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Communication

Access to silver-NHC complexes from soluble silver species in aqueous or ethanolic ammonia



Clémentine Gibard ^{a, 1}, Kévin Fauché ^{a, 1}, Régis Guillot ^b, Laurent Jouffret ^a, Mounir Traïkia ^a, Arnaud Gautier ^a, Federico Cisnetti ^{a, *}

^a Université Clermont Auvergne, CNRS, Sigma Clermont, ICCF, F-63000 Clermont-Ferrand, France
 ^b Institut de Chimie Moléculaire et des Matériaux d'Orsay, Bât. 420, Université Paris-Sud, UMR CNRS 8182, F-91405 Orsay Cedex, France

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ABSTRACT

In this communication, we report the use of aqueous ammonia as original conditions for the metalation of imidazol(in)ium ligands. This reaction, performed in homogenous conditions *via* a soluble silverammine complex is a rapid, scalable and often efficient access to silver-NHC complexes. Moreover, modification of the reported reaction conditions allowed the preparation of unprecedented heteroleptic NHC-Ag-phosphine in case of bulky IPr and SIPr ligands.

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1. Introduction

The preparation of silver(I) complexes of *N*-heterocyclic carbenes (NHC) is a very common step to access NHC complexes with other metallic elements *via* transmetalation [1,2]. Additionally, silver(I)-NHC complexes display intrinsic interests in catalysis either as thermolabile precursors of free carbenes [3] or as active species containing {NHC-Ag} moieties [4–10]. Moreover, silver-NHC complexes are bioactive species, displaying antibacterial properties or cytotoxicity towards cancer cells [11–17]. For all these purposes, the efficiency of the synthetic conditions for the metal-NHC complexes is of paramount importance [18].

For the preparation of silver-NHC complexes, the so-called Ag₂O route (usually performed in organic aprotic solvents) may now be considered as a classical method. Silver(I) oxide acts as base and metal source [2]. Its advantages include the use of stable reactants, the lack of special precautions regarding exclusion of moisture and air, and (in most cases) generally high yields in reasonable reaction times. Despite being successful in most cases, some limitations may arise with some problematic systems [2]. It has been highlighted

that $[Ag(NHC)_2]^+$ complexes with non-coordinating counter-ions are difficult to prepare by this method [19]. Moreover, it has been shown that NHC ligands may yield, either heteroleptic [Ag(NHC)X] or homoleptic [Ag(NHC)₂]⁺ complexes with a variety of counterions, depending on the experimental conditions both for conventional [20] or functionalized [21,22] NHC ligands. Although the metalation by Ag₂O has been modeled at the molecular level [23], one of its obvious characteristics is its heterogeneity. While this is an advantage to separate the excess of silver reactant, the heterogeneity of the reaction may also account for reluctant reactions and for the difficulty to modulate the reaction outcome by variation of experimental conditions. Thieuleux et al. noted that using $Ag(OC(CF_3)_3)$ – a preformed soluble silver metalating agent – may be an asset, especially if the reaction is to be performed with heterogenized azolium salts [24]. Other alternative preparations of silver-NHC complexes have been reported. Gimeno et al. described a procedure using AgNO₃ as the silver source with a mild base – K₂CO₃ – giving only heteroleptic complexes with very high yields [25]. Cazin et al. reported the synthesis of [AgCl(NHC)] type complexes by refluxing the imidazolium chloride and Ag₂O in water for 24 h [26]. Zhu et al. described the efficient (but high temperature) preparation of silver-NHC complexes in unconventional conditions (K₂CO₃/3-chloropyridine) [27]. As an alternative to classical solution conditions, protocols using ball-milling [19] or microwave irradiation [28,29] have been recently reported. Overall, alternative



^{*} Corresponding author.

E-mail address: federico.cisnetti@uca.fr (F. Cisnetti).

¹ These authors contributed equally to this work.

methods to prepare silver-NHC complexes remain scarce.

