such chelation-assisted oxidative additions to gold, DFT calculations were carried out.^[17] In this study, we intended in particular to assess the electron flow and identify the key orbital contributions in the corresponding transition states to shed light into the factors facilitating/disfavouring the oxidative addition to gold. The fact that deprotonation of the SPO moiety triggers the reaction suggests that the more electron-donating is the ligand, the more electron-rich is the metal and the easier is the oxidative addition, meaning gold would in this case follow the *classical* trend and parallels the reactivity profile of palladium. This would be in marked contrast with the *peculiar* behaviour we noticed upon oxidative addition to cationic P/PN-ligated Au(I) complexes (intermolecular reactions).^[21] Here, computations revealed an inverse electron flow in the oxidative addition transition state, with transfer of electron density from the substrate to the metal fragment [(PhI)→Au donation prevails]. A similar behaviour was found by Bower and Russell for (NN)-ligated Au⁺ complexes (with 2,2'-bipyridines as ligands).^[22]

The first point we studied computationally was the donation/back-donation balance in the P-chelation assisted oxidative addition to gold. Since these reactions involve a neutral or anionic LAuX fragment, the electron bias may be different from that encountered with bent L₂Au⁺ fragments. The Natural Orbital for Chemical Valence (NOCV) extension of the EDA (Energy Decomposition Analysis) method was used and applied to the transition states. To this end, the system had to be fragmented. Given the intramolecular nature of the oxidative addition, model transition states were built.^[17] The approach was first applied to the *peri*-iodo diphenyl naphthyl phosphine we initially found to promote oxidative addition to Au.^[4] The



Scheme 2. P-chelation assisted and base-triggered oxidative addition of the C–I bond of the *peri*-iodo naphthyl SPO **2'**.

EDA-NOCV calculations were performed on the 3-center transition state (Figure 3), replacing the P-naphthyl bond for P–H/C–H bonds and changing the naphthyl group for a phenyl ring (to avoid overlap between the added H atoms). In this case, the dominant orbital interaction is Au→(PhI) back-donation (57.8%), while (PhI)→Au donation accounts for 23.3% (Table S3).^[17] Consistently, a charge flow from Au to PhI of about 0.10 electron was estimated from Hirshfeld partitioning. This picture is similar to that predicted for the oxidative addition of PhI to (Ph₃P)₂Pd, but markedly contrasts with that found for the oxidative addition of PhI to the cationic complex gold (MeDalphos)Au⁺, where the main orbital interaction is (PhI)→Au donation (40.0% vs 32.6% for the back-donation) and the electron flow is opposite (PhI to Au by 0.08 electron). Thus, in the oxidative addition of Ar–I bonds to LAuI fragments, as realized experimentally using P-chelation, gold behaves similarly to Pd and back-donation prevails. In terms of ligand effect, this suggests that the reaction should be facilitated by increasing the electron-density at the metal.

The influence of the P-ligand was then examined by computing the reaction profiles for the oxidative addition of the C–I bond to gold assisted by SPO chelation for the protonated complex, its naked deprotonated form and its H-bonded NEt₃ adduct (Figure 4). Calculations were performed at

the SMD(benzene)-B3PW91-D3(BJ)/SDD + f(Au),I(SDD),6-31G** (other atoms)//B3PW91/SDD + f(Au), I(SDD),6-31G** (other atoms) level of theory. In all cases, the formation of the (P=O,C)-cyclometalated Au(III) complex is exergonic, significantly more for the deprotonated and H-bonded complexes (ΔG –30.7 and –25.1 kcal/mol) than for the protonated one (ΔG –15.8 kcal/mol). At the same level of theory (gas phase), the barrier for oxidative addition of the C–I bond amounts to 17.7 kcal/mol for the PPh(OH) ligand, compared to 21.9 kcal/mol for the PPh₂ analog.^[4] It is likely that the barrier for the oxidative addition from **3** is slightly underestimated as the Au(I) complex exists in an intermolecularly H-bonded form, as authenticated crystallographically. The barrier drops by ca. 2 kcal/mol upon H-bonding to NEt₃ (17.0 vs 15.1 kcal/mol, in benzene) and 5 kcal/mol upon deprotonation (17.0 vs 11.7 kcal/mol, in benzene), in line with the results observed experimentally.^[23]

