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Structural elucidation of silver(I) amides and their application as catalysts in the hydrosilylation and hydroboration of carbonyls

Samantha A. Orr, John A. Kelly, Aaron J. Boutland and Victoria L. Blair*[a]

Abstract: *This study details the isolation and characterisation of three novel silver(I) amides in solution and solid-state, [Ag(Cy$_3$P)(HMDS)]* ***2****, [Ag(Cy$_3$P){N(TMS)(Dipp)}]* ***3*** *and [Ag(Cy$_3$P)$_2$(NPh$_2$)]* ***4****. Their catalytic abilities have proved successful in hydroboration and hydrosilylation reactions with a full investigation performed with complex* ***2****. Both protocols proceed under mild conditions, displaying exceptional functional group tolerance and chemoselectivity, in excellent conversions at competitive reaction times. This work reveals the first catalytic hydroboration of aldehydes and ketones performed by a silver(I) catalyst.*

Among the Group 11 coinage metals, silver is often overlooked or neglected in synthesis due to its relatively moderate Lewis acidity, ease of reduction and photosensitivity.[1] Despite these drawbacks, the reasonable cost of silver salts (relative to other expensive transition metals) combined with the ability of silver to act as a σ- and/or π-Lewis acid,[2] have placed them as indispensable reagents in various organic transformations including as additives in Pd-catalysed transformations,[3] as effective Lewis acid catalysts, as well as promoters in carboxylation,[4] enantioselective asymmetric reactions,[5,6] heterocyclisations and cycloadditions.[7]

A key aspect of why silver is so suited to these catalytic transformations is its tunable Lewis acidity. By careful choice of counter-ion (e.g. halide, perchlorate, triflate) the Lewis acidity can be modulated (weaker or stronger) and manipulated to achieve a desired outcome in synthetic organic transformations. However, in most cases these reactions can often require additional additives, such as supporting ligands, base(s), and/or elevated temperatures, with the actual composition of the active Ag(I) species generally unknown. Some silver salts have emerged as promising reagents in catalytic hydrosilylation and more recently hydroboration of unsaturated substrates.[8,9] Both AgOTf[10] (Figure 1) and $AgPF_6$[11] with addition of an appropriate phosphine or NHC co-ligand respectively, have shown to be effective and efficient in the hydrosilylation of aldehydes, albeit at elevated temperatures (70-100°C), while ketones still remain a challenge. Significantly these catalytic hydrosilylation reactions are proposed to involve 'M-H' intermediates[9,10] as the active catalytic species, although characterisation has proved elusive. In marked contrast, progress in Ag(I) catalysed hydroboration reactions are still in their infancy. Yoshida and co-workers,[12] were the first to report catalytic hydroboration of terminal alkynes using B_2Pin_2 (pin = pinacol) employing an Ag(I)-NHC complex and KOtBu.

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The groups of Rit[13] and Bi[14] simultaneously reported the use of silver(I) salts $AgSbF_6$ or AgOAc for the catalytic selective β-hydroboration of terminal alkynes and/or alkenes, respectively, under base and ligand free conditions via a proposed radical pathway.

Moving away from traditional salts, Kobayashi combined Lewis acidic silver with the Brønsted amido base HMDS (HMDS = hexamethyldisilazide) to give AgHMDS which was shown to catalyse asymmetric [3+2] cycloaddition reactions of Schiff bases with α-aminophosphonates[15] and/or olefins[16] in high yields and enantioselectivities in the presence of a supporting chiral bisphosphine ligand (Figure 1).[17] Interestingly, in the absence of the chiral supporting ligand AgHMDS showed little to no catalytic activity. To the best of our knowledge this represents the only example of a silver(I) amide system used in catalysis

Inspired by this study, we sought to design a silver(I) amide pairing that would be successful as a catalyst in hydrofunctionalisation reactions. These typically involve M-H intermediates, which are unstable and extremely rare in silver chemistry with only two examples structurally characterised to date.[18,19] Therefore, designing a pre-catalyst that allows *in-situ* access to a stable silver(I) hydride species would be of benefit in such catalytic systems.

Compelled by the general lack of knowledge on silver(I) amide complexes, from both a structural and reactivity viewpoint, we now describe the synthesis, solution and solid-state characterisation of three monomeric silver(I) amide complexes and their application in the catalytic hydrosilylation and hydroboration of a range of aldehydes and ketones.

