EurJIC European Journal of Inorganic Chemistry

ChemPubSoc Europe

FULL PAPER

DOI:10.1002/ejic.201500771

Organometallic Reactivity of [Silver(I)(Pyridine-Containing Ligand)] Complexes Relevant to Catalysis

Tommaso Pedrazzini,[a] Paolo Pirovano,[a][‡] Monica Dell'Acqua,[b] Fabio Ragaini,[a] Pasquale Illiano,[a] Piero Macchi,[c] Giorgio Abbiati,*[b] and Alessandro Caselli*[a]

Keywords: Silver / N ligands / Macrocyclic ligands / Structure elucidation / Pyridine-containing ligands

Silver(I) complexes of pyiridine-containing macrocyclic ligands (Pc-L) have already been demonstrated as active catalysts for some domino and multicomponent reactions. Here, we report new chiral [Ag^{I}(Pc-L*)] cationic complexes that have been synthesized and fully characterized, including structural determination by single-crystal X-ray diffraction. The complexes show a rich coordination chemistry, demonstrating both the σ-philic (alcohol and nitrile coordination) and the π-philic (alkyne coordination) nature of silver. The η^2 coordination mode of the naphthyl pendant arm of the ligands on silver has been observed in solution by NMR spectroscopic experiments. 2D NMR spectroscopy revealed the presence of positive cross peaks resulting from rotational processes and the rate of rotation was measured by using 2D exchange spectroscopy (EXSY).

Introduction

Macrocyclic ligands have attracted widespread attention, especially because of two of their unique properties:[1] the macrocyclic and the ring size effects. The first was initially described in 1969 in studies on the Cu^{II} complexes of some tetraaza macrocycles.[2] The macrocyclic complexes benefit from extra stability with respect to the common chelate effect.[3] Compared with the acyclic ones, macrocyclic ligands also have the advantage of being conformationally pre-organized and, as a consequence, they are able to discriminate among closely related metal ions based on the metal ion radius (ring size effect).[4] Some nitrogen-containing macrocyclic molecules are also naturally occurring species that play a vital role in biological system, such as porphrins, corrins, and chlorins. Since the report by N. F. Curtis in 1960, in which the first macrocyclic complex was synthesized by the reaction of tris-ethylenediamine nickel(II) perchlorate and acetone,[5] "synthetic" macrocycles have competed with the "natural" ones.[6] Macrocyclic chemistry has focused on the synthesis of species inspired by the naturally occurring systems, which mainly contain nitrogen donor atoms.[7] In general, polyaza macrocycles form extremely stable complexes with transition metals of the later transition series compared with the polyoxa macrocycles.[8] Cyclam (1,4,8,11-tetraazacyclotetradecane) and related unsaturated and homologous systems have been the most studied examples.[9]

The introduction of a pyridine moiety into the skeleton of a tetraaza-macrocycle ligand has a strong influence on both the complexation kinetics and the thermodynamic properties by increasing the conformational rigidity and by changing its basicity.[10] In past years, our attention has turned to the development of synthetic pathways that have allowed us to obtain a new class of tetraaza-macrocyclic ligands containing pyridine.[11] Our efforts were rewarded in 2008 when we published the synthesis of some pyridine-based 12-membered tetraaza-macrocyclic ligands, named pyridine-containing ligands (Pc-L).[12] The synthetic methodology employed is simple and allows us to differently functionalize the macrocyclic framework to increase the molecular diversity and create different stereocenters on the backbone.[13] The copper(I) complexes of these Pc-L* ligands have been fully characterized and successfully employed as catalysts in the Henry reaction[14] and in the enantioselective cyclopropanation of alkenes.[15] Compared with the more extensively studied copper and gold catalysis, reports on the catalytic activity of silver complexes are relatively sparse.[16] We have recently demonstrated that the sil-

[a] Università degli Studi di Milano and ISTM-CNR,
Via Golgi 19, 20133 Milano, Italy
E-mail: alessandro.caselli@unimi.it
http://users.unimi.it/acaselli/
[b] Dipartimento di Scienze Farmaceutiche, Sezione di Chimica Generale e Organica "A. Marchesini", Università degli Studi di Milano,
Via Venezian 21, 20133 Milano, Italy
E-mail: giorgio.abbiati@unimi.it
http://users.unimi.it/istchimorg/giorgio.htm
[c] Department of Chemistry & Biochemistry, University of Bern, Freiestrasse 3, 3012 Bern, Switzerland
[‡] Present Address: School of Chemistry, The University of Dublin, Trinity College,
College Green, Dublin 2, Ireland