The charge flow in the transition states for oxidative addition of the (Ph(HO)P,naphthyl,peri-I)AuI complex, its deprotonated form and its triethylamine adduct was analysed using the same methodology as for the *peri*-iodo diphenyl naphthyl phosphine gold(I) complex. The naphthyl group was replaced by a phenyl ring and the P-naphthyl bond for P–H/C–H bonds. The prevailing orbital interaction in the EDA-NOCV analyses is here also the Au→(PhI) back-donation (Figure 5), weighting

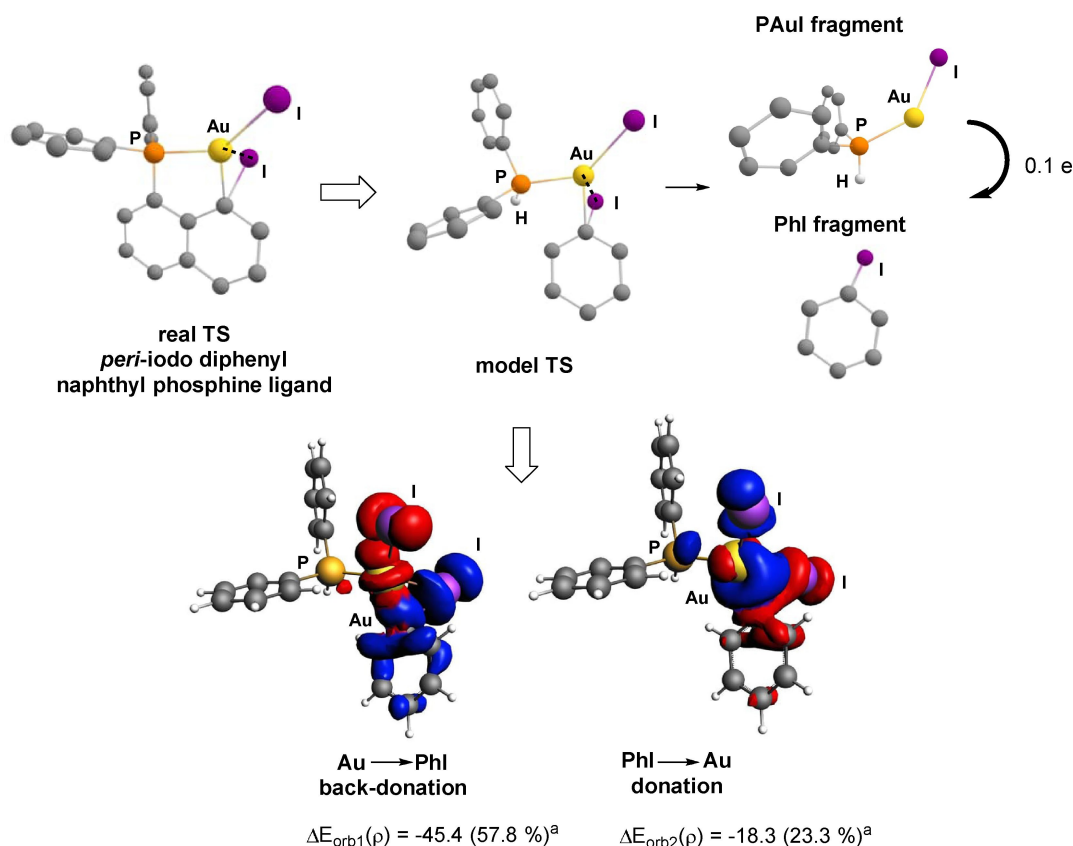


Figure 3. Fragmentation used to carry out EDA-NOCV analysis on the transition state of P-chelation assisted oxidative