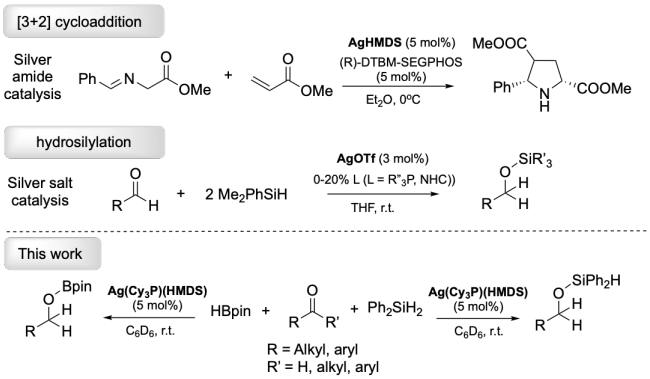

Figure 1. Summary of silver mediated catalysis.

The target silver(I) amide complexes were synthesized using salt metathesis. Addition of the appropriate lithium amide to a THF suspension of AgCl and Cy_3P **1** (Scheme 1) afforded [Ag(Cy$_3$P)(HMDS)] **2**, [Ag(Cy$_3$P){N(TMS)(Dipp)}] **3** and [Ag(Cy$_3$P)$_2$(NPh$_2$)] **4.** Emphasising the importance of the soft phosphine donor, changing to an oxygen or nitrogen Lewis donor, resulted in repeated decomposition and precipitation of Ag(0). Complexes **2** - **4** are pale yellow to colourless solids, hydrocarbon soluble, thermally robust, and stable for weeks at 25°C upon exclusion of light. Interestingly, addition of an excess Cy_3P to

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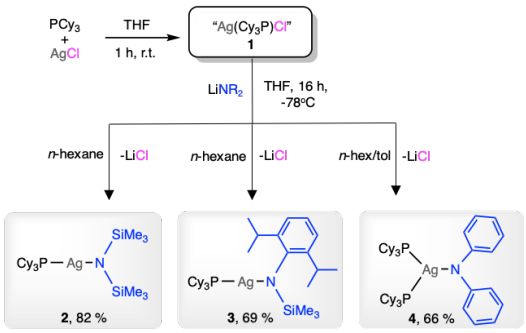
complexes **2** and **3** did not result in any additional phosphine coordination to silver.



Scheme 1. Synthesis of Ag(I) amide complexes **2** - **4**.

Single crystals suitable for X-ray diffraction studies were obtained for complexes **2** - **4**. Due to the isostructural nature of **2** and **3** (see ESI) only **2** will be discussed in detail. All three complexes **2** - **4** are monomeric in the solid state. The silver atom in **2** adopts an almost perfect P-Ag-N linear angle of 177.02 (4)° with a short Ag-N bond length of 2.0746 (17) Å (Figure 2). This is similar to that of 2.079 (2) Å reported in the NHC silver(I) amide complex [Ag(SItBu)(HMDS)][20] (SItBu = 1,3-di-tert-butyl-imidazolin-2-ylidene) while being significantly shorter than that found in tetrameric [{Ag(HMDS)}$_4$][21] (average Ag-N = 2.147 Å). In contrast, **4** adopts a distorted trigonal planar geometry due to the large steric constraint of the two coordinated Cy_3P ligands. This steric constraint results in the lengthening of the Ag-N bond to 2.258 (2) Å. To the best of our knowledge structural characterisation of monomeric silver(I) amide complexes, in which a Brønsted base is bound to the silver centre are scarce[20] though tetrameric and dimeric structures are more common.[22–24]

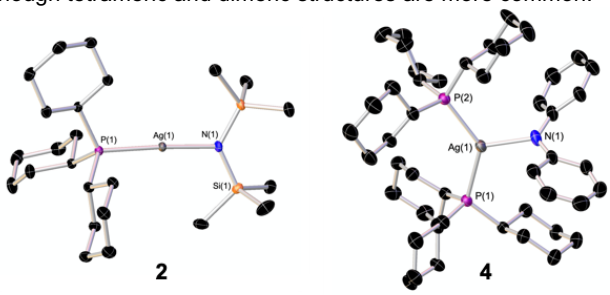


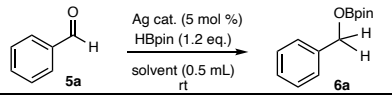
Figure 2. Molecular structure of [Ag(Cy_3P)(HMDS)] **2** and [Ag(Cy_3P)$_2$(NPh_2)] **4** in the solid state. Ellipsoids are set at 50% and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] for **2**: Ag(1)-N(1), 2.0746(17); Ag(1)-P(1), 2.3404(10), N(1)-Ag(1)-P(1), 177.02(4); and **4**: Ag(1)-N(1), 2.258 (2); Ag(1)-P(1), 2.4680(6); Ag(1)-P(2), 2.4718(7); N(1)-Ag(1)-P(1), 114.84(8); N(1)-Ag(1)-P(2), 114.94(8); P(1)-Ag(1)-P(2), 130.23(2).

