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# Approaching monocoordination at a silver(I) cation†

Matthew M. D. Roy, Michael J. Ferguson, Robert McDonald and Eric Rivard *

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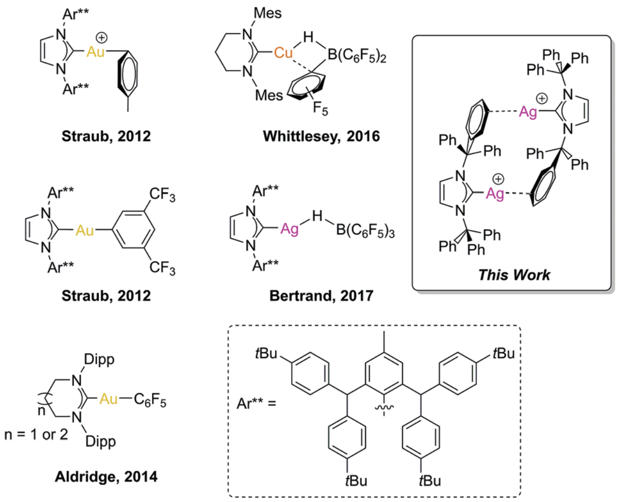
**The recently reported bulky N-heterocyclic carbene ITr (ITr = [(HCNCPh$_3$)$_2$C:]) was found to stabilize low-coordinate Ag(I) environments. These electrophilic species were crystallographically identified as the weak solvates [(ITr)Ag(sol)]$^+$ (sol = PhF, MesH or CH$_2$Cl$_2$) and as a solvent-free dimer [(ITr)Ag]$_2$$^{2+}$. The highly electrophilic nature of the [(ITr)Ag]$^+$ cation was further demonstrated by the calculation of a very high methyl ion affinity (MIA) and the synthesis of [(ITr)Ag(PCO)] which features substantial side-on electron donation from a P–C π bond to Ag.**



Scheme 1 Examples of NHC-supported group 11 species generated during the attempted syntheses of monocoordinate [NHC–M]$^+$ compounds.

Group 11 elements in +1 oxidation states are widely used as catalysts to activate carbon–carbon multiple bonds.[1] In many instances the active species in these transformations is presumed to be a monocoordinate ligand-stabilized metal cation, [L–M]$^+$ (L = phosphines or N-heterocyclic carbenes (NHCs); M = Cu, Ag or Au),[1d] yet truly monocoordinate coinage metal cations have not yet been observed. Recently, several research groups have attempted to synthesize monocoordinate cations of the general form [NHC–M]$^+$ supported by very hindered NHCs such as IPr** [IPr** = (HCNAr**)$_2$C:] (Scheme 1). Arguably, the closest approach to monocoordination amongst the coinage metals was achieved by Straub and co-workers with their toluene adduct [(IPr**)Au(PhMe)]$^+$, prepared from [(IPr**)AuCl] and Na[SbF$_6$].[2] Replacement of the [SbF$_6$]$^-$ counterion by the less coordinating [BAr$^F$$_4$]$^-$ anion (Ar$^F$ = 3,5-(F$_3$C)$_2$C$_6$H$_3$) led to Ar$^F$ abstraction by gold to yield the Au(I) aryl complex [(IPr**)Au(Ar$^F$)].[3] Attempts to obtain low-coordinate M(I) species *via* hydride abstraction from metastable [(NHC)MH]$_{1,2}$ complexes afforded the aryl gold species [(NHC)Au(C$_6$F$_5$)]$^4$ or hydride-bridged products such as [(NHC)M(μ-H)B(C$_6$F$_5$)$_3$] where M = copper[5] and silver.[6] The electrophilic nature of silver(I) ions has also been demonstrated by the coordination of the unsaturated substrates ethylene, acetylene and carbon monoxide.[7] Furthermore, the large size of Ag(I) often leads to coordination of multiple NHC equivalents (*i.e.* in [(NHC)$_2$Ag][AgX$_2$] or [(NHC)$_2$Ag$_2$(μ-X)]X; X = halide or triflate) rather than simple [(NHC)Ag-X] adducts.[8]