addition to Au. Charge transfer from PAuI to PhI fragment (Hirshfeld partitioning). Plot of the contour of the deformation densities contributions (ΔQ_{orb}) of the pairwise orbital interactions between PhI and Ph₂P(H)AuI with associated orbital interaction energy (ΔE_{orb} , in kcal/mol) for the model transition state, computed at ZORA-BP86-D3/TZ2P level of theory. The charge flow is red→blue ($\Delta Q < 0$ in red and $\Delta Q > 0$ in blue). The contour value for density is 0.001. ^a Contribution of each term to the total orbital energy ΔE_{orb} .

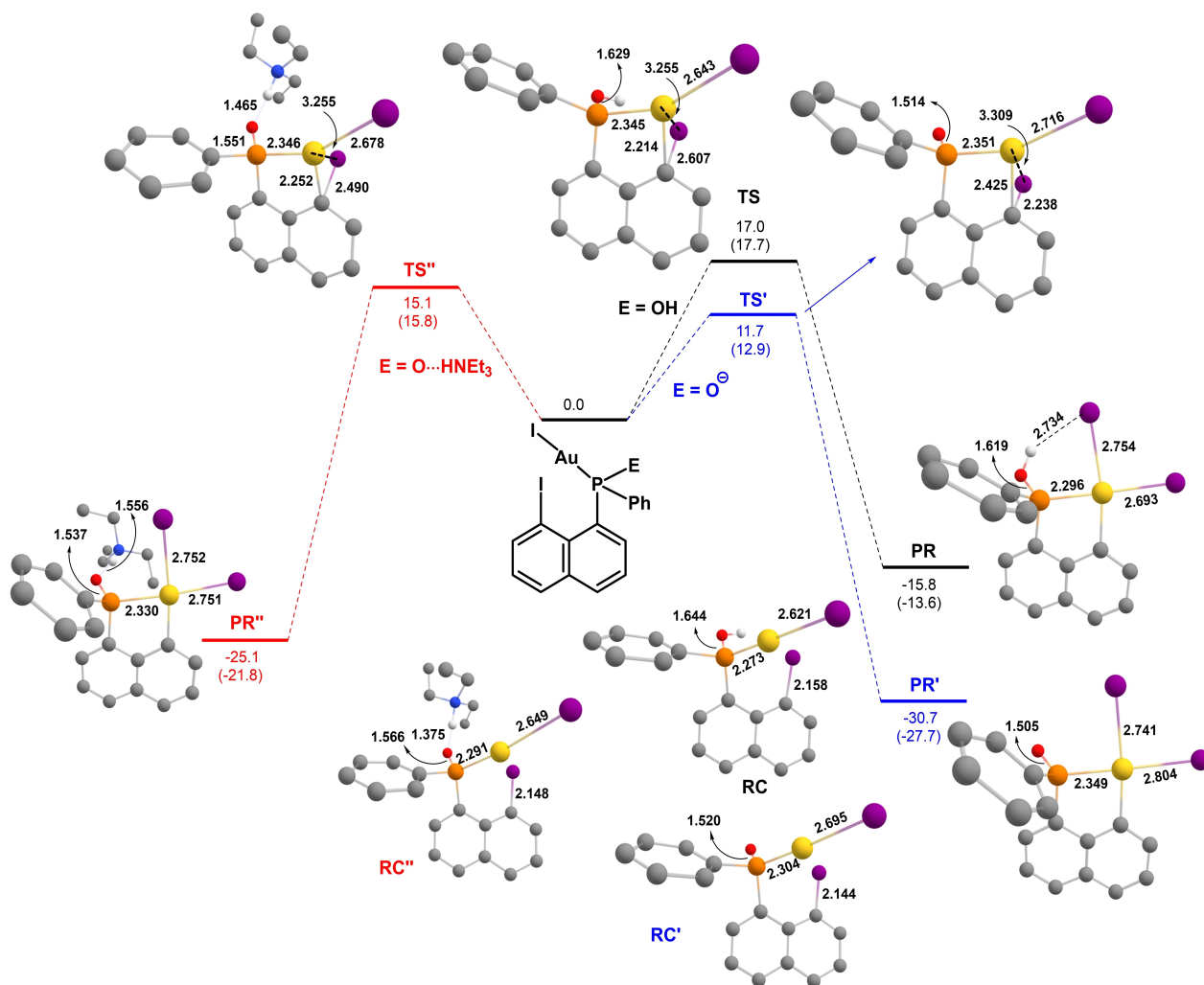
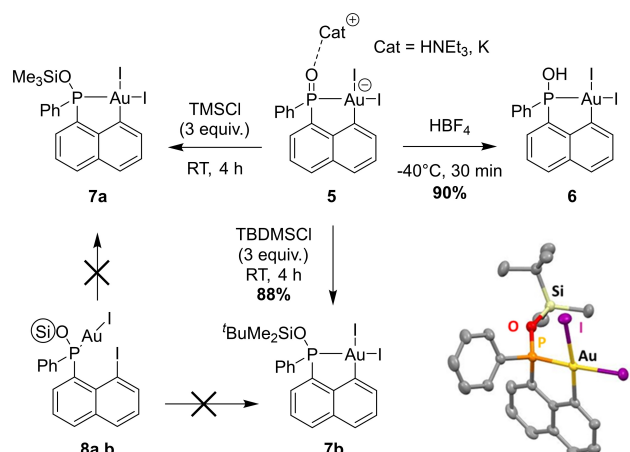