We report herein the use of ammonia as modifying reagent in Ag_2O metalations performed in aerobic aqueous or ethanolic conditions. A similar protocol has already proven its interest for the preparation of copper(I)-NHC complexes [30]. The efficient and scalable preparation of several widely used metal-NHC complexes in aqueous aerobic medium is reported. Interestingly, these conditions inspired by classical aqueous coordination chemistry allow in some cases the determination of the reaction outcome by the modulation of the experimental conditions. Also, we discovered that $[Ag((S)IPr)(NH_3)]^+$ are stable, soluble species in ethanolic solution and that their reactivity may be harnessed to prepare $[Ag((S)IPr)(phosphine)]^+$ complexes in very practical one-pot conditions.

2. Experimental

General protocol for the synthesis of Ag-NHC complexes from azolium chlorides: conditions 1), NHC.HCl (1.0 mmol) was dissolved/suspended in 5 mL water. Tollens' reagent was prepared by mixing silver(I) oxide (127 mg, 0.548 mmol) and concentrated ammonia (0.73 mL, 15.3 mol/L, 11 mmol) until complete dissolution. The reagent was diluted with *quantum satis* water for a final volume of 5 mL. An instantaneous precipitation was observed. After 30 min at RT, the white solid was filtered and washed with water. Conditions 2), NHC.HCl (1.0 mmol) was dissolved/suspended in 10 mL of water or ethanol. Silver(I) oxide (127 mg, 0.549 mmol) and ammonia (0.65 mL, 15.3 mol/L, 9.9 mmol) were added. After 30–200 min at RT, the white solid was isolated by filtration and washed with water (IMes, SIMes) or ethanol (IPr, SIPr).

General protocol for the synthesis of Ag-NHC complexes from azolium hexafluorophosphates: NHC.HPF₆ (1.0 mmol) was suspended in 5 mL ethanol. Silver(I) oxide (64.3 mg, 0.277 mmol) and ammonia (0.65 mL, 15.3 mol/L, 9.9 mmol) were added. The mixture was stirred at RT during 30 min and filtered. The white solid was washed with cold ethanol.

General protocol for the synthesis of heteroleptic [Ag((S)IPr) (phosphine)](PF₆) complexes: (S)IPr.HPF₆ (1.0 mmol) was suspended in 10 mL absolute ethanol. Silver(I) oxide (116 mg, 0.50 mmol), followed by aqueous ammonia (0.65 mL, 15.3 mol/L, 9.9 mmol) were added and the mixture was treated in an ultrasound bath until total dissolution of the product (approximately 5 min). The phosphine (0.95 mmol) was added. The mixture was treated with ultrasounds during 10 min and stirred at room temperature for a further 30 min. It was filtered and the resulting white solid was washed with ethanol then with ether.

3. Results and discussions

As a first set of experiments, we decided to investigate the scope and limitations of the use of ammonia as basic and complexing reagent in silver metalation. Hence, we sought to prepare heteroleptic [AgCl(NHC)] complexes (NHC = IPr, SIPr, IMes, SIMes) and homoleptic [Ag(NHC)₂]⁺ complexes (NHC = IMes, SIMes) as PF₆ salts.

Initially, by analogy to our previously reported copper metalation protocol (aqueous ammonia and copper(I) chloride in water as metalation medium) [30], silver chloride was considered as the metal source to prepare [AgCl(NHC)] complexes. The desired complexes were indeed obtained in these conditions, albeit in very limited conversions (~30%) after several hours. This could be rationalized by considering that solubility of AgCl is ~25 times lower than the one of CuCl [31]. As the efficient formation of a soluble metalating agent is crucial in our approach, we decided to prepare [Ag(NH₃)₂]⁺ in solution. This may be achieved using two protocols, 1) the preparation of a solution corresponding to the