Recently our group has reported the synthesis of the extremely bulky NHC, ITr (ITr = [(HCNCPh$_3$)$_2$C:]), which was used to isolate low-valent main group element-based cations.[9] We now report the formation of various Ag(I) complexes which show coordination behavior that approaches monocoordination, as evidenced by the identification of the weakly associated solvates [(ITr)Ag(sol)]$^+$ (PhF, MesH and CH$_2$Cl$_2$) and the dicationic dimer [(ITr)Ag]$_2$$^{2+}$ in the solid state; the latter represents the closest crystallographic observation of a highly elusive monocoordinate [L–M]$^+$ (M = Cu, Ag, or Au) fragment to date. Additionally, [(ITr)Ag(PCO)] was synthesized which exhibits η$^2$-PCO coordination to silver *via* a P–C π-bond, in line with the high electrophilicity of the [(ITr)Ag]$^+$ unit.

Looking to form a suitable [(ITr)AgX] precursor for our studies, the free ligand ITr was combined with AgOTf (OTf = O$_3$SCF$_3$$^-$) in

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*Department of Chemistry, University of Alberta, 11227 Saskatchewan Drive, Edmonton, Alberta, T6G 2G2, Canada. E-mail: erivard@ualberta.ca; Web: http://www.chem.ualberta.ca/~erivard/*

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toluene to yield [(ITr)Ag(OTf)] (**1**) as an analytically pure solid in 93% yield; this compound can be stored under ambient lighting (under $N_2$) for weeks without noticeable decomposition [mp = 187 °C (decomp.)], thus highlighting the stabilizing influence of the ITr ligand. X-ray crystallography (Fig. S1, ESI†)[10] showed the presence of a Ag–OTf interaction [Ag–O bond length = 2.172(4) Å; *cf.* 2.137(2) Å in (SIPr)AgOTf;[8b] SIPr = $(H_2CNDipp)_2C$:] and a significantly distorted $C_{NHC}$–Ag–OTf angle of 162.31(13)°, similar to what is found in the Cu(I) halide complex [(ITr)CuI] [165.91(9)°].[9]

With [(ITr)Ag(OTf)] (**1**) in hand, we looked to abstract the triflate to form the potentially one-coordinate $[(ITr)Ag]^+$ cation (**2**). When **1** and Na[BAr$^F_4$] were combined in fluorobenzene, the yellow crystalline fluorobenzene adduct, [(ITr)Ag(η$^2$-PhF)][BAr$^F_4$] (**3**) was formed (Fig. 1). The η$^2$-coordination of $C_6H_5F$ to Ag(I) shows long Ag–C contacts [2.381(4) and 2.435(4) Å] which compare well with known Ag–$C_6H_6$ adducts[11] and are significantly longer than the coordinative $C_{NHC}$–Ag bond in **3** [2.115(3) Å]. Additionally, we estimated the affinity of $[(NHC)Ag]^+$ for fluorobenzene by determination of the enthalpy of the following reaction: $[(NHC)Ag]^+ + PhF \rightarrow [(NHC)Ag(PhF)]^+$ ($\Delta_rH = -111$ kJ mol$^{-1}$) using a truncated model for the NHC.[10] When the reaction between **1** and Na[BAr$^F_4$] was conducted in mesitylene, the corresponding mesitylene adduct [(ITr)Ag(η$^3$-MesH)][BAr$^F_4$] (**4**) was formed (Fig. S2, ESI†)[10] which exhibits similarly long Ag–C(arene) interactions in the range of 2.322(4)–2.719(5) Å.[10]