Figure 4. Energy profiles (ΔG values in kcal/mol) for the SPO-chelation assisted oxidative addition to gold (in black OH, in blue naked anion, in red H-bonded O–H...NEt₃) computed at the SMD(benzene)-B3PW91-D3(BJ)/SDD + f(Au),I(SDD),6-31G**(other atoms)//B3PW91/SDD + f(Au),I(SDD),6-31G**(other atoms) level of theory. Values in brackets are computed in the gas phase at the B3PW91/SDD + f(Au),I(SDD),6-31G** level. P in orange, Au in yellow, I in violet, N in blue. RC: reactant, TS: transition state, PR: product.

52.9% for PPh(OH), 62.6% for PhPO...HNEt₃ and 59.8% for PPh(O)⁻ while (PhI)→Au donation contributes for only 11.0–11.9% (Table S6).^[17] As for the PPh₂ ligand, Hirshfeld partitioning shows charge transfer (CT) from the Au complex to PhI in the transition state, by 0.13 e for PPh(OH), 0.21 e for PhPO...HNEt₃ and 0.22 e for PPh(O)⁻.

Reactivity of the (P=O,C)-cyclometalated Au(III) complex

Here we aimed to assess the ability of the SPO moiety installed for the first time at Au(III) in complex 5 to be chemically derivatized. First, we targeted protonation and reacted 5 with a Brønsted acid, HBF₄ (Scheme 3). The corresponding hydroxyphosphine Au(III) complex 6 rapidly formed, as substantiated by NMR spectroscopy:^[17] the ³¹P NMR signal shifts further downfield to δ 91.0 ppm, a broad ¹H NMR signal is observed at δ 9.71 ppm for the OH group and retention of the (P=O,C)Au(III)



Scheme 3. Protonation/silylation of the P=O group of 5, molecular structure of 7b.

