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Structure and bonding of [(SIPr)AgX] (X = Cl, Br, I and OTf)†

Valerie H. L. Wong,[ab] Andrew J. P. White,[a] T. S. Andy Hor[b] and King Kuok (Mimi) Hii*[a]

A series of iso-structural complexes [(SIPr)AgX] (X = Cl, Br, I, OTf; SIPr = 1,3-bis(2,6-diisopropylphenyl)imidazolidene) were synthesised, including the first example of a N-heterocyclic carbene silver(I) complex containing an O-bound triflate. Bond Energy Dissociation and Natural Orbitals for Chemical Valence bond analyses (BEDA & ETS-NOCV) revealing a significant NHC → M σ-back-donation, which influences the stability and sigma-donicity of these complexes.

The discovery of a stable free N-heterocyclic carbene (NHC) by Arduengo in 1991[1] is an important milestone that has transformed many areas of chemistry.[2] In a little over two decades, NHC's have been shown to be a privileged ligand class for important metal-catalysed reactions with broad applicability, such as cross-coupling and olefin metathesis, as well as being active organocatalysts in their own right. Additionally, metal–NHC complexes have also found applications as valuable functional materials, and anti-microbial and anti-tumour agents for the treatment of multi-drug resistant infection and cancer.[3] Interests in their chemical, physical and biological activities have stimulated many studies of the metal–carbene bond.[4]

Monomeric Ag(I)–NHC complexes with the structure [(NHC)AgX], where X = anion ligand, are relatively uncommon.[5] Generally, a combination of strong σ-donor ability of the NHC ligand and a relatively weak Ag–X bond makes these complexes unstable; they tend to undergo rapid exchange in solution with the homoleptic species $[(NHC)_2Ag][AgX_2]$,[6] which may be isolated as ionic pairs,[7] or as discreet bis-NHC complexes $[(NHC)_2Ag][X]$ (when X = counter-anion, *e.g.* BF_4).[8] Concurrently, [(NHC)AgX] complexes where NHC = imidazolidin-2-ylidene derivatives ('saturated carbenes') are even less common.[9] Saturated NHC ligands are generally thought to be better σ-donors than their unsaturated analogues, thus can impose greater *trans*-effect on the opposite anion, making these complexes even more unstable.

To date, there are no reported examples of mononuclear [(NHC)AgX] complexes containing a bound triflate anion ($X = CF_3SO_3^-$), although the synthesis of [(SIPr)AgOTf] (**1**) had been reported to be prepared by the addition of AgOTf to a suspension of [(SIPr)AgCl].[10] Within our work programme on silver catalysis,[11] the procedure was repeated to afford a white crystalline solid that has similar characterisation data to that described: the key observation being a downfield shift of the ^{13}C NMR resonance signal corresponding to the metal-coordinated carbene to 205.3 ppm, with ^1J coupling to $^{109}Ag/^{107}Ag$ isotopes of 304 and 264 Hz, respectively. Subsequently, a crystal suitable for X-ray crystallography was obtained, revealing that it is, in fact, a chloride-bridged dinuclear complex, $\{[(SIPr)Ag]_2(\mu\text{-}Cl)\}[OTf]$ (**2**) (Fig. 1), consisting of two $[Ag(SIPr)]^+$ units connected by a bridging chloride, structurally analogous to a fluoride-bridged dimer $[(SIPr)_2Ag_2(\mu\text{-}F)][BF_4]$ reported recently.[12] The Ag–C bond distance of 2.08 Å in complex **2** is longer than that found in the fluoride congener (2.05 Å), reflecting the greater *trans*-effect of Cl. Interestingly, very similar ^{13}C NMR data were reported for the two complexes, suggesting that the halide bridges in these complexes may not be retained in solution.

