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PAPER

The interplay of metal and supporting ligand in labile coordination to pincer complexes of Ag(I)[†]

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The bis(imino)pyridine scaffold provides support for the synthesis and characterization of unique Ag(t) pincer complexes [{ArN=CPh}₂(NPh)]Ag⁺(OTf)⁻ (Ar = 2,5^{-t}Bu₂C₆H₃ **3**; 2,6⁻ⁱPr₂C₆H₃ **4**). The bonding interactions between the cation–anion and between the bis(imino)pyridine ligand and the Ag centre are presented. Coordination of pyridine, toluene, 2-butyne and cyclooctene to the Ag centre led to the isolation and crystallographic characterization of labile transient adduct species. Bonding analysis of the adducts revealed conventional ligand–Ag coordination and important unconventional electron donation from the ligand to a π^* -orbital of the bis(imino)pyridine group.

Introduction

Lability and reactivity are fundamental objectives in chemistry that are in opposition to isolation and characterization of stable species. The capture and analysis of weakly bonded complexes has important implications on reactivity and can challenge and enhance concepts of bonding and stability. Because such species are fragile and vulnerable to transformation only some characterization tools may be applicable to their analysis, in contrast to the examination of unreactive, stable compounds. Computations can enhance the characterization and provide a springboard for defining more subtle features of intermolecular interactions that go beyond conventional electron transfer–donor bonds.

With the goal of discovering unprecedented bonding features and concomitant reactivity, we were attracted to the bis(imino) pyridine scaffold; a neutral ligand that presents three electron pairs in a well-defined, planar, pincer array. The modular stereoelectronic features and the relative ease of synthesis of these ligands has inspired their application to a range of transition metal ions.¹ To avoid reactivity of the imino methyl groups we replaced these moieties with phenyl groups and tuned the steric demands of the N-aryl substituents by employing a range of substituted aryl groups.^{2,3} For example, the new ligands 1 and 2 afforded a series of low-valent, In(I) complexes $[{ArN=CPh}_2(NC_5H_3)]In^+(OTf)^-$ where the In⁺ accepts little covalent donor-acceptor interaction from the ligand.³ These investigations were extended to the synthesis of analogous Ag⁺ complexes and yielded unique pincer complexes with an orbital array and geometry that allows for interesting coordination and

† Electronic supplementary information (ESI) available: Infrared data on compounds **3**, **4** and **3a–d** and **4a**. Combined cif for structures **3a**, **4a**, **3c** and **3d**. CCDC 849370–849373. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt12112c

adduct formation. In particular, the coordination of a toluene molecule to the $[\{(2,5-tBu_2C_6H_3)N=CPh\}_2(NC_5H_3)]Ag^+$ cation was examined and the interaction was shown to involve an interesting combination of conventional electron donation from the toluene π -orbital to Ag with an unusual donation to an essentially bis(imino)pyridine-based π^* -orbital. This unconventional bonding interaction points to the important role of the bis(imino) pyridine ligand not only in stabilizing the pincer geometry of Ag⁺ but in adduct formation.

The increasing profile of the complexes of the coinage metals in catalysis and medicine encourage the exploration of ligand environments that promote interesting and pertinent metal coordination geometries for potential precatalysis species.⁴ For example, a general feature of reactivity and transformations that are promoted by metal complexes is the role of σ - and/or π -Lewis acidity used for substrate activation. Herein we report the vital and unanticipated role of a supporting ligand in the labile coordination of a variety of pertinent ligands to an Ag centre.

Results and discussion

The first reported Ag complexes of the bis(imino)pyridine ligand frame were prepared by the reaction of **1** and **2** with Ag (O₃SCF₃) (eqn (1)), which provided **3** and **4** as bright yellow crystalline solids.^{3*a*} The ¹H and ¹³C NMR spectra of these materials were consistent with the proposed formulations. Broadened resonances and the appearance of diastereotopic methyl groups for the iPr groups in **4** suggested hindered rotation of the Ar–N_{imine} bonds. The identities and structural details of these compounds as bis(imino)pyridine complexes [{ArN=CPh}₂ (NPh)]Ag⁺(OTf)⁻] (Ar = 2,5-^tBu₂C₆H₃ **3**; 2,6-ⁱPr₂C₆H₃ **4**) were established by single crystal X-ray analysis.^{3*a*} These Ag(1) species are not only unique in possessing the bis(imino)pyridine ligand, but the constrained geometry and coplanar tridentate