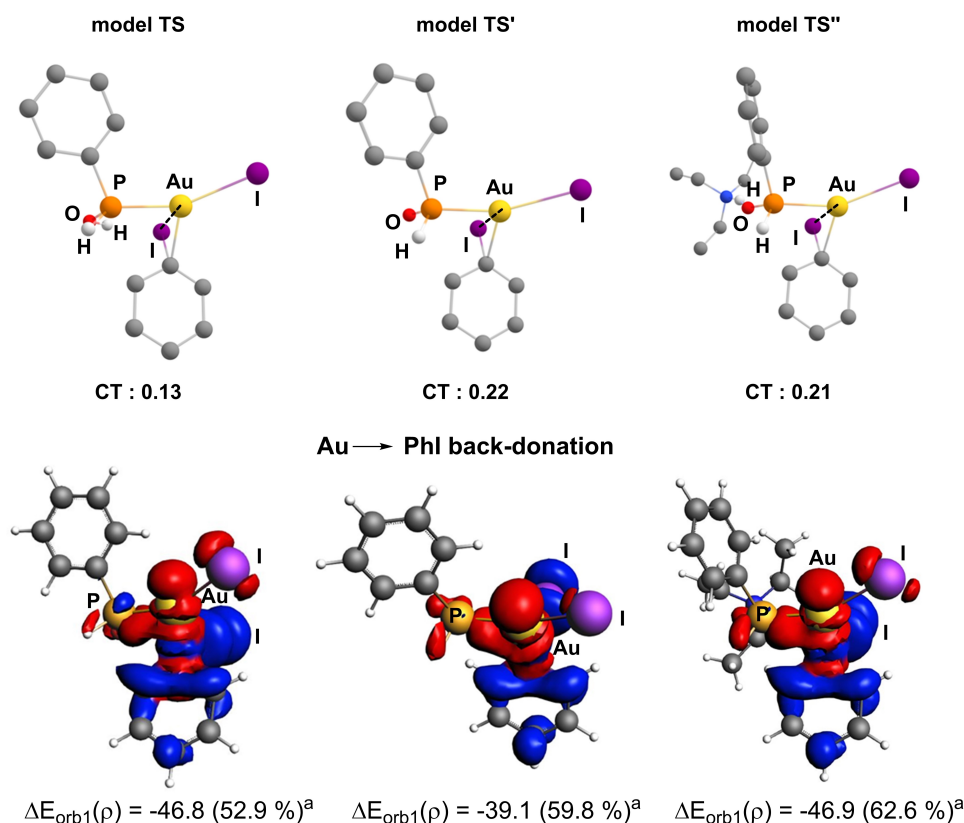


Figure 5. Structures of the model transition states for the SPO-chelation assisted oxidative addition to gold. Charge transfer (CT) from the Au complex to PhI. Plot of the contour of the main deformation density contribution ($\Delta\rho_{orb1}$) of the pairwise orbital interactions (back-donation term) between PhI and the Au complex with associated orbital interaction energy (ΔE_{orb1} in kcal/mol) for the transition states of the protonated complex, naked deprotonated form and H-bonded NEt_3 adduct, computed at ZORA-BP86-D3/TZ2P level of theory. The charge flow is red→blue ($\Delta\rho < 0$ in red and $\Delta\rho > 0$ in blue). The contour value for density is 0.001. ^aContribution of each term to the total orbital energy ΔE_{orb} .

framework is apparent from the ^1H NMR signal δ 8.97 ppm for the CH(naphthyl) next to Au. The reaction stops at the stage of O-protonation. Reductive elimination to reform the C–I bond and regenerate the hydroxy-phosphine Au(I) complex **3** is uphill in energy, with an activation barrier > 30 kcal/mol (Figure 4). Silylation was then investigated. Treating **5** with Me_3SiCl (3 equiv., 4 h, RT) led to the O-silylated Au(III) complex **7a**. This species proved unstable towards work-up under vacuum (to remove the excess of Me_3SiCl) and was characterized in situ.^[17] Increasing the steric demand of the silyl group (from Me_3Si to $^t\text{BuMe}_2\text{Si}$) resulted in an isolable complex **7b**, which was fully characterized by multi-nuclear NMR spectroscopy, high-resolution mass spectrometry and XRD.^[17] Most diagnostic for the silylation of the P=O moiety are the doublets found at δ 32–34 ppm ($^2J_{\text{P-Si}} = 10\text{--}15$ Hz) in the ^{29}Si NMR spectra of **7a,b**, while the deshielded ^1H NMR signals at δ 9.3–10.0 ppm for the CH(naphthyl) next to Au indicate the retention of the (P=O,C)Au(III) framework. The molecular structure of **7b**^[17] shows that the introduction of the silyl group at oxygen induces only small geometric modifications: the square-planar environment around the Au(III) center is marginally distorted while the P-naphthyl-Au skeleton slightly deviates from planarity (torsion angle P–C3...C1–Au $-4.9(1)^\circ$). Compared with the (P=O,C) Au(III)