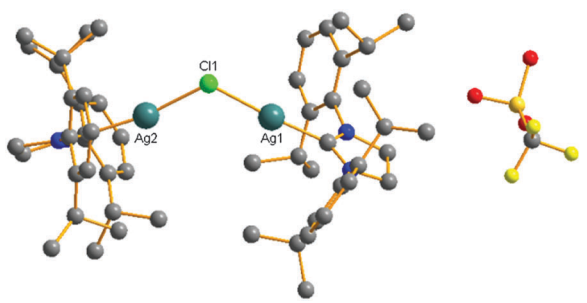
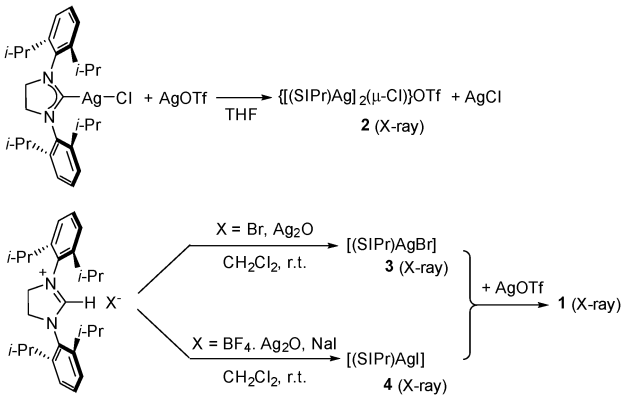


Fig. 1 X-ray crystal structure of compound **2** (H atoms omitted for clarity).

[a] Department of Chemistry, Imperial College London, Exhibition Road, South Kensington, London SW7 2AZ, UK. E-mail: mimi.hii@imperial.ac.uk
[b] Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543

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Scheme 1 Preparation of Ag–NHC complexes **1–4**.

Addition of further equivalents of AgOTf to complex **2** did not lead to further halide abstraction. This led us to explore the use of the corresponding bromide and iodide precursors (**3** and **4**, respectively) for the metathesis reaction. These were prepared separately from different imidazolinium salts and fully characterized as monomeric [(NHC)AgX] complexes (Scheme 1), as confirmed by X-ray crystallography (see ESI†).

The addition of AgOTf to either **3** or **4** led to the formation of a new compound that is distinct from that obtained from the chloride precursor. In this case, the product was found to be highly fluxional in solution. The structure of [(SIPr)AgOTf] (**1**) was eventually confirmed by X-ray diffraction study (Fig. 2), showing that Ag is coordinated in a linear arrangement to SIPr and the triflate anion, providing the first unequivocal evidence that a Ag–O bond can be forged between a triflate anion and (NHC)–silver(I). The stability of **1** is both unique and surprising, as the corresponding experiments with IPr (unsaturated carbene) and SIMes analogues (where i-Pr is substituted with Me) resulted only in the formation of homoleptic $[(NHC)_2Ag][X]$ complexes. While the latter can be attributed to greater kinetic lability due to the smaller ligand, the former suggests that electronic factors are also important.

In order to understand this, the electronic structures of these iso-structural series of complexes were investigated. Bond energy decomposition analysis (BEDA)[13] is a popular method used for the analysis of NHC–metal complexes by partitioning

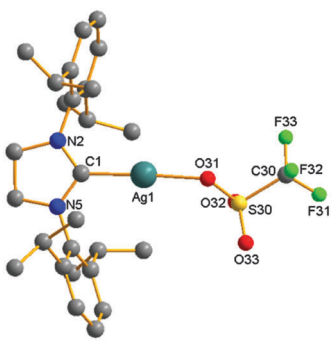


Fig. 2 X-ray crystal structure of [(SIPr)Ag(OTf)], **1**. H atoms omitted for clarity. SIPr = 1,3-bis(2,6-diisopropylphenyl)imidazolidene.

Table 1 Bond energy decomposition analysis of Ag–C bond in [(SIPr)AgX] complexes (kcal mol^{-1}), experimental and calculated Ag–C bond distances (Å), δ_C (ppm) and ^1J(Ag–C) coupling constants (Hz)

Energies (kcal mol^{-1})	X = Cl	X = Br (**3**)	X = I (**4**)	X = OTf (**1**)
ΔE_{int} [a]	−50.71	−49.28	−47.37	−59.20
Steric int	−13.68	−12.22	−11.11	−16.30
ΔE_{Pauli}	120.04	119.96	115.60	126.71
ΔE_{elstat}	−133.72	−132.19	−126.71	−143.01
ΔE_{oi}	−37.04	−37.06	−36.26	−42.90
Ag–C (expt)	2.081(9)	2.080(3)	2.094(3)	2.072(3)
Ag–C (calc)	2.071	2.083	2.099	2.058
δ_C [b]/ppm	207.7	209.9	210.8	— [d]
^1J(Ag–C) [c]	253, 219	249, 216	238, 207	— [d]