Examination of the ^{1}H, ^{13}C and ^{31}P NMR spectra in C_6D_6 of complexes **2** - **4** reveal the solid-state structure is retained in solution with characteristic resonances of the amido and phosphine (Cy_3P) ligands (see ESI). Most characteristic is their differing ^{31}P spectra due to deshielding of the phosphine ligand upon complexation to silver. In complex **2** a broad doublet at 37.0 ppm with a $^1J(^{107/109}Ag\text{-}^{31}P)$ coupling constant of 503 Hz is observed, whilst for **3** a set of doublets of doublets at 41.9 ppm and 37.7 ppm are detected due to spin-spin coupling of ^{107}Ag and ^{109}Ag nuclei. This results in $^1J(^{107}Ag\text{-}^{31}P)$ and $^1J(^{109}Ag\text{-}^{31}P)$ coupling constants of 480 Hz and 556 Hz respectively, which fall in the range of previously reported silver(I) complexes.[25] Whereas complex **4** shows a singlet at 28.8 ppm belonging to the Cy_3P ligand, attributed to rapid exchange equilibria in solution.

The relative stability of complexes **2** - **4** prompted us to probe their reactivity in catalytic systems. Although hydroboration and hydrosilylation reactions have been studied extensively with various metal systems,[26–29] to the best of our knowledge, there are no examples employing silver(I) amides.

Employing our benchmark reagent benzaldehyde, we investigated the most effective candidate for catalyzing carbonyl hydroboration, **2**-**4**, probing the structure activity relationship if any. The reaction was performed with pinacolborane (HBpin) and 5 mol% of each catalyst (Entries 1-3, Table 1) at room temperature in an amber J. Young's NMR tube and monitored by ^{1}H NMR spectroscopy. Catalysts **2** and **4** performed well reaching quantitative conversion in less than 30 minutes (Entries 1 and 3, Table 1), whereas catalyst **3** required extended reaction times not yielding a single product.[23] Catalyst **2** was selected for further studies owing to its ease of synthesis using commercially available starting reagents and a stoichiometric amount of Cy_3P ligand. Initial studies were performed in benzene, owing to the hydrocarbon solubility of our catalysts. However, we explored a more polar solvent, D_8-THF, to contrast the reaction outcome (Entry 4, Table 1). Comparatively, this inhibited the reaction considerably, reaching only 18 % conversion after 0.5 hours. Finally, to confirm the silver(I) amide is more catalytically active than the silver(I) chloride, complex **1** was studied (Entry 5, Table 1) which showed less than 50% conversion after 3 days.

Table 1. Hydroboration of benzaldehyde optimization.[a]



Entry	Catalyst	Solvent	Yield [%]	Time [h]
1	**2**	C_6D_6	99	0.5
2	**3**	C_6D_6	81[b]	7
3	**4**	C_6D_6	>99	0.3
4	**2**	D_8-THF	18	0.5
5	**1**	C_6D_6	43	72

[a] Reaction conditions: substrate (1 mmol), HBpin (1.2 mmol), 5 mol% catalyst and 10 mol% internal standard hexamethylcyclotrisiloxane in 0.5 mL of solvent at room temperature. [b] 97% conversion of aldehyde.

To study the scope of these Ag-mediated transformations, a range of carbonyls were studied. Preparing one equivalent of substrate in an amber J. Young's NMR tube, along with 5 mol% catalyst loading of **2**, and 1.2 equivalents of HBpin, they were monitored by ^{1}H and ^{11}B NMR spectroscopy. The successful outcome is an atom economical method that proved efficient for both aldehydes and ketones, resulting in excellent yields (88 – 99 %) of the desired valuable boronic acids **6a-n**, Table 2. Exceptional tolerance of sensitive functional groups and chemoselectivity was displayed by the catalyst, including electron withdrawing groups (**6a-d**, Table 2), as well as electron donating, coupled with steric hindrance **6e-f**, Table 2. Hydroboration of aliphatic substrate **6g** was also achieved, reaching 94% in a moderate two hours. Acetophenone derivatives (**6h-6l**, Table 2) underwent hydroboration albeit reaction times were generally