complexes **5**, the P–O bond in **7b** is longer [1.560(2) Å] in line with single bond character.

Note that attempts to prepare the Au(III) complexes **7a,b** by inverting the order of steps (O-silylation first, then P-chelation assisted oxidative addition to Au) failed. The corresponding siloxy-phosphine Au(I) complexes **8a,b** did not evolve spontaneously into **7a,b** and upon heating, only degradation was observed. This confirms the determinant impact of the electron density at P for the *peri* C–I bond to oxidatively add to Au, even when the Au(I) complex is sterically congested and geometrically constrained.

Conclusion

The P-chelation assisted strategy to promote oxidative addition of $\text{C}(\text{sp}^2)\text{--I}$ bonds to gold has been extended to the SPO moiety. In contrast with related phosphines, the reaction was found to require a base (NEt_3 , K_2CO_3) to proceed efficiently. Suspecting that the electron-donating properties of the P-ligand and thus the electron density at gold play a major role in this process, the electron flow and key orbital contributions in such oxidative additions have been analysed in-depth computationally. Accordingly, back-donation prevails over donation in the oxidative

additions of Ph-I to LAuI complexes, as for PdL₂ species. This markedly contrasts with that found previously for the activation of aryl iodides by cationic complexes featuring chelating PP/NN or hemilabile PN ligands, where the electron flow was opposite. The properties of gold towards oxidative addition thus finely depend on the charge and geometry of the metal.

The reaction gives access to (P=O,C)-cyclometallated Au(III) complexes, the first Au(III) complexes with SPO ligands. The possibility for chemical derivatization of the P=O moiety has been substantiated by protonation and silylation reactions. Future work will aim to explore further and exploit the reactivity of (P=O,C)-cyclometallated Au(III) complexes. Special interest will be given to transformations involving metal-ligand cooperativity, which is still very scarce with gold.^[15,24]

Experimental Section

General Remarks: Unless otherwise stated, all reactions and manipulations were carried out under an atmosphere of dry argon using standard Schlenk techniques or in a glovebox under an inert atmosphere. Dry, oxygen-free solvents were employed. Solution ¹H, ¹³C, ³¹P, ²⁹Si NMR spectra were recorded on Bruker Avance 300, 400 or 500 spectrometers at 298 K unless otherwise stated. Chemical shifts are expressed with a positive sign, in parts per million, calibrated to residual ¹H and ¹³C solvent signals. The following abbreviations and their combinations are used: br, broad; s, singlet; d, doublet; t, triplet; q, quartet; quin, quintuplet; m, multiplet. Mass spectra were recorded on a Waters GCT premier apparatus and Waters Xevo G2 QTOF apparatus. All starting materials were purchased from Aldrich and used as received unless otherwise stated.