classical Tollens' reagent (reactive dissolution of Ag₂O [32] with excess ammonia in water) and its addition to a solution of the azolium salt and 2) the addition of ammonia to a suspension of Ag₂O in a solution of the azolium salt. Noteworthy, silver(I) ammonia complexes – chiefly $[Ag(NH_3)_2]^+$ – are not oxidizable. Hence, all syntheses were performed without any experimental precaution under aerobic conditions. (no improvement of the isolated vields was observed if the reactions were performed under argon atmosphere). The preparation of heteroleptic complexes [AgCl(NHC)] (NHC = IPr, SIPr) proceeded using either conditions (Scheme 1, Table 1). In all cases, silver was introduced in nearly stoichiometric proportions (1.1 equiv.). With IPr and SIPr, the reaction was performed in water and ethanol in both conditions (Table 1, entries 1–6). For conditions 2, longer reaction times were necessary, as detected visually by the disappearance of black Ag₂O (entries 2,3,5,6). Although the desired [AgCl(NHC)] complexes were recovered in all cases, the use of water in conditions 2 resulted in lower yields in some cases, most probably due to solubility issues, (entries 2 and 5). As unreacted azolium salts were removed washing the recovered solids, this reduced yield is indicative of limited conversion. Solubility issues could be mitigated by using ethanol as solvent (entries 3 and 6) [33]. Finally, to check the scalability of the present protocol, entries 1 and 6 were repeated at the 10 mmol scale (~5 g of starting material). The procedure demonstrated to be easily scalable as the same yields of products were obtained as in the mmol scale. For IMes and SIMes (entries 7-10), the starting material experienced a full conversion, but complexes were isolated as mixture of homoleptic [Ag(NH-C)₂](AgCl₂) and heteroleptic [AgCl(NHC)] species, with the former being predominant, whatever the conditions. It is well-known that silver complexes may undergo ligand redistribution equilibria [34], and the use of a solvent with a high dielectric constant may favor the cationic homoleptic complex. The obtention of a mixture of species was also observed for the metalation of the same azolium salts with copper in aqueous ammonia [30], although in the latter case heteroleptic complexes predominated.

The reported reaction times were dependent on solubility issues rather than chemical reactivity. Indeed, a modification of the protocol in which both partners were soluble before reaction (IPr.HCl in ethanol and Tollens reagent in water) resulted in reactions proceeding apparently instantaneously upon mixing both solutions (Video 1). However, conditions 1 or 2 were more convenient from a practical point of view [35].

Supplementary video related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2017.04.009.

The propensity of IMes and SIMes to form homoleptic complexes was turned into a facile synthetic procedure (Scheme 2 and Table 2). Due to the insolubility of azolium salt starting materials in water (hexafluorophosphate as the counter-ion), ethanol and conditions 2 were selected. Again, silver(I) was introduced in very slight excess (0.275 equiv. Ag₂O). NMR analysis indicated complete conversions within 30 min following Ag₂O dissolution. At this point, the complexes could be isolated by filtration as [Ag(NHC)₂](PF₆) salts.

To further exemplify the present method, a new complex



Scheme 1. Preparation of silver-NHC complexes from azolium chlorides. Ar = dipp, Mes.

Table 1

Preparation of silver complexes with IPr, SIPr, IMes and SIMes ligands: conditions 1 (preformed Tollens' reagent) or 2 (*in situ* addition of ammonia).

Entry	Ligand	Cond.	Solvent	Time (min)	Isolated yield
1	IPr	1	H ₂ O	30	84% ^a
2	IPr	2	H ₂ O	200	51% ^a
3	IPr	2	EtOH	200	82% ^a
4	SIPr	1	H ₂ O	30	91% ^a
5	SIPr	2	H ₂ O	200	57% ^a
6	SIPr	2	EtOH	200	92% ^a
7	IMes	1	H ₂ O	30	81% (36:64) ^b
8	IMes	2	H ₂ O	30	93% (24:76) ^b
9	SIMes	1	H ₂ O	30	92% (29:71) ^b
10	SIMes	2	H ₂ O	30	79% (46:54) ^b

^a 100% heteroleptic [AgCl(NHC)] complex.

^b Obtained as a mixture of heteroleptic and homoleptic complexes.





Table 2

Preparation of homoleptic silver complexes with IMes and SIMes ligand (isolated as ${\rm PF}_6$ salts).

