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Silver-mediated intramolecular P–C coupling

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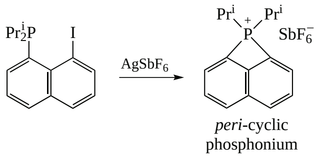
Silver(I) salts mimic copper(I) but not gold(I) salts in the reaction with *peri*-iodo naphthyldiisopropylphosphine. The formation of the corresponding *peri*-cyclic phosphonium derivatives represents the first example of silver-mediated P–C coupling through a two-electron redox sequence.



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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 reagents, one-electron oxidants, (2) halide scavengers and (3) π-activators for olefins and alkynes.[1] In terms of reactivity, silver shows some resemblance to its heavier analogue, 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.[3–7] Indeed, two-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 $C(sp^2)$–X oxidative addition (OA) to coinage metals. The initial *peri*-iodo naphthylphosphine **1** was transformed into (P,C)-cyclometallated gold(III) complex **2**, which provided the first evidence for such a process at a single gold center (Figure 1).[12] The same chelation 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 four-membered cyclic phosphonium diiodocuprate **3a**.[13] The reaction turned to be catalytic in copper, providing a direct and efficient access to relative iodide **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.

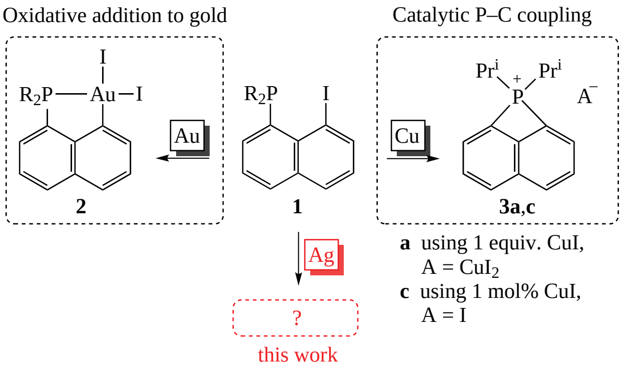
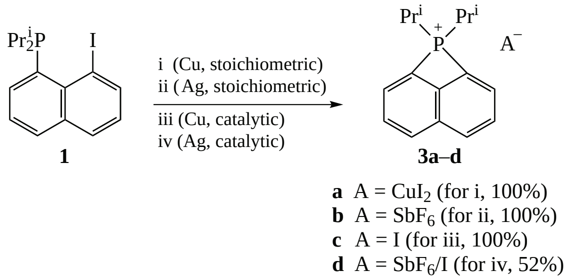


Figure 1 Reactions of the *peri*-iodo naphthylphosphine **1** with gold, copper and silver salts.

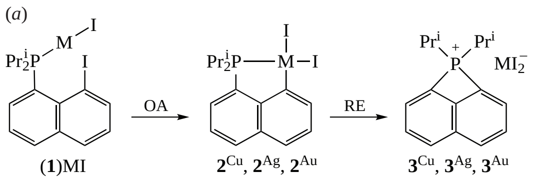
First, *peri*-iodo naphthylphosphine **1** was reacted with $AgBF_4$ in MeCN (Scheme 1). ^{31}P NMR monitoring revealed the instantaneous formation of a new species (see Online Supplementary Materials, Figure S1). The observed chemical shift (25.1 ppm) and $^1J_{P-Ag}$ couplings (480.1/555.6 Hz) are indicative of a P-coordinated silver(I) complex. After 1 day at room temperature, phosphonium salt **3b** ($A = BF_4$) 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, CH_2Cl_2, THF, DMF, $MeNO_2$), MeCN provided the cleanest and fastest formation of phosphonium derivatives **3**. In terms of silver salts, $AgSbF_6$ performed better than $AgPF_6$, $AgBF_4$, AgOTf and AgI. Finally, the temperature effect was investigated. Full conversion required 7 h at 45 °C, but only 10 min at 85 °C. Under the optimized conditions, phosphonium salt **3b** was synthesized in 92% isolated yield. From these results, the *peri*-iodo naphthylphosphine is found to react with silver(I) in the same way as with copper(I), but differently to gold(I). The