Preparation of ligand 2: 1,8-Diiodonaphthalene (1.3 g, 3.4 mmol) was dissolved in 40 mL THF and cooled to -78 °C. To this solution, 2.3 mL of a 1.5 M solution of ⁿBuLi (3.4 mmol, 1.0 equivalent) were added over 5 min under stirring. Color turns deep yellow/dark orange. After stirring at the same temperature for 1 h, Ph(NEt₂)PCl (733 mg, 3.4 mmol) was added as a solution in 2 mL THF via syringe. The reaction was allowed to warm back to room temperature overnight. The solution was treated with 2.2 equiv. of HCl in CPME (4 M) for 2 h, then quenched with aqueous NaHCO₃ and left stirring for 2 h. The solvents were evaporated and the residue was extracted with ethyl acetate (3 × 20 mL) and washed with brine. The combined organic phases were evaporated, dried over Na₂SO₄. The crude was purified through column chromatography on silica pretreated with acetone/water 9:1 for at least 1 h (note: the acetone/water solution must be removed completely before performing the column, otherwise the purification is compromised). The column was performed with DCM/EtOAc/EtOH 7.5:2:0.5 to afford **2** as a pure beige solid (880 mg, 60% yield). If necessary, **2** can be recrystallized from CH₂Cl₂/pentane.

¹H NMR (500 MHz, CDCl₃) δ 9.74 (d, *J* = 519.3 Hz, 1H), 8.47 (ddd, *J* = 17.0, 7.2, 1.4 Hz, 1H), 8.27 (dd, *J* = 7.3, 1.3 Hz, 1H), 8.02 (d, *J* = 8.2 Hz, 1H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.72–7.44 (m, 4H), 7.40 (td, *J* = 7.7, 2.9 Hz, 2H), 7.18 (t, *J* = 7.7 Hz, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 143.2, 138.5 (d, *J* = 8.3 Hz), 136.6–135.9 (m), 135.0 (d, *J* = 3.0 Hz), 133.8, 132.9, 131.9 (d, *J* = 1.9 Hz), 131.2 (d, *J* = 10.9 Hz), 130.5 (d, *J* = 2.1 Hz), 128.7 (d, *J* = 12.8 Hz), 127.9 (d, *J* = 91.2 Hz), 127.3, 125.2 (d, *J* = 13.3 Hz), 91.3 (d, *J* = 3.8 Hz).

³¹P NMR (121 MHz, CDCl₃) δ 15.8 (d, *J* = 522.6 Hz).

HRMS: (DCI, CH₄) calculated for C₁₆H₁₃IOP⁺: 378.9749; found: 378.9746

Preparation of complex 5b: A solution of **2** (18.9 mg, 0.05 mmol) in THF (1 mL) was added to a suspension of AuI (16.2 mg, 0.05 mmol) in THF (1 mL). After 10 min, the solution was filtered through cannula into a schlenk flask containing K₂CO₃ (8.3 mg, 0.06 mmol) and stirred at room temperature for 2.5 h. The solution was then filtered again with a cannula, and then precipitated with 3 mL of pentane obtaining **5b** (26.3 mg, 71% yield) as a crystalline yellow solid. ¹H NMR (500 MHz, THF-*d*₈) δ 9.28 (d, *J* = 7.5 Hz, 1H), 7.88 (dd, *J* = 6.8, 3.3 Hz, 1H), 7.81 (dd, *J* = 7.6, 3.2 Hz, 1H), 7.62–7.48 (m, 3H), 7.45–7.36 (m, 2H), 7.34–7.30 (m, 1H), 7.25 (td, *J* = 7.4, 3.0 Hz, 2H). ¹³C NMR (126 MHz, THF-*d*₈) δ 155.6 (d, *J* = 7.5 Hz), 147.8 (d, *J* = 74.1 Hz), 143.0 (d, *J* = 31.6 Hz), 141.3 (d, *J* = 76.9 Hz), 140.0 (d, *J* = 2.3 Hz), 135.3 (d, *J* = 18.4 Hz), 131.7 (d, *J* = 2.8 Hz), 131.4 (d, *J* = 3.3 Hz), 131.0 (d, *J* = 12.2 Hz), 129.4 (d, *J* = 3.5 Hz), 128.6, 128.5 (d, *J* = 13.3 Hz), 126.8, 126.6 (d, *J* = 11.0 Hz). ³¹P NMR (121 MHz, THF) δ 75.1. **HRMS:** (ESI⁻) calculated for C₁₆H₁₁OPAu₂: 700.8302; found: 700.8304.