The attempted synthesis of $[(ITr)Ag]^+$ by combining **1** and Na[BAr$^F_4$] in dichloromethane gave some very interesting results. $^{19}F\{^1H\}$ and $^{11}B\{^1H\}$ NMR spectroscopy of the soluble reaction product revealed that the [BAr$^F_4$]$^-$ anion remained intact, which was not the case when [(IPr**)AuCl] was combined with Na[BAr$^F_4$] in $CH_2Cl_2$ (*vide supra*).[3] Repeated crystallization attempts yielded yellow block-like crystals which proved to be the $CH_2Cl_2$ adduct of **2**, [(ITr)Ag($CH_2Cl_2$)][BAr$^F_4$] (**5**) (Fig. S3, ESI†)[10] (co-crystallized with 30% of the 1 : 1 toluene adduct [(ITr)Ag(toluene)][BAr$^F_4$]). In the same product mixtures, yellow crystalline rods were also always present, which were identified as the weakly associated dimer of the target monocoordinate silver(I) cation [(ITr)Ag]$_2$[BAr$^F_4$]$_2$ (**6**) (Fig. 2). When mixtures of **5** and **6** were re-dissolved in $CH_2Cl_2$ and the solvent removed, elemental analysis of the final product was consistent with a solvent-free species "[(ITr)Ag][BAr$^F_4$]". The bonding situation in **6** is reminiscent of the previously observed terphenyl-substituted copper(I) dimer, $[(2,6\text{-}Mes_2H_3C_6)Cu]_2$.[1g]

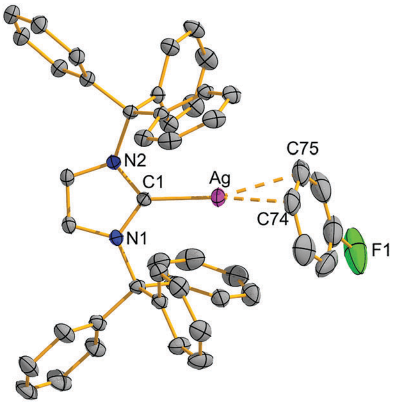


Fig. 1 Molecular structure of [(ITr)Ag(PhF)][BAr$^F_4$] (**3**) with thermal ellipsoids plotted at the 30% probability level. All hydrogen atoms and the [BAr$^F_4$]$^-$ counterion have been omitted for clarity. Selected bond lengths [Å] and angles [°]: C1–Ag 2.115(3), Ag–C74 2.381(4), Ag–C75 2.435(4); C1–Ag–C74 159.33(16), C1–Ag–C75 163.92(16).

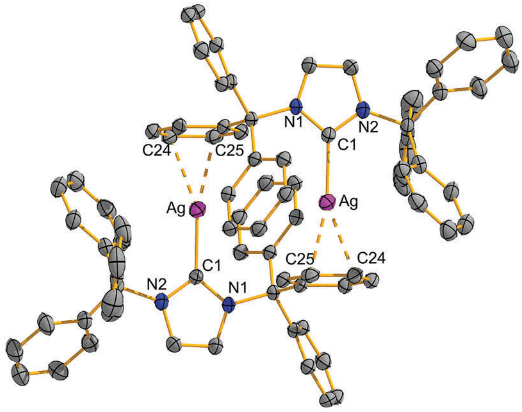
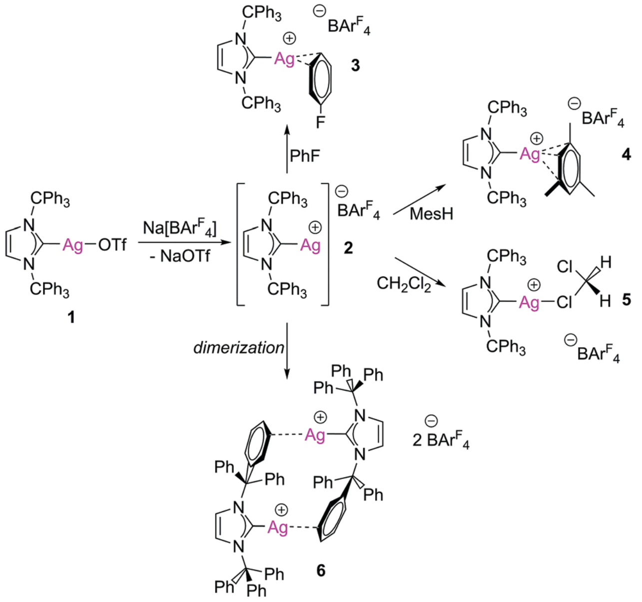


Fig. 2 Molecular structure of [(ITr)Ag]$_2$[BAr$^F_4$]$_2$ (**6**) with thermal ellipsoids plotted at the 30% probability level. All hydrogen atoms and the two [BAr$^F_4$]$^-$ counterions have been omitted for clarity. Selected bond lengths [Å] and angles [°]: C1–Ag 2.110(4), Ag–C24 2.444(4), Ag–C25 2.348(4); C1–Ag–C24 157.96(15), C1–Ag–C25 168.04(15).