Scheme 1 *Reagents and conditions*: i, CuI (1 equiv.), CH_2Cl_2, 25 °C, inst.; ii, $AgSbF_6$ (1 equiv.), MeCN, 45 °C, 7 h; iii, CuI (1 mol%), MeCN, 25 °C, 5 min; iv, $AgSbF_6$ (20 mol%), MeCN, 85 °C, 3 h.

reaction does not stop at the silver(III) stage following oxidative addition, but would progress further until the P–C coupling affords the *peri*-bridged phosphonium product. In this sequence, copper displays much higher activity than silver (100% conversion, 25 °C, inst. *vs.* 100% conversion, 45 °C, 7 h respectively, see Scheme 1). Of note, the formation of phosphonium iodide **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 $AgSbF_6$ (50 mol% and 20 mol%) were used. When reacting iodo phosphine **1** in the presence of 20 mol% $AgSbF_6$, the desired product **3c** was formed in 52% NMR yield after 3 h at 85 °C, 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 al.* showed that adding PPh_3 cocatalyst or a strong halide scavenger (TlOTf) can improve catalytic turnovers.[8] Therefore, the reaction of **1** with 20 mol% $AgSbF_6$ was further tested in the presence of 20 mol% PPh_3, and also 1 equiv. TlOTf; unfortunately, these additives did not improve the outcome. This experiment may reveal some catalytic turnover in the formation of the phosphonium with $AgSbF_6$. 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% $AgSbF_6$, 3 h, 85 °C, 52%).

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 $\mathbf{2}^{M}$. In the case of copper, the formation of the phosphonium $\mathbf{3}^{Cu}$ is highly favoured. It is exergonic (ΔG_{RE} = –13.7 kcal mol^{-1}) and the activation barrier is very small ($\Delta G^{\ddagger}_{RE}$ = 6.3 kcal mol^{-1}). On the contrary, the Au^{III} intermediate $\mathbf{2}^{Au}$ is formed preferentially. The RE step is thermodynamically unfavorable (ΔG_{RE} = 8.4 kcal mol^{-1}) and kinetically inaccessible ($\Delta G^{\ddagger}_{RE}$ = 35.8 kcal mol^{-1}). As for silver, the formation of the phosphonium $\mathbf{3}^{Ag}$ is thermodynamically favored (ΔG_{RE} = –20.1 kcal mol^{-1}) and kinetically accessible upon heating ($\Delta G^{\ddagger}_{RE}$ = 15.7 kcal mol^{-1}). It is worth noting that energy barrier for the OA to silver (18.4 kcal mol^{-1}) is the largest in the coinage metal series. It slightly exceeds that of gold (16.1 kcal mol^{-1}). The Ag^{III} complex $\mathbf{2}^{Ag}$ lies only 3.1 kcal mol^{-1} higher in energy than the phosphine complex **1**·AgI and displays slightly distorted square-planar geometry [Figures 2(*b*) and S7].[15]



M	$\Delta G^{\ddagger}_{OA}$	ΔG_{OA}	$\Delta G^{\ddagger}_{RE}$	ΔG_{RE}
Cu	7.8	–1.4	6.3	–13.7
Ag	18.4	3.1	15.7	–20.1
Au	16.1	–15.0	35.8	8.4

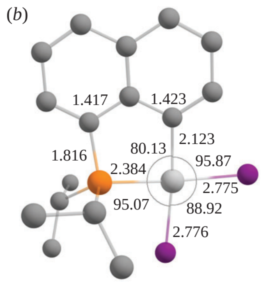


Figure 2 (*a*) Energy profiles computed for the reaction of **1** copper, silver and gold iodides: P-chelated oxidative addition of the C–I bond to M (OA) and intramolecular reductive elimination leading to P–C coupling (RE) (*G* in kcal mol^{-1}). (*b*) Structure of the key Ag^{III} intermediate $\mathbf{2}^{Ag}$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

In conclusion, silver(I) salts were found to react with the *peri*-iodo naphthylphosphine **1** to give the *peri*-cyclic phosphonium salts **3**, mimicking copper(I) rather than gold(I). This transformation represents the first example of a P–C coupling operating by a two-electron Ag^{I}/Ag^{III} redox sequence.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.01.025.

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