[a] $\Delta E_{int} = \Delta E_{oi} + \Delta E_{electostat} + \Delta E_{Pauli}$; steric int = $\Delta E_{Pauli} + \Delta E_{electostat}$. [b] Resonance signal of coordinated carbene. Recorded in CD_2Cl_2. [c] Values corresponding to $^1J(^{109}Ag–^{13}C)$ and $^1J(^{107}Ag–^{13}C)$ respectively. [d] Not observed (fluxional).

the M–C bond into ionic and covalent components.[4a,14] This was employed by Frenking and co-workers in a computational study of [(NHC)AgX] complexes, where the NHC = unsubstituted imidazol-2-ylidene.[15]

The results of our study are summarized in Table 1. In agreement with previous studies, the metal–carbene bond is largely ionic in nature, dominated by repulsive ΔE_{Pauli} and attractive ΔE_{elstat} terms, with a small, but not insignificant, orbital contribution. The binding energies between SIPr and AgX decrease slightly in the order: Cl > Br > I; this is supported experimentally by a corresponding increase in the Ag–C bond length, downfield shift of the ^{13}C resonance signal, and reduced ^1J(AgC) coupling constants. In comparison, the Ag–C bond in the triflate complex **1** is notably stronger than the halide compounds, due to an increase in both the ionic (steric int) and covalent (ΔE_{oi}) components. This is also supported by the shortest Ag–C bond.

Charge transfer and a breakdown of σ and π interactions between SIPr and AgX fragments were quantified by ETS-NOCV analysis. For all four complexes, similar pairs of NOCV were found to have significant contribution to the Ag–C bond ($|\nu_\kappa| \geq 0.1$, Fig. 3 and Table 2): one depicts a σ-donation of electron density from NHC → Ag (σ_d), and the rest with electron density transferring in the opposite direction (back-bonding) comprising of two π- (in- and out-of-plane, $\pi_\parallel$ and $\pi_\perp$, respectively), and a σ-back donation (σ_{bd}). The latter is a particularly striking feature. Energetically, σ_{bd} is comparable in magnitude to the $\pi_\perp$-back-bonding and, in the triflate complex **1**, overrides $\pi_\perp$ as the major contributor to back-donation.

In similar studies of [(NHC)MX] complexes, where NHC = unsaturated NHC and M = Ag or Au,[15,16] M → NHC back-donation were always found to be dominated by $\pi_\perp$, followed closely by $\pi_\parallel$ interactions; σ_{bd} is often discarded as an insignificant contributor. The only exception is a theoretical study by Huynh and co-workers of [(NHC)AuCl] complexes,[4b] where σ_{bd} contributions to ΔE_{oi} of *ca.* 11% was recorded – a similar result obtained in our present study with the Ag complexes. Therefore, a simple σ/π-partitioning analysis will show that the Ag–C bond has *ca.* 75% σ-character, comparable to reported values for unsaturated [(NHC)AgX] complexes.[15] However, with the σ_{bd} back-bonding

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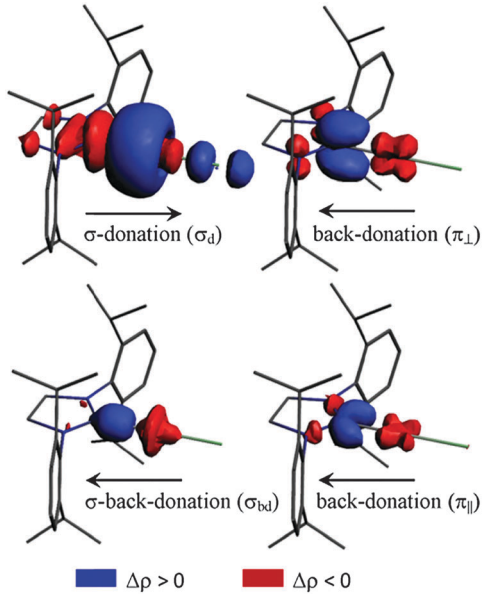


Fig. 3 Contribution to deformation density between NOCV pairs of SIPr and AgX fragments, illustrated with [(SIPr)AgCl]. Red surfaces = loss of electron density; blue surfaces = gain of electron density.