Entry	Ligand	Cond.	Solvent	Time (min)	Isolated yield
1	IMes	1	EtOH	30	97%
2	IMes	2	EtOH	30	97%
3	SIMes	1	EtOH	30	88%
4	SIMes	2	EtOH	30	97%

containing a 1,2,4-triazol-3-ylidene was prepared. The synthesis of a 1,2,4-triazolium hexafluorophosphate (triaz.HF₆) was made easier in comparison to the method reported by Rovis et al. [36,37] (see ESI). This starting material was used to prepare a homoleptic complex in 94% yield (Scheme 2) adapting directly the conditions described for IMes and SIMes (30 min reaction time). For the sake of comparison, 1,2,4- triazol-5-ylidene complexes of silver have been obtained previously using conventional procedures (Ag₂O in dichloromethane) which required lengthy reaction times (12–48 h) [20,38]. X-ray diffracting crystals of this compound were obtained. Although the crystals displayed twinning, this was handled as described in the supporting information and the structure depicted in Fig. 1 was obtained.

When IPr.HPF₆ and SIPr.HPF₆ were considered for the preparation of homoleptic complexes, only unreacted azolium salts were isolated by filtration. ¹H-NMR analysis of a sample of the reaction medium afforded interesting information. In addition to the signals corresponding to the azolium salt, another set of signals with approximately the same integrations was detected (Fig. S7). We hypothesize that a soluble [Ag(NHC)(NH₃)]⁺ (NHC = IPr, SIPr) species may be stable in solution and not reactive in the conditions



Fig. 1. Thermal ellipsoid plot (50% probability) of the cationic moiety of $[Ag(triaz)_2]^+$ deduced from X-ray structural data (PF₆⁻ anion and hydrogen atoms omitted for the sake of clarity). Key structural parameter: Ag-C = 2.0872 (11) Å.²¹

of the experiment towards the formation of a homoleptic complex. This may be connected to our previous hypothesis of the existence of a similar $[Cu(IPr)(NH_3)]^+$ as an intermediate in the synthesis of a $[Cu_2(IPr)_2 (\mu-OH)]^+$ dinuclear complex [39]. In the case of IPr, we decided to perform detailed experiments to prove this hypothesis. First, as the putative $[Ag(IPr)(NH_3)]^+$ species is soluble in ethanol, we precipitated it by addition of diethyl ether and *n*-pentane in the medium. We obtained a material containing this species at > 95%purity (with a trace of homoleptic bis-NHC complex as contaminant). The IR spectrum of this solid shows a strong PF₆ absorption at 830 cm⁻¹ as well as two bands at high wavenumbers (3394 and 3312 cm⁻¹). The IR data is consistent with a [Ag(IPr)(NH₃)](PF₆) composition. Although we were not able to obtain crystals suitable for X-ray diffraction, the assumption that the compound possesses a 1:1 metal-NHC ratio is strongly supported spectroscopically by the ${}^{1}J_{Ag-C}$ coupling constants deduced from the ${}^{13}C$ NMR spectrum (ESI) [40]. The values (265 Hz and 229 Hz) confirm that only one NHC ligand is bound to silver. Also, in the ¹H NMR spectrum, a signal displaying an integral of 3H is observed at δ ~3 ppm (concentration and temperature sensitive signal) which could be attributed to the ammonia protons (a similar signal was present for copper [39]). IR and ¹H NMR data are fully consistent with a previous example of a well-defined ligand-silver-ammine complex [41].

To further proof the mononuclear nature of this species, a mixture corresponding to the outcome of the metalation reaction of IPr.HPF₆ described in Fig. S7 was subjected to a diffusion ordered 2D NMR (DOSY) analysis [42]. This sample contained IPr.H⁺, minor amounts of [Ag(IPr)₂]⁺ and the putative [Ag(IPr)(NH₃)]⁺ species in an approximate ~1.63:0.12:1 ratio. The diffusion coefficients as determined from the DOSY NMR data (Fig. S12) were 1,82. 10^{-10} m² s⁻¹, 1,54. 10^{-10} m² s⁻¹ and 1,94. 10^{-10} m² s⁻¹, respectively. As the measured diffusion coefficient of the latter species is intermediate between the one of the corresponding azolium cation and homoleptic complex, the formation of higher nuclearity complexes may be excluded, and the assignment of the observed set of signals to [Ag(IPr)(NH₃)]⁺ is confirmed.