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array provided by the ligand makes these compounds unusual pincer complexes for silver. $^{5-7}$



A more intimate examination of the electronic features of compounds **3** and **4** was obtained through a density functional theory (DFT) computational study using the B3LYP functional and the mixed DZVP–TZVP basis set.^{3a} The electronic interaction energy between the Ag[bis(imino)pyridine]⁺ (LAg⁺) cation and the OTf⁻ anion was determined to be similar for **3** and **4** with values of -85.7 and -84.5 kcal mol⁻¹, respectively. Furthermore, these compounds displayed similar cation–anion bond orders of 0.31–0.32, which corresponded to approximately 0.18–0.19 electrons transferred from the triflate to the LAg⁺ fragment. Two unoccupied acceptor orbitals on the LAg⁺ fragment (LUFO and LUFO + 2) participated in covalent bonding with the OTf⁻ anion. The Ag character of these fragment orbitals (FOs) was dominated by the empty Ag 5s orbital.

These computational results also provided details for the bonding interaction between the bis(imino)pyridine ligand and the silver centre within the LAg⁺ cation, and revealed that greater than 50% of the electronic interaction energy (average energy = $-88.4 \text{ kcal mol}^{-1}$) is due to covalent bonding between the metal ion and the ligand. In both compounds the bis(imino) pyridine ligands donate 0.4 electrons to the Ag⁺ ion. This donation comes primarily from the four highest occupied orbitals of the ligand that are shown in Fig. 1. Four orbitals on the Ag⁺ cation fragments accept this electron density: LUFO-LUFO + 3. The major (60%) contribution to covalent bonding is between the LUFO of the Ag⁺ centre, with 100% 5s character, and the HOFO-6 ligand orbital. The three remaining unoccupied acceptor orbitals on the Ag cation are of 5p character; two of these orbitals (LUFO + 1 and LUFO + 2) lie in the ligand plane and accept σ -type electron density from the ligand donor orbitals HOFO and the HOFO-5/HOFO-1 combination respectively. The remaining metal acceptor orbital, LUFO + 3, is the 5p Ag orbital oriented perpendicular to the ligand plane and is of π -symmetry and accepts very little electron density from the bis(imino)pyridine ligand.

The ligand array and geometry of cationic complexes **3** and **4** provide an interesting set of compounds to investigate the nature of interactions with common Lewis base ligands. The reactivity of the open face of compounds **3** and **4** with σ and π ligands was probed by the reactions shown in Scheme 1. The addition of pyridine, toluene, 2-butyne or cyclooctene to the LAg⁺ centres of **3** or **4** led to weak coordination of these species to the open site of the cation species. In fact, the LAg⁺-donor interactions produce labile species that could be captured and examined by single crystal X-ray analysis but these adducts did not exhibit distinct NMR signals, indicating that the coordinating species is released when compounds **3a**–**d** and **4a** were dissolved in solution. Furthermore, preparation of samples of compounds **3a**–**d** and **4a** for



Fig. 1 The four most significant donor orbitals of the pincer ligand in 3. The energy of each orbital is provided with the label.

microanalysis led to results consistent with the loss of the coordinating species (*i.e.* pyridine, toluene, 2-butyne, cyclooctene).

When **3** and **4** are recrystallized from pyridine, single crystals of the pyridine adducts **3a** and **4a** were repeatedly obtained, which were analysed by single crystal X-ray diffraction. The results are summarized in Fig. 2 and 3 and Table 1. Both compounds display $LAg(pyridine)^+$ cations with an LAg^+ fragment in a pincer geometry of a planar tridentate bis(imino)pyridine ligand array.



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Fig. 2 Structure of compound 3a with the hydrogen atoms and triflate counterion omitted for clarity.

