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Silver-mediated intramolecular P–C coupling

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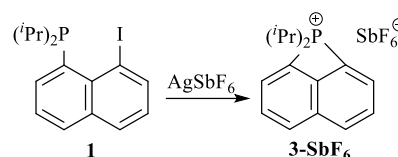
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Abstract: Silver(I) salts mimics copper(I) not gold(I) salts

in the reaction with the *peri*-iodo naphthyl phosphine **1**.

The formation of the *peri*-cyclic phosphonium **3**

represents the first example of silver-mediated P–C coupling through a 2-electron redox sequence.



Keywords: silver, complexes, cross-coupling, oxidative addition, phosphonium, DFT, naphthalene, *peri* substitution

Main text: Among the coinage metals, silver is quite peculiar. Its molecular chemistry is by far less developed and explored than those of copper and gold. Inorganic salts and coordination complexes of silver(I) have been mostly used as (1) sacrificial, 1-electron oxidants, (2) halide abstractors and (3) π -activators for olefins and alkynes.¹ In terms of reactivity, silver shows some resemblance to its heavier analog, gold, that is widely used and extremely powerful in π -activation.² On the other hand, while C–C and C–heteroatom cross-coupling chemistry is well-known with copper and rapidly developing with gold, such reactivity has been very rarely demonstrated for silver.^{3,4,5} Indeed, 2-electron redox cycling between M(I) and M(III) has only been recently and scarcely evidenced for silver, mainly under stoichiometric conditions.⁸⁻¹¹

In 2014, our group introduced a chelating strategy to promote C(sp²)-X oxidative addition (OA) to coinage metals. The formation of the (P,C)-cyclometallated gold(III) complex **2** from the *peri*-iodo naphthylphosphine **1** provided the first evidence for such a process at a single gold center (Figure 1)¹² The same approach was later explored with copper in order to compare the reactivity of the two metals. Surprisingly, the outcome of the reaction was different: OA to copper was followed by intramolecular P-C coupling to afford the original 4-membered cyclic phosphonium diiodocuprate **3a**.¹³ The reaction turned to be catalytic in copper, providing a direct and efficient access to **3c**.¹⁴ Given that silver(I) salts are known to readily form complexes with phosphines, we wondered about the fate of their reaction with the *peri*-iodo naphthylphosphine **1** and the possibility to apply the P-chelation strategy to promote oxidative addition to silver (see Figure 1). The results we obtained are described hereafter, comparing silver with copper and gold.

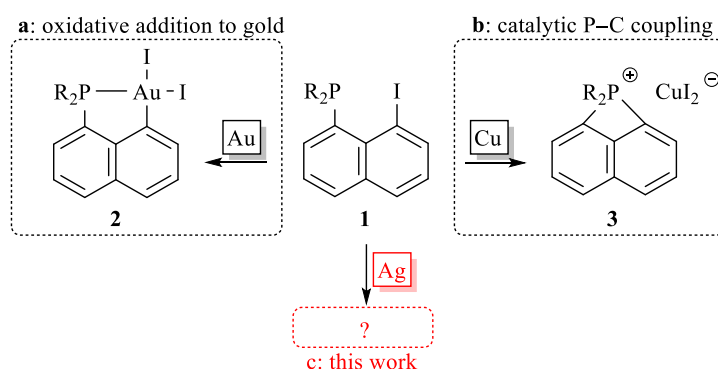
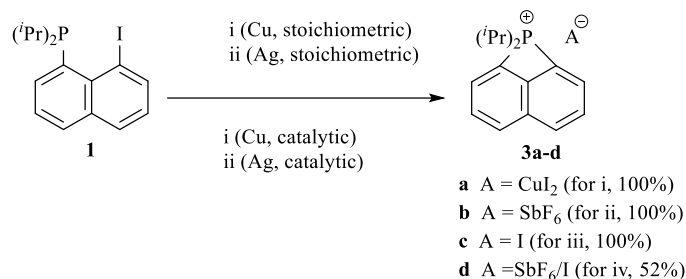


Figure 1 Reactions of the *peri*-iodo naphthyl phosphine **1** with gold, copper and silver salts.

First, the *peri*-iodo naphthylphosphine **1** was reacted with AgBF₄ in CH₃CN. ³¹P NMR monitoring revealed the instantaneous formation of a new species (S1). The observed chemical shift (25.1 ppm) and ¹J_{P-Ag} couplings (480.1 / 555.6 Hz) are indicative of a P-coordinated silver(I) complex. After 1 day at room temperature, the phosphonium salt **3b** (A = BF₄) was observed as the major product along with a small amount of

remaining intermediate Ag(I) complex. Following this preliminary result, a quick optimization was carried out. Among the tested solvents (MeCN, CH₂Cl₂, THF, DMF, MeNO₂), MeCN provided the cleanest and fastest formation of phosphonium derivatives **3**. In terms of silver salts, AgSbF₆ performed better than AgPF₆, AgBF₄, AgOTf and AgI. Finally, the effect of the temperature was also investigated. Full conversion required 7 hours at 45°C, but was reached within only 10 minutes at 85°C. Under the optimized conditions, the phosphonium **3b** was synthesized in 92% isolated yield. From these results, the peri-iodo naphthyl phosphine is found to react with silver(I) in the same way than with copper(I), but differently to gold(I). The reaction does not stop at the silver(III) stage following oxidative addition, but would progress further until the P–C coupling to afford the *peri*-bridged phosphonium. In this sequence, copper displays much higher activity than silver (100% conv. 25°C, inst. vs. 45°C, 7h respectively, Scheme 1). Of note, the formation of phosphonium **3c** was shown to require only a catalytic amount of copper(I) salt.¹² In order to test the feasibility of such a catalytic P–C coupling with silver, substoichiometric amounts of AgSbF₆ (50 mol% and 20 mol%) were used. ³¹P NMR monitoring revealed the full conversion of **1** after 30 hours. However, the reaction was not clean. The desired product **3c** formed along with other unidentified products (see Online Supplementary Materials, Figures S4 and S5). The precipitation of AgI, which decreases the amount of active silver(I) species in solution, may explain why the reaction is sluggish and incomplete. In the study of C–O couplings of *N*-based macrocycles mediated by silver, Ribas *et coll.* showed that adding PPh₃ cocatalyst or a strong halide scavenger (TIOTf) can increase catalytic turnovers.⁸ Therefore, the reaction of **1** with 20 mol% AgSbF₆ was further tested in the presence of 20 mol% PPh₃, and also 1 equiv. TIOTf; unfortunately, these additives did not improve the outcome. This experiment may reveal some catalytic