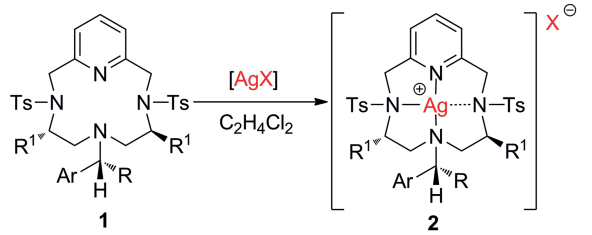
Supporting Information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201500771.

ver(I) complexes of achiral Pc-L ligands are effective catalysts in the regiospecific synthesis of 1-alkoxy-isochromenes under mild reaction conditions.[17] The same silver(I) catalysts have shown a good catalytic activity in the microwave-enhanced synthesis of propargylamines starting from aldehydes, terminal alkynes, and amines (A^3-coupling).[18]

The great advantage of the [Ag^I(Pc-L)] complexes with respect to simple silver salts, is their enhanced stability and the ease of handling. In fact, they can be stored indefinitely in open air/light conditions at room temperature without any appreciable decomposition. However, they have the tendency to adsorb an additional ligand, for example, a water molecule from moisture, which can sometimes modify and/or reduce their catalytic behavior. Although from our previous studies we were able to propose some mechanistic hypotheses, the structure of the silver catalysts was not yet completely elucidated. In this paper, we report the study of the organometallic reactivity of those silver(I) complexes with substrates relevant to the catalytic reactions studied, that is, alkynes and alcohols and with other neutral ligands, such as CO, water, and acetonitrile. In some cases, the structures of the reaction products were unambiguously determined by X-ray analysis of single crystals.

Results and Discussion

The silver(I) complexes, **2**, of Pc-Ls, **1**, the syntheses of which have been previously reported,[13] have been obtained in almost quantitative yields from different sources; respectively, silver tetrafluoroborate (**X¹**), silver triflate (**X²**), and silver bis-triflimidate (**X³**) (Scheme 1).



1a, **2a**: R = R^1 = H, Ar = Ph
1b, **2b**: R = CH_3, R^1 = H, Ar = Ph
1c, **2c**: R = R^1 = H, Ar = Naphthyl
1d, **2d**: R = CH_3, R^1 = H, Ar = Naphthyl
1e, **2e**: R = CH_3, R^1 = *i*Pr, Ar = Naphthyl

2a–e¹: X^1 = BF_4
2a–e²: X^2 = OTf
2a³, **2d–e³**: X^3 = $N(Tf)_2$

Scheme 1. Synthesis of [Ag^I(Pc-L)] complexes **2**.

Each silver(I) salt was added at room temperature to a solution of the ligand **1** in DCE (DCE = 1,2-dichloroethane) and the reaction mixture was stirred for one hour, keeping the flask in the dark and under a protective atmosphere until isolation of the final product. Silver complexes **2** were easily obtained as white crystals in yields up to 91% by precipitation, concentrating the solvent, and adding *n*-hexane. Complexes **2a¹⁻³** and **2c¹,²** have been already described,[17,18] and experimental details for all others complexes can be found in the Experimental Section and in the Supporting Information. All the obtained silver complexes **2** have been fully characterized by ^{1}H and ^{13}C NMR spectroscopy, ESI-MS, and IR and UV/Vis spectroscopy.

All attempts to synthesize a complex with chloride as the counterion met with failure. In fact, when we conducted the reaction between ligand **1a** and silver chloride, we did not observe the dissolution of the silver salt, and when we tried an anion-exchange reaction between complex **2a¹** and tetrabutylammonium chloride, silver chloride precipitated immediately from the solution. This fact suggested that silver complexes **2** could be quite sensitive to any free halide source present in the environment. In particular, when using chloroform, care must be taken to avoid the presence of HCl in the solvent.