Fig. 3 Structure of compound 4a with the hydrogen atoms and triflate counterion omitted for clarity.

The bonding parameters within the [bis(imino)pyridine]Ag⁺ fragments of 3a and 4a are very similar to the parent species. The coordinated pyridine fragment lies in the open face of the LAg⁺ moiety to yield a distorted square planar metal centre within the limits due to the restrictions of the bis(imino)pyridine ligand. Interestingly, the plane of the coordinated pyridine ligands in these two compounds is nearly co-planar/coincides with that of the bis(imino)pyridine ligands. In the case of 3a, the angle between the planes defined by the pyridyl group of the bis (imino)pyridine ligand and the coordinated pyridine ligand was $10.2(1)^{\circ}$ with an analogous angle for 4a of $25.9(1)^{\circ}$. This disposition appears to be a result of the steric pocket provided by the NAr' groups. In both compounds, the triflate anion is more removed than in the parent compounds. The shortest Ag-triflate contact for **3a** was Ag(1)-O(2) at >3.0 Å and in **4a** it was Ag (1)–O(1) at ≈ 2.7 Å. The lability of the coordinated pyridine in compounds 3a and 4a was demonstrated during efforts to obtain elemental analysis, whereby loss of pyridine adduct was evident even in samples subjected to minimal sample preparation/handling prior to combustion.

There is a growing literature reporting the formation of stable crystalline Ag–arene π -complexes with the arene bonded in the η^2 or η^3 mode.⁸ As previously reported, when **3** was crystallized from toluene, crystals of **3b** were isolated that demonstrate the Lewis acidity of the LAg⁺ pincer cation (Fig. 4).^{3a} The coordination of toluene has displaced the OTf⁻ anion to a distance >

	Bis(imino)pyridine ligand		T :0 /	Coordinated ligand						
	Ag– N _{py}	Ag– N _{imine}	Ag– OTf	Ag– N(4)	Ag– C _{arene}	Ag– C _{alkyne}	Ag– C _{olefin}			
3 ³	2.270(9)	2.523(7) 2.526(6)	2.331(8) 2.638(6)							
4 ³	2.347(6)	2.492(6)	2.04	2 197(2)						
3a	2.255(2)	2.537(3)	3.04	2.187(3)						
4a	2.298(2)	2.556(2) 2.559(2)	2.66	2.212(2)						
3b ³	2.287(2)	2.556(3) 2.581(3)	6.94		2.447(4) 2.464(4)					
3c	2.276(2)	2.596(2) 2.703(2)	2.95			2.373(3) 2.369(3)				
3d	2.296(4)	2.622(4) 2.503(4)	17.02				2.418(5) 2.360(6)			

Table 1 Selected bond lengths (Å) for 3, 4, 3a-d and 4a

Fig. 4 The structure of compound 3b, with the hydrogen atoms and triflate counterion omitted for clarity.

6.3 Å and the silver centre bonds symmetrically to the *m*- and *p*-carbons of the toluene molecule. The distance between the Ag centre and the mean aromatic plane of 2.279 Å and Kochi's geometric criteria gave a hapticity for **3b** of $\eta = 2.02$.⁹ Again, while the formation of crystals of **3b** was reproducible, attempts to obtain microanalysis of this species was hindered by the loss of toluene during sample isolation and transport.

Similarly, the alkyne adduct of 3 was obtained when this silver complex was crystallized in excess 2-butyne. The results of a single crystal X-ray analysis of this new compound 3c are presented in summary form in Fig. 5 and Table 1. As with the pyridine and toluene adducts, **3a** and **3b**, the alkyne complex, **3c**, displayed a silver centre coordinated by the tridentate pincer ligand. Overall the Ag-N distances in the LAg⁺ fragment (Ag- N_{py} and Ag– $N_{imine})$ are similar to those observed for $\boldsymbol{3}$ and 3a-b. Similarly, the Ag-OTf distance is increased relative to the starting material 3. The 2-butyne is coordinated symmetrically to the Ag centre with Ag-C distances of 2.373(3) and 2.369(3) Å. This coordination only very slightly lengthens the $C \equiv C$ bond distance with the observed value of 1.186(4) Å vs. the reported value of 1.1160 Å.¹⁰ In addition, the alkyne moiety exhibits only a minor deviation from linearity with a C(49)-C(50)-C(51)angle of 169.14(3)°. Overall, these features suggest little, if any,