The dimeric dication [(ITr)Ag]$_2^{2+}$ unit in **6** arises from a set of aryl–Ag(I) η$^2$-interactions [2.444(4) and 2.348(4) Å] involving ligand-containing –$CPh_3$ groups of a neighbouring $[(ITr)Ag]^+$ cation (Fig. 2); these Ag–arene distances are similar to those in compounds **3** and **4** [*ca.* 2.32–2.72 Å]. The formation of a weakly associated dimer motif in **6** leads to effective encapsulation of two electrophilic Ag(I) centers within a hydrophobic core provided by the –$CPh_3$ groups.

The NMR spectra of isolated crystals of compounds **3**–**6** in $C_6D_6$ were each consistent with the formation of the same [(ITr)Ag($C_6D_6$)][BAr$^F_4$] adduct, with release of free solvate (PhF, MesH and $CH_2Cl_2$) in the case of compounds **3**–**5**. This indicates the labile nature of the secondary Ag(I)–arene interactions in solution, in line with the high degree of steric protection offered by the ITr ligand (Scheme 2).

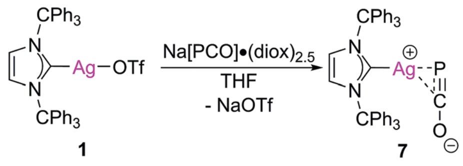
Natural population analysis (NPA) of $[(ITr)Ag]^+$ (**2**) revealed a high degree of positive charge on silver (+0.71), consistent with substantial electrophilic character.[10] We also attempted to quantify the Lewis acidity of **2** using the Childs method[12] by coordination of crotonaldehyde.[10] The chemical shift difference between the H3 proton of free and coordinated crotonaldehyde ($\Delta\delta$ = 0.08 ppm) compares well with the relatively weak Lewis acids $BPh_3$ ($\Delta\delta$ = 0.05 ppm) and $B(OPh_3)$ ($\Delta\delta$ = 0.03 ppm) but shows a weaker interaction compared with $B(C_6F_5)_3$ ($\Delta\delta$ = 1.05 ppm).[12b] Given that strong coordination of crotonaldehyde to **2** may be limited by the bulky nature of ITr and the soft character of the Ag(I) center, we decided to investigate the methyl ion affinity (MIA) of this species computationally.[10,13] Using a truncated model for ITr, the overall reaction: $[NHC\text{–}Ag]^+ + :CH_3^- \rightarrow [NHC\text{–}Ag\text{–}CH_3]$ ($\Delta_rH$ = –MIA) revealed an MIA of 780 kJ mol$^{-1}$. Notably, the $[(NHC)Ag]^+$ fragment has an affinity for the methyl



Scheme 2 Formation of solvent adducts **3–5** of the parent $[(\text{ITr})\text{Ag}]^+$ (**2**) and its dimerization to form **6**.

anion on the same order of magnitude as $\text{SiMe}_3^+$ (1000 kJ mol$^{-1}$), $[\text{MeZn}]^+$ (1025 kJ mol$^{-1}$), $\text{Ph}_3\text{C}^+$ (836 kJ mol$^{-1}$) and the recently reported tin cation $[\text{CpSn}]^+$ (765 kJ mol$^{-1}$).[10,13] Interestingly, $[(\text{NHC})\text{Ag}]^+$ has a slightly lower MIA than its copper and gold analogues (814 and 861 kJ mol$^{-1}$, respectively).[10]