Even though all silver complexes **2** can be used in an air atmosphere without any observable decomposition, they are quite sensitive to atmospheric moisture and tend to form monoaquo species, as demonstrated by single-crystal X-ray structure for complex **2a¹** (Figure 1). Interestingly, there are two molecules in the asymmetric unit, showing significantly different conformations and coordination modes of the ligand. The ideal geometry of the complex is a square pyramid, with a water molecule occupying the vertex and the four N atoms at the base. However, the base is irregular because the coordination of the N–Ts groups to Ag is weaker than that of the pyridine and the N–benzyl groups (see bond lengths in caption of Figure 1). In addition, the O atoms of the Ts groups are very close to the coordination sphere (Ag···O distances are in the range 3.2–3.9 Å). One of the two independent molecules of **2a¹** has a distorted conformation of one N–Ts group, which is due to the hydrogen-bond linkage with one co-crystallized water molecule. This produces a conformational change that brings one O atom, O(23), into a position with a rather short distance to Ag(2) (see caption of Figure 1). The ideal square pyramid is substantially distorted and the coordination at the Ag is extended to six atoms. This demonstrates the rather unstable configuration of the complex, which is easily subjected to severe deformations induced even by a weak intermolecular perturbation. The stereochemistry of the complex in solution is very likely even more flexible.

We evaluated the effect of the counterion on the NMR spectra of silver complexes **2**, choosing **2a¹⁻³** as case studies and, as expected, we observed the same signals in the ^{1}H, ^{13}C, and ^{15}N NMR spectra without any dependence on the coordinating features of the counterion. These complexes showed an apparent *Cs* symmetry of the structure in solution, with two signals for each couple of equivalent methylene groups. The ^{1}H-^{19}F heteronuclear Overhauser effect spectroscopy (HOESY) experiment conduced in $CDCl_3$ showed that the tetrafluoroborate anion in complex **2a¹** has proximity interactions, mainly with the pyridine ring of the ligand (Figure S1 in the Supporting Information).

The UV/Vis spectra of complexes **2a¹** and **2a²** in chloroform showed the absence of absorption bands at wavelength higher than 290 nm, which is consistent with the observed absence of color and the d^{10} electronic configuration for the metal – no d–d transitions are allowed (Figure S2). The shape of the UV/Vis spectra of ligand **1a** does not vary