Fig. 5 Structure of compound **3c**, with the hydrogen atoms and triflate counterion omitted for clarity.

back donation from the metal centre to the 2-butyne. The alkyne is coordinated along the same vector as was observed for the pyridine coordination in **3a** and, like that compound, the C(50)–Ag(1)–C(49) plane approaches a co-planar orientation with that of the bis(imino)pyridine ligand with an observed angle between pyridine ring and alkyne plane of $31.8(5)^{\circ}$.

This compound can be compared to both trigonal planar and tetrahedrally coordinated Ag–alkyne complexes. The Ag–C_{alkyne} distances in **3c** are longer than those observed in the trigonal planar hexyne adduct of a triazapentadienyl Ag complex with Ag–C distances of 2.233 and 2.241 Å¹¹ as well as those in Ag (hfac)(Me₃SiCCSiMe₃) (hfac⁻=(CF₃COCHCOCF₃)⁻) with Ag–C_{alkyne} distances of 2.255(4) and 2.267(4) Å.¹² A trispyrazolyl borate complex of Ag(1) is coordinated by both acetylene (Ag–C_{alkyne} = 2.293(4) Å) and phenylacetylene (Ag–C_{alkyne} = 2.263 (5), 2.407(5) Å) to yield a tetrahedral species.¹³

We explored the coordination of alkenes to the LAg⁺ fragment by crystallizing compound **3** in excess cyclooctene. Single crystal X-ray analysis revealed this species to be compound **3d**, $[LAg^+(cyclooctene)][OTf^-]$, with the results presented in Fig. 6 and Table 1. The triflate anion in **3d** is well separated from the cation with the shortest contact, Ag1–O3, greater than 17 Å.

Similar to compounds **3** and **3a–c**, the bis(imino)pyridine ligand provides a planar pincer coordination with a typical Ag (1)–N(2) distance (2.296(4) Å) and only slightly asymmetrically to the N_{imine} sites of the ligand. The Ag–C_{olefin} distances (2.418 (5), 2.360(6) Å) are slightly longer than those of the four coordinate species [HB(3,5-(CF₃)₂Pz)₃]Ag-(H2CCH2) (Ag–C = 2.294 (7) and 2.307(7) Å).¹³ The cyclooctene adduct, **3d**, exhibited a C=C distance (C(48)–C(49) 1.361(8) Å) slightly elongated from the free cyclooctene value of 1.22(4) Å.¹⁴ Like the pyridine and the alkyne adducts, the olefin displays a rather small angle with the bis(imino)pyridine ligand plane; the angle between the pyridine ring and olefin–Ag fragment is 27.8 (0.4)°.

Fig. 6 Structure of compound 3d, with hydrogen atoms and triflate counterion omitted for clarity.

The combination of our experimental observations on the nature of compounds 3a-d and the analysis of the crystallographic features of these compounds indicated that they exhibit weak interactions between the LAg⁺ cation and the ligands. In order to quantify the degree and details for the interactions between the [bis(imino)pyridine]Ag⁺ cation and the coordinated moieties we examined the interaction of these fragments using computations with the resulting data summarized in Table 2. Frequency analysis on the optimized structures confirmed that they were minima and provided the data for the calculation of free energy of adduct formation (ΔG_f) and sum of electronic and zero-point energies, ΔE , according to eqn (2).