turnover in the formation of the phosphonium with AgSbF₆. However, the activity of silver(i) lags far behind that of copper(i) in this P–C coupling reaction (1 mol% CuI, 5 min, room temperature, 100% vs. 20 mol% AgSbF₆, 3 h, 85 °C, 52%)



Scheme 1 Reagents and conditions: i, CuI (1 equiv.), CH₂Cl₂, 25 °C, inst.; ii, AgSbF₆ (1 equiv.), MeCN, 45 °C, 7 h; iii, CuI (1 mol%), MeCN, 25 °C, 5 min; iv, AgSbF₆ (20 mol%), MeCN, 85 °C, 3 h.

In order to get more insight into this silver-mediated P–C coupling and compare the coinage metals, DFT calculations were performed. The energy profiles of the reaction of **1** with copper, silver and gold iodides were computed at the same level of theory [Figure 2(a), see also Online Supplementary Materials, Figures S6 and S8]. The reaction sequence proceeds in two steps: P-chelated oxidative addition of the C–I bond to the coinage metal (OA) followed by intramolecular reductive elimination leading to P–C coupling (RE). The outcome can be explained by the thermodynamic and kinetic stability of the M(III) diiodo intermediate **2^M**. In the case of copper, the formation of the phosphonium **3^{Cu}** is highly favored. It is exergonic ($\Delta G_{\text{RE}} = -13.7$ kcal/mol) and the activation barrier is very small ($\Delta G^{\ddagger}_{\text{RE}} = 6.3$ kcal/mol). On the contrary, for gold, the Au(III) intermediate **2^{Au}** is formed preferentially. The RE step is thermodynamically unfavorable ($\Delta G_{\text{RE}} = 8.4$ kcal/mol) and kinetically inaccessible ($\Delta G^{\ddagger}_{\text{RE}} = 35.8$ kcal/mol).

As for silver, the formation of the phosphonium **3^{Ag}** is thermodynamically favored ($\Delta G_{(1)AgI-3Ag} = -20.1$ kcal/mol) and kinetically accessible upon heating ($\Delta G_{RE}^{\ddagger} = 15.7$ kcal/mol). It is worth noting that energy barrier for the OA to silver (18.4 kcal/mol) is the largest in the coinage metal series. It slightly exceeds that of gold (16.1 kcal/mol). The Ag(III) complex **2^{Ag}** lies only 3.1 kcal/mol higher in energy than the phosphine complex **(1)AgI** and displays slightly distorted square-planar geometry (Figure 2b and S7).⁶

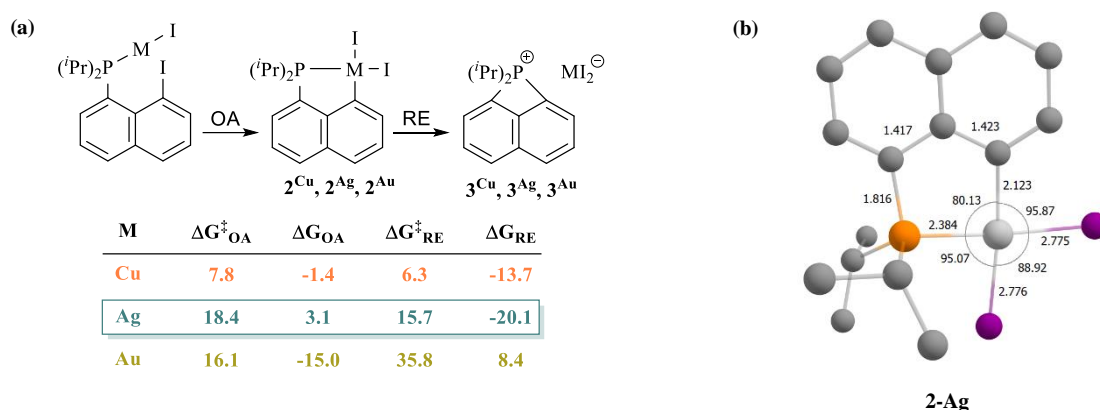


Figure 2 (a) Energy profiles computed for the reaction of **1** copper, silver and gold iodides: P-chelated oxidative addition of the C–I bond to M (OA) and intramolecular reductive elimination leading to P–C coupling (RE). (b) Structure of the key Ag(III) intermediate **2^{Ag}**. (distances in Å and bond angles in °) optimized at SMD(CH₃CN)-B3PW91/SDD+f(M), I(SDD), 6-31G** (other atoms) level of theory. Hydrogens omitted for clarity.

In conclusion, silver(I) salts react with the *peri*-iodo naphthyl phosphine **1** to give the *peri*-cyclic phosphonium **3**, mimicking copper(I) not gold(I). This transformation represents the first example of a P–C coupling operating by a 2-electron Ag(I)/Ag(III) redox sequence.

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