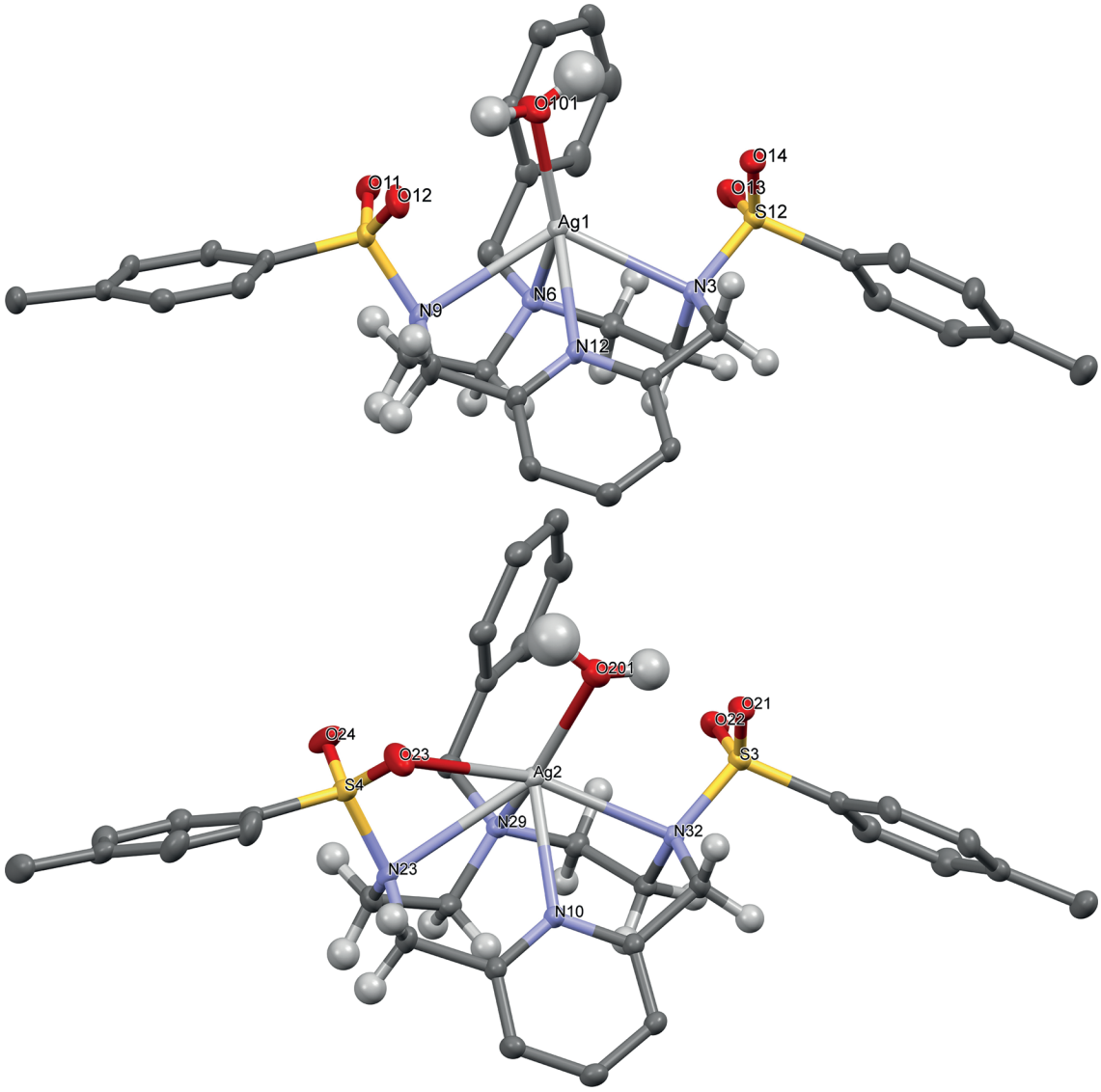


Figure 1. The structure of **2a**[1] with a molecule of water coordinated to the metal center. Two independent molecules are present in the asymmetric unit and both are shown here (with similar orientation). H atoms of the aryl groups are omitted for clarity. Atomic ellipsoids are drawn at 30% probability level. Principal bond lengths [Å]: Ag(1)–O(101) 2.258(4); Ag(1)–N(3) 2.549(3); Ag(1)–N(9) 2.785(4); Ag(1)–N(6) 2.384(4); Ag(1)–N(12) 2.448(3); Ag(2)–O(201) 2.394(3); Ag(2)–N(23) 2.830(4); Ag(2)–N(32) 2.608(3); Ag(2)–O(23) 2.847(4); Ag(2)–N(29) 2.387(4); Ag(2)–N(10) 2.407(3). Note that O(24) is involved in a rather strong intermolecular hydrogen bond with a co-crystallized water molecule (not shown in the figure).

as a result of complexation; however, the intensities of the absorptions are slightly different. For this reason, the bands recorded in the near-UV region can be assigned to ligand-centered transitions.

As previously reported for copper(I) complexes,[13] the effect of the metal complexation to the ligand was clearly disclosed by ^{1}H and ^{13}C NMR spectroscopy. The partial desymmetrization of the ligand backbone is more evident in the complexes with a pendant naphthyl group on the amine nitrogen (**2c**–**e**). For example, the ^{1}H NMR spectrum of complex **2d**[1] in $CDCl_3$ displays a very low degree of symmetry: the proton directly bound to carbon i, H^i, shifts to higher frequencies (δ = 9.42 ppm compared with δ = 8.16 ppm for the free ligand **1d**; Figure 2). Moreover, instead of being the expected doublet, it appears as a pseudo-triplet (J = 7.1 Hz) as a result of coupling with vicinal proton H^h (which in the free ligand resonates at δ = 7.43 ppm compared with δ = 8.00 ppm in the complex).[19] This is due to the η^2 coordination mode of the naphthyl group on silver(I), a feature that can also be observed by ^{13}C NMR spectroscopic studies in $CDCl_3$. The shift to low frequencies of the naphthyl carbon i, which is involved in the η^2 bond with silver, from δ = 124.0 ppm in the free ligand to δ = 104.7 ppm in the complex, is associated with a small frequency shift for carbon h from δ = 126.4 ppm in **1d** to δ = 125.1 ppm in **2d**[1]. This kind of unsymmetrical shift of the signals of the carbon atoms involved in η^2 coordination bonds is common for strongly distorted alkenes coordinated to a metal atom.[20] In the complex **2d**[1], carbon i is held in close proximity to the silver atom by steric requirements