The LAg⁺-pyridine interactions in compound 4a were examined with a DFT computational study using the B3LYP functional and the mixed DZVP/TZVP basis set. Full optimization of this compound yielded a structure in accord with the cation in 4a including the features of the Ag-pyridine bonding. Our analysis indicated that the electronic interaction energy between the two fragments was -23.9 kcal mol⁻¹ with donation of only 0.11 electrons from the N-based lone pair of the pyridine (e.g. 5.5% of the population of the HOFO). This corresponded to a bond order of 0.25 between the fragments. The two LAg⁺ acceptor orbitals, LUFO and LUFO + 2 (Fig. 7), receive nearly equal components of this electron donation (2.3 and 3.9% respectively). In terms of Ag contribution, both of these orbitals consist mainly of the empty Ag 5s orbital with the LUFO being 25% 5s and 6% 5p and the LUFO + 2 being 53% 5s and 7% 5p. Significantly, almost 70% of the LUFO is actually based on the bis (imino)pyridine ligand. Furthermore, even the LUFO + 2 is about 40% bis(imino)pyridine in character. Although the

 Table 2
 Summary of computational results on compounds 4a, 3a-d

	Ligand, L'	$E_{\rm int}$ (kcal mol ⁻¹)	Bond order	Charge donation (electrons)	$\Delta G_{\rm f} (\rm kcal \ mol^{-1})$	$\Delta E (\mathrm{kcal} \mathrm{mol}^{-1})$
4a	Pyridine	-23.9	0.25	0.11	-6.2	-18.9
3b ^{3a}	Toluene	-12.9	0.44	0.19	1.2	-9.4
3c	2-Butyne	-17.1	0.53	0.28	1.6	-9.6
3d	Cyclooctene	-17.6	0.62	0.26	1.2	-11.0

[Ag(L)]⁺ Fragment

Fig. 7 FOs for the optimized cation fragment, [$\{(2,5-tBu_2C_6H_3)N=CPh\}_2(NC_5H_3)$]Ag⁺. These are the FOs with the largest electron acceptor contributions to bonding in **4a**, and **3a–d**, as discussed in the text.

donation of electron density from a coordinated pyridine to the Ag 5s orbital is as expected, the important role of the supporting ligand in this bonding, revealed in this analysis, is unexpected. The small value for the free energy of formation of this adduct is in agreement with our observations that the pyridine ligand is only weakly bound to the Ag centre.

A similar analysis of the bonding interactions between the LAg⁺ cation and the toluene moiety was carried out. In order to facilitate the computations, the $LAg(toluene)^+$ cation in **3b** was modelled by replacing the $2{,}5{}^{-t}\mathrm{Bu}_2\mathrm{C}_6\mathrm{H}_3$ groups with simple phenyl rings. Using the B3LYP functional and the mixed DZVP/ TZVP basis set on this model yielded a structure in agreement with the cation in 3b. The electronic interaction energy between the [bis(imino)pyridine]Ag⁺ and the toluene fragments was determined to be -12.9 kcal mol⁻¹ with a corresponding bond order of 0.44 and a charge transfer of 0.19 electrons from toluene to the silver fragment. The toluene–Ag interaction is $\boldsymbol{\sigma}$ in nature and involves the π -orbitals on toluene and LAg⁺ FOs shown in Fig. 7. As was observed with compound 4a, the silver fragment acceptor orbitals LUFO and LUFO + 2 are the major recipients of electron donation from the toluene HOFO (4.4%) and HOFO-4 (2.5%).^{3a} Again, the LUFO + 2 is predominantly an Ag orbital. Again, it was both interesting and unexpected that the other acceptor orbital was the bis(imino)pyridine-based π^* orbital. This unusual bonding points to the important role of the bis(imino)pyridine ligand not only in stabilizing the pincer geometry of Ag⁺ but in adduct formation. The interaction between the supporting bis(imino)pyridine ligand and the coordinated

toluene is a key component in the adduct formation. The nearly zero value of the $\Delta G_{\rm f}$ is, once again, consistent with the labile nature of this interaction.