We also combined **1** with the recently reported, thermally stable phosphaketene salt Na[PCO]·(diox.)$_{2.5}$.[14] As expected, the –OTf group was substituted for a –PCO ligand to give [(ITr)Ag(PCO)] (**7**) (Scheme 3 and Fig. 3); a similar reaction has been noted between Na[PCO]·(diox.)$_{2.5}$ and CAAC gold and copper halide complexes (CAAC = cyclic(alkyl)aminocarbene).[15] Compound **7** has a $\text{C}_{\text{NHC}}$–Ag–P bond angle that is slightly distorted from linearity [175.22(5)°], with Ag–P and Ag–C(6) distances of 2.4015(6) and 2.770(3) Å, respectively, indicating $\eta^2$-coordination between the $\text{PCO}^-$ anion and Ag(I). Compound **7** yielded a broad signal in the $^{31}\text{P}\{^1\text{H}\}$ spectrum at −406 ppm at room temperature which was resolved as a sharp doublet at −80 °C due to $^{107/109}$Ag–P coupling (Fig. S12 and S13, ESI†).[10] The Kohn–Sham molecular orbitals[10] associated with the optimized geometry of **7** support $\eta^2$-PCO coordination (Fig. 3) as the HOMO−1 shows electron delocalization about the Ag–P–C unit, arising from side-on overlap of a P–C π bond with an empty s orbital on silver. The natural bonding orbitals (NBOs) further corroborate this bonding description, with the highest energy donor–acceptor interaction (second-order perturbation theory) between the $[(\text{ITr})\text{Ag}]^+$ fragment and $\text{PCO}^-$ being donation from a P–C π bond to an empty silver-centered s orbital (62.8 kcal mol$^{-1}$). A related bonding situation has been observed for [(CAAC)Cu(PCO)][15] and within phosphalkyne Ag(I) complexes,[16] and supports the presence of a highly electron-deficient Ag(I) center in $[(\text{ITr})\text{Ag}]^+$.



Scheme 3 Formation of $[(\text{ITr})\text{Ag}(\eta^2\text{-PCO})]$ (**7**) from **1**.

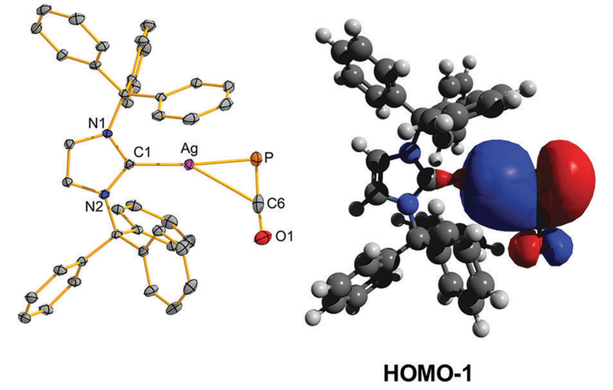


Fig. 3 Molecular structure of $[(\text{ITr})\text{Ag}(\eta^2\text{-PCO})]$ (**7**) with thermal ellipsoids plotted at the 30% probability level (left) and the HOMO−1 (right) of the optimized geometry of **7**. All hydrogen atoms and THF solvate have been omitted for clarity. Selected bond lengths [Å] and angles [°]: C1–Ag 2.140(2), Ag–P 2.4015(6), P–C6 1.588(3), C6–O1 1.211(4), Ag–C6 2.770(3); C1–Ag–P 175.22(5), Ag–P–C6 85.35(9), P–C6–O1 174.5(2).

We have reported the formation of $[(\text{ITr})\text{Ag}]^+$ complexes from the readily accessible, thermally and light, stable precursor [(ITr)Ag(OTf)]. The electrophilic $[(\text{ITr})\text{Ag}]^+$ unit engages in weak/reversible 1 : 1 complexation with fluorobenzene, mesitylene and dichloromethane, and yields the solvent-free, weakly associated dimer $[(\text{ITr})\text{Ag}]_2^{2+}$. These compounds represent rare examples of silver(I) complexes that approach monocoordination. Future work will involve exploring the catalytic activity of the thermally stable and electron-deficient $[(\text{ITr})\text{Ag}]^+$ unit.

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## Conflicts of interest

There are no conflicts to declare.

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