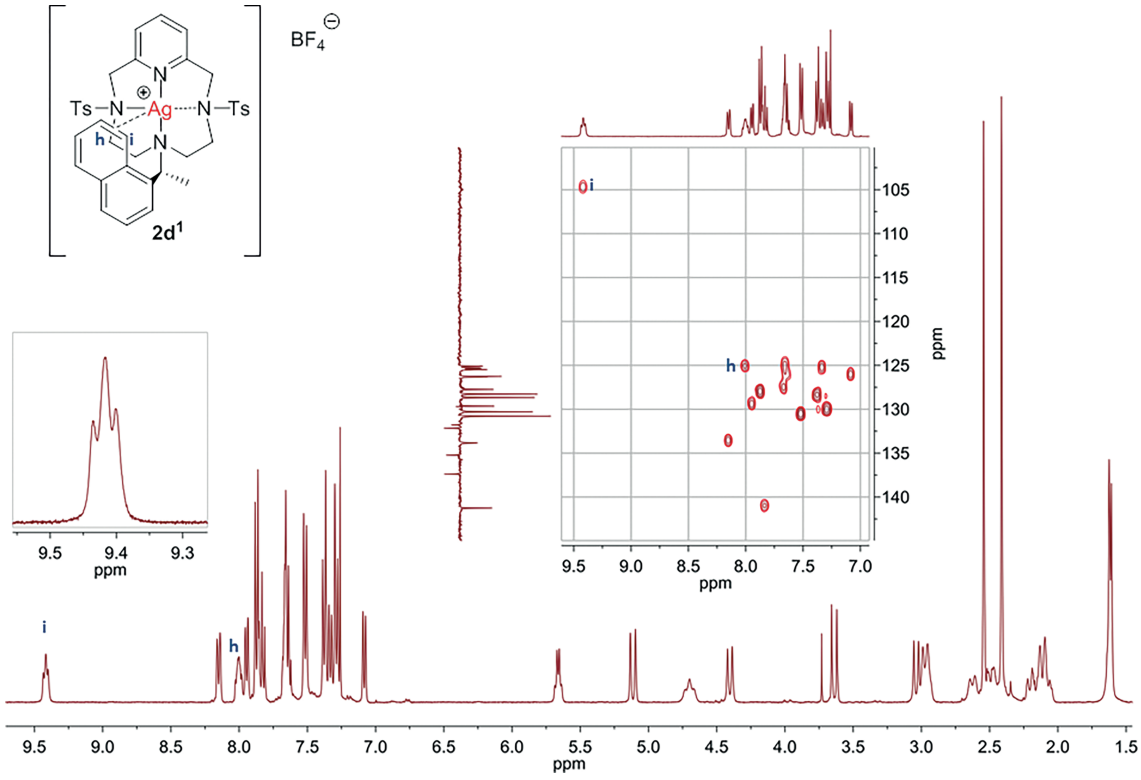


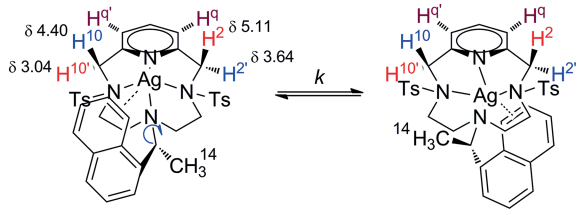
Figure 2. ^{1}H NMR spectrum of complex **2d^{1}** with highlighted carbon atoms, h and i, involved in η^2 coordination of the naphthyl on silver(I). Inset: Expansion of the signal corresponding to proton i as a triplet (J = 7.1 Hz). In the box, the ^{13}C-^{1}H heteronuclear single quantum correlation (HSQC) NMR spectrum of complex **2d^{1}**.

and, as a consequence, carbon h is less strongly coordinated. The resonance signal of carbon i can barely be located in the ^{13}C NMR spectrum when using the attached proton test pulse sequence, which is probably due to coupling with ^{107}Ag and ^{109}Ag nuclei.