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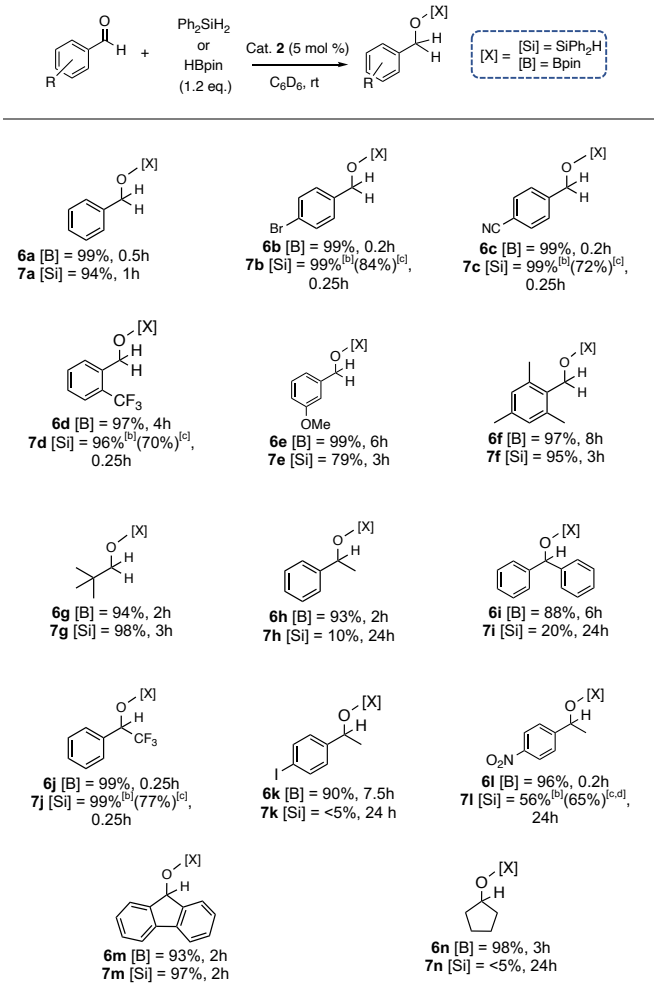
longer than for aldehydes. Exceptions were electron deficient substrates **5j** and **5l,** where greater than 95% conversion was obtained in less than 15 minutes. Aliphatic and aromatic cyclic systems also work well (**6m** and **6n**, Table 2) in this catalytic system. To the best of our knowledge this is the first report of a silver catalyzed hydroboration of aldehydes and ketones.

Encouraged by our findings we extended our study to the hydrosilylation of carbonyls, employing Ph_2SiH_2 due to optimum selectivity's and conversion times noted (see ESI).[23] The same range of aromatic substituted benzaldehydes bearing various functional groups were investigated (Table 2) which underwent successful hydrosilylation. Monitoring by ^{1}H NMR spectroscopy, revealed more than one species was forming for products **7b**, **7c**, **7d**, **7j** (Table 2), hence these were isolated (ESI) to determine the yield of desired alcohol product.

Table 2. Hydroboration and hydrosilylation of carbonyls using HBpin or Ph_2SiH_2 catalyzed by **2**.[a]

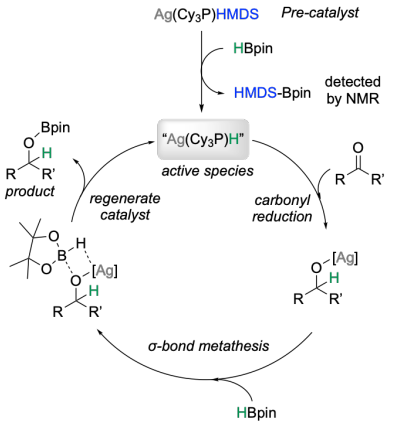


[a] Reaction conditions: substrate (1 mmol), Ph_2SiH_2 or HBpin (1.2-1.5 mmol), 5 mol% [$Ag(Cy_3P)(HMDS)$] (**2**) and 10 mol% internal standard hexamethylcyclotrisiloxane in C_6D_6 at room temperature. [b] Conversion of substrate. [c] Yield of corresponding alcohol product. [d] Reaction quenched after 30 h.