Table 2 ETS-NOCV decomposition energy contributions characterising σ_d, $\pi_{\parallel}$, $\pi_{\perp}$, and σ_{bd} interactions (kcal mol^{-1}). NOCV eigen values, $|\nu_k|$, are given in parenthesis

Complex	σ_d	$\pi_{\perp}$	σ_{bd}	$\pi_{\perp}$
X = Cl	−19.51 (0.40)	−5.63 (0.22)	−5.32 (0.15)	−2.54 (0.10)
C = Br (**3**)	−19.60 (0.40)	−5.43 (0.22)	−5.25 (0.15)	−2.47 (0.10)
X = I (**4**)	−19.72 (0.41)	−4.96 (0.21)	−4.91 (0.15)	−2.27 (0.10)
X = OTf (**1**)	−21.81 (0.44)	−5.85 (0.20)	−6.53 (0.17)	−2.83 (0.10)

taken into account, the σ-donation related to NHC → Ag is reduced to <55%. In this respect, SIPr is a weaker σ-donor than its saturated equivalent IPr, where σ_{bd} is negligible. This is supported by experimental data, where [(IPr)AgX] (2.06–2.07 Å)[9b,17] have shorter Ag–C bond lengths than [(SIPr)AgX] (2.08–2.09 Å, Table 1) complexes, reflected by a greater shielding for the coordinated carbene (δ_C 185 *vs.* 210 ppm, respectively). This will also account for the greater stability of complex **1**.[18]

The relative σ-donor ability of saturated and unsaturated NHC ligands has been a subject of some debate. It is generally accepted that the pK_a of the imidazolium/imidazolinium salts is not an adequate indicator for the σ-donicity of their corresponding carbenes. In NMR and calorimetric studies of ruthenium(II),[19] palladium(II)[20] and platinum(II)[21] complexes, unsaturated carbenes (IPr and IMes) were reported to be less σ-donating than their saturated analogues (SIPr and SIMes). However, the reverse appears to be true in IR spectroscopic studies of nickel(0)[22] and iridium(I)[23] carbonyl complexes; explained by evoking synergistic relationships between NHC and CO ligands. In this study, however, we have shown that SIPr can be a weaker σ-donor than IPr in the absence of other π-acceptor ligands. For Ag(I) complexes, the presence of a full-shell of electrons (d^{10}) prevents effective $\pi_{\parallel}$ and $\pi_{\perp}$-back donation, particularly as saturated carbenes are poor π-acceptors. Consequently, the excess electron density on the metal is dispelled back towards the metal *via* σ_{bd}, reducing the σ-donicity of the NHC ligand, and correspondingly, its *trans*-effect on the opposite anion.

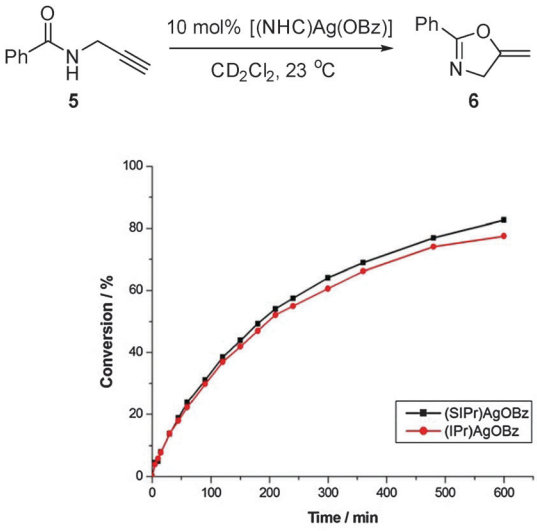


Fig. 4 Catalytic activity of [(SIPr)Ag(OBz)] and [(IPr)Ag(OBz)] in the intramolecular cyclization of propargylamide (OBz = benzoate).

This electronic 'levelling' effect is bound to have important implications in the application of these metal complexes as catalysts. Given that the [(IPr)Ag(OTf)] cannot be prepared, preliminary catalytic experiments were performed using SIPr and IPr complexes of silver(I) benzoate so as to afford direct comparisons. Nearly identical rates in the cyclization of propargyl amide **5** to the oxazolidine **6** were observed (Fig. 4), supporting the view that that the two complexes are not electronically different.[24,25]

In summary, a series of monomeric [(SIPr)AgX] compounds have been prepared and fully characterised; including the first report of a triflate-coordinated complex. BDEA showed that the Ag–C binding energy increases in the order of X = I < Br < Cl < OTf, while ETS-NOCV analyses revealed significant involvement of a σ-component in the back donation of electron density from Ag → NHC, making the SIPr ligand a weaker σ-donor than its saturated analogues in these complexes. This implies that, at least for group 11 metals, that the choice between saturated or unsaturated NHC ligands may not make much of a difference in their catalytic activities as may be expected.

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