Preparation of complex 7b: A solution of **2** (50 mg, 0.132 mmol) in THF (2 mL, plus 2 mL for rinsing) was added at room temperature to a suspension of AuI (43 mg, 0.132 mmol) in dry THF (4 mL). After 1 h, the clear yellow solution was filtered through cannula directly to a schlenk containing flame dried K₂CO₃ (23 mg, 0.159 mmol). After 12 h, the suspension was filtrated via cannula to remove the excess of K₂CO₃ to afford a clear intense yellow solution (complex **4b**). Then, a solution of TBDMSCl (60 mg, 0.396 mmol) in THF (2 mL) was added and the reaction mixture was stirred at room temperature for 4 h. The reaction mixture was then evaporated and the obtained residue was dissolved in DCM (1.5 mL). Upon addition of pentane (30 mL), pure **7b** was isolated after filtration via cannula and drying under vacuum as a pure yellow solid (95 mg, 88%). ¹H NMR (500 MHz, CD₂Cl₂) δ 9.32 (ddd, *J* = 7.5, 1.6, 0.9 Hz, 1H), 8.28–8.07 (m, 1H), 8.07–7.96 (m, 1H), 7.79–7.68 (m, 2H), 7.68–7.61 (m, 2H), 7.61–7.52 (m, 4H), 0.91 (s, 9H), 0.35 (s, 3H), -0.06 (s, 3H). ¹³C NMR (126 MHz, CD₂Cl₂) δ 154.3 (d, *J* = 6.3 Hz), 144.1 (d, *J* = 38.2 Hz), 139.8 (d, *J* = 2.2 Hz), 138.7 (d, *J* = 65.9 Hz), 135.3 (d, *J* = 19.7 Hz), 134.8 (d, *J* = 2.2 Hz), 134.1 (d, *J* = 3.6 Hz), 132.4 (d, *J* = 2.9 Hz), 131.4 (d, *J* = 14.0 Hz), 129.2 (d, *J* = 14.5 Hz), 127.1 (d, *J* = 10.9 Hz), 25.5, -2.7, -3.2. ³¹P NMR (202.45 MHz, CD₂Cl₂) δ 89.6 (t, *J*_{P-Si} = 14.17 Hz). ²⁹Si NMR (99.36 MHz, CD₂Cl₂) δ 34.7 (d, *J*_{P-Si} = 14.9 Hz). **HRMS:** (DCI) calculated for C₂₂H₂₆Au₂OPSi: 815.9246; found: 815.9254.

Deposition Number(s) 2212158 (for **3**), 2212155 (for **4a**), 2212157 (for **4b**), 2212160 (for **7b**) contain(s) the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

Additional references cited within the Supporting Information.^[25–36]

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

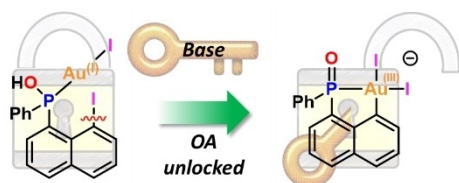
The data that support the findings of this study are available in the supplementary material of this article.

Keywords: DFT calculations · gold · oxidative addition · secondary phosphine oxides · XRD analyses

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The P-chelation assisted strategy to promote oxidative addition of $C(sp^2)-I$ bonds to gold has been extended to secondary phosphine oxides, but in contrast with related phosphines, a base (NEt_3 , K_2CO_3) is needed. Back-

donation prevails over donation in such oxidative additions. The reaction gives access to (P=O,C)-cyclometalated Au(III) complexes whose SPO moiety can be chemically derivatized.

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Base-Triggered Oxidative Addition to Gold