The 2-butyne ligand interacts more strongly with the LAg⁺ cation of 3c than the toluene in adduct 3b as evidenced by a greater electronic interaction energy between the LAg⁺ cation and the alkyne of -17.1 kcal mol⁻¹ as well as a higher bond order (b.o. = 0.53) and a greater degree of charge transfer from the alkyne to LAg^+ of 0.23 electrons. The only significant interaction is σ in nature and is donation of 8.9% of the electronic population from the alkyne HOFO (π bonding) to Ag. There was no significant back donation contribution to the Ag-alkyne interaction (i.e. into the LUFO of the alkyne) a feature consistent with the crystallographic data and supported by the observed lability of this adduct. In this case the donation from the alkyne moiety is distributed between the LUFO (3%) and LUFO + 2 (5.9%) (see Fig. 7). Once again, adduct bonding involves acceptor orbitals that have significant bis(imino)pyridine ligand-based components. For example, the LUFO is only 20% Ag-centred with 80% bis(imino)pyridine character while the LUFO + 2 is 68% on Ag 32% on the tridentate ligand. Consistent with the previous observations, the Ag contribution is dominated by the 5s orbital (*i.e.* 65.4% 5s for LUFO + 2).

The degree and nature of the interaction between the LAg⁺ cation and olefin in **3d** is similar to that observed in the alkyne complex **3c**. Specifically, the interaction energy between the fragments was determined to be -17.6 kcal mol⁻¹ with a bond order of 0.62 and corresponding charge donation of 0.26 electrons. In this case, the olefin contributes 10.8% of the electron density in the HOFO (olefin π) through a σ interaction with the two cation acceptor orbitals: the LUFO (4.7%) and LUFO + 2 (6.3%). The nature of these two orbitals was as observed for the other adducts, with the LUFO being largely bis(imino)pyridine in nature (71 *vs*. 29% Ag) and the LUFO + 2 being 66% Ag with a substantial contribution (33%) from the supporting bis (imino)pyridine ligand.

Conclusions

The bis(imino)pyridine ligand scaffold does more than provide a supporting framework for unique pincer complexes of Ag. In the complexes $[{ArN=CPh}_2(NPh)]Ag^+(OTf)^-]$ (Ar = 2,5-^tBu₂C₆H₃ 3; 2,6-ⁱPr₂C₆H₃ 4), important charge transferbonding interactions between the triflate anion and the ligand are a significant component in the stability of these species. Furthermore, we have shown that the interplay of the bis(imino)pyridine ligand with weakly coordinating ligands, ranging from pyridine to arene, alkyne and olefin species, is a significant general feature with impact on geometry and complex formation. In addition to the conventional electron donation from the ligand to the metal centre, a remarkable contribution to the bonding in these species is an unusual donation to an essentially bis(imino) pyridine-based π^* -orbital. This unconventional bonding interaction involving a non-innocent role of the bis(imino)pyridine ligand in adduct formation may have broader implications on the application of these and other transient species to organic transformations. Our continuing efforts are focused on expanding on the reactivity of pincer Ag complexes and on elaborating our

understanding of features that favour labile bonding and its relevance to chemical transformations.

Experimental

General methods

All reactions were performed in a glovebox with a nitrogen atmosphere, with the exception of ligand synthesis, which was performed using standard Schlenk technique under a flow of N₂. All solvents were sparged with nitrogen and then dried by passage through a column of activated alumina using an apparatus purchased from Anhydrous Engineering. Deuterated chloroform was dried using activated molecular sieves. All other chemicals were purchased from Aldrich and used without further purification. Compounds **1** and **2** were synthesized according to literature procedure.¹⁵ NMR spectra were run on a Bruker Avance 300 MHz spectrometer with CDCl₃ as solvent and internal standard. Elemental analyses were performed by Midwest Microlab LLC, Indianapolis, IN.

Synthesis of [Ag-2,6-bis{1-[(2,5-ditertbutylphenyl)imino]-benzyl} pyridine][SO₃CF₃] (3)