Benzaldehyde (**7a**) underwent hydrosilylation employing conditions comparable with typical coinage metal catalysts.[30–32] Noteworthy, is the efficient hydrosilylation of *tert*-butylaldehyde in 3 hours at room temperature, improving upon limitations of an earlier reported protocol by Stradiotto which required 24 hours at 70 °C to reach 48 % of silyl ether product **7g**.[10] Moving to slightly more challenging ketone substrates, the 'pre-catalyst' highlighted its boundaries. Substrates, acetophenone and benzophenone, displayed low conversions even after 24 hours monitoring by ^{1}H NMR spectroscopy (Table 2). This is unsurprising when compared with a recently reported silver(I) system ($AgPF_6$:Ligand:Base) that observed negligible conversion after 24 hours at 100 °C[11] and a copper(I) catalyst requiring 44h to reach full conversion of benzophenone.[30] Replacing the methyl with a trifluoromethyl group, dramatically enhanced reactivity (**7j**) whilst, introducing a *p*-NO_2 group facilitated successful hydrosilylation reactivity. Polycyclic aromatic hydrocarbon, 9-fluorenone, showed quantitative formation of the corresponding silyl ether **7m**. However, conversion of an aliphatic cyclic species **7n** was negligible.

In contrast to complex silver systems that require additional ligands, metal(s) or base(s) to achieve catalytic activity, our simple pre-catalyst is molecularly well defined. To gain mechanistic insights and to understand the active catalytic species, we performed a series of stoichiometric control experiments. Precedence in the literature suggests a metal hydride pathway, however recent studies of silver catalyzed hydroboration of olefins postulated a radical based mechanism.[13,14]

To determine the first step in the cycle, generally accepted to be the formation of the 'active catalyst', the stoichiometric reaction of [$Ag(Cy_3P)(HMDS)$] (**2**) and HBpin in an equimolar ratio was performed at room temperature in C_6D_6. After 2 hours ^{1}H and ^{11}B NMR spectra indicated the complete formation of HMDS-Bpin with a singlet resonance corresponding to the newly formed B-N bond in the ^{11}B NMR at δ 25.8 ppm. Interestingly, this resonance can be observed in our catalytic measurements (Figure S55). This outcome is in keeping with both metathesis and radical pathways, arising from either the by-product of forming of a 'AgH' containing species, (Scheme 2) or as a result of generating a $^{\cdot}$Bpin radical from homolytic cleavage of HBpin (see ESI). For clarity, a control reaction was performed employing standard conditions in the presence of a radical scavenger TEMPO. This did not influence the outcome of the reaction, with ^{11}B NMR showing full conversion to the desired product, along with an extremely broad ^{1}H NMR spectrum. This would support a dominant σ-bond metathesis pathway for hydroboration, albeit a secondary radical pathway must not be overlooked.



Scheme 2. Proposed catalytic mechanism for hydroboration of carbonyls by silver(I) amides via a silver(I) hydride intermediate.

We propose our molecular (Cy_3P)-solvated silver(I) amide 'pre-catalysts' acts as a support for a transient catalytically active 'AgH' species formed upon reaction with HBpin (Scheme 2). The carbonyl then inserts the silver(I) hydride yielding a silver alkoxide intermediate that undergoes σ-bond metathesis via a transition state with HBpin to yield the desired alkoxyboronate ester product and regenerate the catalyst.

Performing the same control study for the hydrosilylation mechanism it was found that, the presence of the radical scavenger TEMPO hinders reactivity, extending the reaction time. This would suggest that both a hydride and radical pathway are feasible, with reaction conditions determining the optimum route.

In conclusion, we have fully characterized three rare monomeric silver(I) amides in the solid and solution state and explored their preliminary catalytic abilities, taking the first steps in catching up with other coinage metal based catalytic systems. This study represents the first hydroboration of carbonyls, employing a silver(I) amide pre-catalyst. The advantageous mild conditions used for hydroboration and hydrosilylation are competitive in the catalytic arena, with non-activated ketones remaining a challenge. Mechanistically, our silver(I) amide pre-catalyst is proposed to proceed predominantly via a traditional σ-bond metathesis pathway, for hydroboration reactions, although further studies are ongoing to elucidate the mechanism in more detail.

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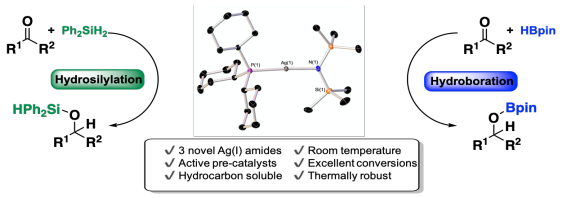

The Allure of Silver: Utilizing monomeric silver(I) amides as molecular defined pre-catalysts, the first silver mediated hydroboration of a range of aldehydes and ketones has been achieved. Catalytic hydrosilylation of carbonyls has also shown success employing Ph_2SiH_2. Both mechanisms are proposed to proceed via a 'AgH' intermediate.

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