Interestingly, prolonged heating in refluxing water resulted in the obtention of a solid consisting essentially in $[Ag(IPr)_2](PF_6)$ [43] along with a black insoluble solid (likely Ag₂O). The homoleptic complex could be obtained as monocrystals suitable for X-ray diffraction. This structure is very similar to the previously reported SbF₆ salt of the same complex [44] (Fig. S39, see ESI for details). In stark contrast, the same reaction performed with NHC = SIPr resulted – even in anoxic conditions – in the oxidative degradation of the NHC as an urea along with the formation of a silver mirror. Hence, for the obtention of a fairly stable $[Ag(NHC)(NH_3)]^+$ species in solution, the imidazol-2-ylidene core seems to be required.



Scheme 3. Preparation of heteroleptic NHC-silver-phosphine complexes (R = Cy, Ph, o-tolyl).

Table 3 Isolated yield of the hexafluorophosphates salts of [Ag(NHC)(Phosphine)]⁺.

NHC	Phosphine	Isolated yield
IPr	PPh ₃	89%
SIPr	PPh ₃	87%
IPr	PCy ₃	94%
SIPr	PCy ₃	66%
IPr	P(o-tol) ₃	88%
SIPr	P(o-tol) ₃	59%



Fig. 2. Thermal ellipsoid plot (50% probability) of the cationic moiety of $[Ag(IPr)(PCy)_3]^+$ deduced from X-ray structural data (PF₆⁻ anion, solvent molecule and hydrogen atoms omitted for the sake of clarity). Key structural parameters: Ag-C = 2.119 (8); Ag-P = 2.344 (2) Å; P-Ag-C = 177.34 (19)°.

The relative stability of $[Ag(NHC)(NH_3)]^+$ prompted us to investigate whether it could be used to prepare heteroleptic NHC-Ag-phosphine complexes. Indeed, unlike for their gold and copper congeners [45-47], there is a lack of reliable methods to prepare these potentially useful compounds. To exemplify this reaction, we prepared six $[Ag(NHC)(PR_3)]^+$ complexes (NHC = IPr, SIPr, R = Cy, Ph, o-tolyl) as hexafluorophosphate salts (Scheme 3). In optimized conditions, the addition of 0.95 equiv. of the phosphine ligand to a solution of $[Ag(NHC)(NH_3)]^+$ prepared as above afforded the heteroleptic NHC-Ag-phosphine complexes. These were isolated as hexafluorophosphate salts by simple filtration after 30 min reaction at room temperature. Isolated yields of the complexes are reported in Table 3. All compounds were characterized by ¹H, ¹³C and ³¹P NMR spectroscopy, high resolution mass spectrometry and elemental analysis (supporting information).

For $[Ag(IPr)(PCy_3)](PF_6)$ X-ray diffracting (albeit twinned) crystals were obtained. The structure was resolved as described in the SI (See Fig. 2).

4. Conclusions

We have reported herein a variant of silver oxide-based

metalation proceeding in aqueous conditions. By conducting the reaction with a dissolved silver reagent, the reactions were performed akin to classical aqueous coordination chemistry with very short reaction times and predictable outcomes. In the most favorable cases, the crudes proved to be pure NHC complexes, thus removing the need of purification. This protocol may be helpful for chemists working in the various areas where silver-NHC complexes are considered. Moreover, for the bulky imidazol-2-ylidene (S)IPr ligand, the presence of a relatively stable [Ag ((S)IPr)NH₃]⁺ intermediate could be harnessed to prepare unprecedented [Ag((S) IPr)(PR₃)]⁺ complexes. Finally, perspectives of this work may arise in the area of metalation of azolium salts used in (nano)materials functionalization [24,48,49] where the use of soluble metalating agents is critical.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2017.04.009.

Abbreviations

dipp	2,6-diisopropylphenyl
Mes	mesityl
IPr	<i>N,N'</i> -Bis(2,6-diisopropylphenyl)imidazol-2-ylidene
SIPr	<i>N,N'</i> -Bis(2,6-diisopropylphenyl)imidazolin-2-ylidene
IMes	<i>N,N'</i> -Bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene
SIMes	2-Phenyl-6,7-dihydro-5H-pyrrolo[2,1-c][1,2,4]triazol-3-
Triaz	ylidene

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² CCDC 1518573, 1519227 and 1519228 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/ Community/Requestastructure.

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