AgOSO₂CF₃ powder (38 mg, 0.150 mmol) was added to a clear yellow solution of 1 (100 mg, 0.151 mmol) in 8 mL of toluene. The reaction mixture was sealed and wrapped in aluminium foil, due to the light sensitivity of AgOSO₂CF₃, and allowed to stir for 14 hours. During this time the reaction gradually became opaque yellow. The mixture was cooled to -20 °C and a bright yellow precipitate formed. The solid was removed by filtration, washed with 5 \times 2 mL hexanes, and allowed to dry under vacuum. A bright yellow powder was isolated in 69% yield. Large yellow cubic crystals suitable for single-crystal X-ray analysis were grown by diffusion of hexanes into a saturated CDCl₃ solution with cooling to -20 °C. ¹H NMR (CDCl₃, 300 MHz): δ 7.89 (br t, 1 H, py, p-CH), 7.60 (br d, 2 H, py, m-CH), 7.40-7.10 (br m, 12 H, aromatic), 6.96 (br d, 1H, aromatic), 6.93 (br d, 1 H, aromatic), 6.53 (br d, 2 H, aromatic), 1.49 (br s, 18H, ^tBu), 0.96 (br s, 18H, ^tBu). ¹³C NMR (CDCl₃, 75 MHz). δ 165.6 (C=N imine), 152.7 (py, o-C=N), 149.9 (Ar-CH), 148.3 (Ar-CH), 138.9 (Ar, i-C), 138.1 (Ar-CH), 134.3 (Ar, i-C), 129.8 (Ar-CH), 129.3 (Ar-CH), 128.3 (Ar-CH), 126.1 (Ar–CH), 125.0 (Ar–CH), 121.9 (Ar–^tBu, C–^tBu), 120.7 (Ar ^{-t}Bu , C ^{-t}Bu), 35.5 (Ar ^{-t}Bu , C $^{-t}$ (CH₃)₃), 34.2 (Ar ^{-t}Bu , $C-(CH_3)_3$, 31.2 (Ar-^tBu, CH₃), 30.9 (Ar-^tBu, CH₃). A sample for elemental analysis was obtained by recrystallization from toluene, resulting in a 1:1 toluene adduct of 3. Calculated (%) for [C₄₈H₅₅AgF₃N₃O₃S][C₇H₈]: C 65.34, H 6.28, N 4.16, found C 64.92, H 5.97, N 3.90.

Synthesis of [Ag-2,6-bis{1-[(2,6-diisopropylphenyl)imino]benzyl}pyridine][SO₃CF₃] (4)

AgOSO₂CF₃ powder (42 mg, 0.164 mmol) was added to a clear yellow solution of **2** (100 mg, 0.165 mmol) in 8 mL of hexanes : toluene (5:1) solution. The reaction mixture was sealed, wrapped in aluminium foil due to the light sensitivity of

AgOSO₂CF₃, and allowed to stir for 14 hours. During this time the reaction gradually became opaque yellow. The mixture was cooled to -20 °C and a bright yellow precipitate formed. The solid was removed by filtration, washed with 5×2 mL hexanes, and allowed to dry under vacuum. A bright yellow powder was isolated in 84% yield. Large yellow cubic crystals suitable for single-crystal X-ray analysis were grown in a saturated solution of toluene : hexanes (1 : 1) that was cooled to -20 °C. ¹H NMR (CDCl₃, 300 MHz): δ 7.98 (t, 1H, py, p-CH), 7.79 (d, 2H, py, m-CH), 7.42-6.95 (br m, 16H, aromatic), 2.92 (br m, 4H, iPr-CH), 1.21 (br d, 12H, CH₃), 0.91 (br d, 12H, CH₃). ¹³C NMR (CDCl₃). δ 165.6 (C=N imine), 152.3 (py, o-C=N), 144.5 (py, m-CH), 139.3 (py, p-CH), 136.7 (Ph, m-CH), 133.2 (Ph, o-CH), 130.7 (Ar-iPr, C-iPr), 129.4 (Ar-iPr, CH), 129.3 (Ph, i-C), 128.4 (Ph, p-CH), 125.8 (Ar-iPr, C-iPr), 123.6 (Ar-iPr, CH), 28.7 (Ar-iPr,CH₃), 24.6 (Ar-iPr, CH-(CH₃)₂), 22.6 (Ar-iPr, CH₃). A sample for elemental analysis was obtained by recrystallization from toluene, resulting in a 1:1 toluene adduct of 4. Calculated (%) for [C₄₄H₄₇AgF₃N₃O₃S][C₇H₈]: C 64.15, H 5.81, N 4.40, found C 64.83, H 5.78, N 4.19.

Formation of adducts 3a-d, 4a

Adducts **3a–d** and **4a** were prepared by dissolution of either **3** or **4** in a neat solution of the appropriate ligand species (~15 mg of Ag complex in 1.5 mL of solvent). The solutions were allowed to stir for 1 hr and then filtered through a Celite plug into a small vial. This vial was left uncovered and placed within a larger vial with hexanes. The large vial was sealed and placed in the freezer at -30 °C for several d. During this time some hexane diffused into the smaller, internal vial and crystals suitable for single-crystal X-ray crystallography formed. All of these species produced crystals that were bright yellow and these were either plates (**3a–c**) or blocks (**3d, 4a**).

Crystal structure determination of complexes 3a, 4a, 3c, 3d

Adducts 3a-d and 4a were isolated from neat solution of either compound 3 or 4 in compounds a-d respectively (~15 mg of Ag complex in 1.5 mL of solvent). Vials were sealed and placed in the freezer at -30 °C for several d while crystals suitable for single-crystal X-ray crystallography formed. All crystals were bright yellow and were either plate (3a, 3b, 3c) or block like (3d, 4a). Crystals were mounted in inert oil and transferred to the cold stream of the diffractometer for data collection.

Crystal data $C_{53}H_{60}AgF_3N_4O_3S$ (**3a**). $M_r = 997.98$, triclinic, a = 11.1402(4), b = 15.4794(5), c = 15.6244(6) Å, $\alpha = 98.249(3)^\circ$, $\beta = 110.516(2)^\circ$, $\gamma = 91.383(2)^\circ$, V = 2489.27(15) Å³, T = 200 K, space group $P\bar{1}$, Z = 2, reflections collected/unique 40 097/8451 ($R_{int} = 0.0689$). The final w R_2 was 0.0942 (all data).

Crystal data $C_{44}H_{47}AgF_3N_3O_3S(C_5H_5N)(C_4H_6)_{0.35}$ (**4a**). $M_r =$ 960.81, monoclinic, a = 14.3389(16), b = 18.947(2), c = 18.189 (2) Å, $\beta = 98.286(5)^\circ$, V = 4890.0(10) Å³, T = 200 K, space group $P2_1/c$, Z = 4, reflections collected/unique 99 977/12 077 ($R_{int} = 0.0213$). The final w R_2 was 0.1183 (all data).

Crystal data $C_{60}H_{76}AgF_3N_3O_3S$ (**3d**). $M_r = 1084.17$, orthorhombic, a = 31.0722(11), b = 9.7664(4), c = 19.8728(7) Å, V =

6030.7(4) Å³, T = 200 K, space group $Pca2_1$, Z = 4, reflections collected/unique 91 642/7330 ($R_{int} = 0.0584$). The final w R_2 was 0.1277 (all data).

Crystal data C₄₈H₅₅AgF₃N₃O₃S(C₄H₆)_{1.5} (**3c**). $M_r = 1000.01$, monoclinic, a = 32.106(3), b = 20.658(2), c = 19.954(2) Å, $\beta = 118.949(5)^\circ$, V = 11581(2) Å³, T = 200 K, space group C2/c, Z = 8, reflections collected/unique 94 508/14 448 ($R_{int} = 0.0382$). The final w R_2 was 0.1600 (all data).

Computational details

DFT calculations have been performed using the Gaussian 03 package.¹⁶ Wave function stability calculations were performed to confirm that the calculated wave functions corresponded to the electronic ground state. The structures of all species were optimized using the B3LYP exchange-correlation (XC) functional with the mixed basis set (DZVP on Ag and TZVP on all other atoms). Tight SCF convergence criteria (10^{-8} a.u.) were used for all calculations. Harmonic frequency calculations with the analytic evaluation of force gradients were used to determine the nature of the stationary points. The analysis of the molecular orbital (MO) compositions in terms of occupied and unoccupied orbitals of the fragment species (HOFOs and LUFOs, respectively), the construction of the MO diagram and Mayer bond orders were calculated using the AOMix program.^{17,18} Atomic charges and Wiberg bond orders in the natural atomic orbital basis were evaluated by using the natural population analysis.¹⁹ Frequency calculations of the optimized structures provided zero-point corrections and confirmed that the structures represent energy minima.

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