The presence of a strong interaction between the naphthyl moiety and the silver atom allowed us to locate the resonance frequency of the ^{109}Ag atom by heteronuclear multiple bond correlation (HMBC) and HSQC techniques; the resonance was found at δ = 536 ppm (referenced to $AgNO_3$ 1 M in $CDCl_3$ at δ = 41.52 ppm). The main interactions of silver are seen with H^{i} and H^{h}, but other protons of the macrocyclic skeleton also correlate with the metal center (Figure S3). Proton-decoupled experiments allowed us to estimate the coupling constant between H^{i} and ^{109}Ag as $J^{2}_{Ag\text{-}H}$ = 6.0 Hz, which is close to the typical value of J^{ortho} for aromatic rings and justifies the appearance of H^{i} as a pseudo-triplet in the ^{1}H NMR spectrum. The ^{15}N NMR spectrum shows a marked shift from δ = 313 ppm to δ = 265 ppm for the pyridine nitrogen atom, N^{12} (see Exp. Sect. for numbering scheme). Notably, the sp^{3} nitrogen atom, N^{6}, bonded to the asymmetric carbon is almost not affected by coordination of the silver atom (δ = 39 ppm in the free ligand; δ = 40 ppm in the complex). From ^{1}H-^{19}F HOESY experiments conducted in $CDCl_3$, it is possible to determine the position of the BF_4^- anion, which is located on the opposite side to the naphthyl moiety and shows interactions with the methyl protons (H^{14}), the pyridine protons (H^{q}), and some of the protons of the macrocyclic backbone, which by 2D NMR spectroscopic techniques have been assigned as those pointing away from the silver ion (Figures S4 and S5). Unfortunately, we were not able to obtain single crystals of **2d**, but all the spectroscopic evidence we have collected points to a structure very close to that observed for the already reported analogous copper(I) complex of ligand **1d**.[12,13]

Interestingly, some signals were found to have positive cross peaks in the 2D NOESY experiments. On the basis of the attribution of chemical shift, it is evident, for example, that H^{2} must exchange with H$^{10'}$ (responsible for the resonances at δ = 5.11 and 3.04 ppm, respectively) and that H$^{2'}$ must exchange with H^{10} (responsible for the resonances at δ = 3.64 and 4.40 ppm, respectively). The observed exchange has been attributed to the flipping of the naphthyl moiety from one side to the other, with a complete inversion of the molecule (Scheme 2). To confirm the occurrence of this dynamic process, ^{1}H NMR exchange spectroscopy (EXSY) of complex **2d^{1}** in $CDCl_3$ was performed by varying the mixing times (τ_m = 5, 40, 60, 90, 250 ms; Figure 3). The integrated cross peak intensities and diagonal peak intensities determined from EXSY experiments (Table S1 in the Supporting Information) were used to determine the exchange rate for the process.[21] At 299.9 K, the pseudo first-order rate constant, k, was determined to be 0.20 ($\pm$0.02) s^{-1}. It should be pointed out that the calculated k_{xy} values for exchange of CH_2^{2} and CH_2^{10} protons in complex **2d^{1}** showed only little variation with different τ_m, as expected since J cross peaks arising from scalar cou-

pling make a negligible contribution to the intensities of the exchange cross peaks.[21d]



Scheme 2. Schematic view of the possible rotational process occurring in complex **2d**[1].

All silver complexes of ligands **1c**–**1e** are characterized by the coordination of the naphthyl pendant arm to the metal center, although from NMR spectroscopic data it is evident that in the case of ligand **1e**, the presence of the isopropyl substituents on the macrocyclic skeleton weakens the η^2 bond as a result of steric crowding. Having explored the coordination behavior of the naphthyl double bond to the silver(I) atom, we started to look at other coordinating ligands. By exposing a dichloroethane/hexane solution of **2c**[1] to acetonitrile vapor, we obtained the [(**2c**)(CH_3CN)]-BF_4 complex, which precipitated upon concentration of the solution. The complex [(**2c**)(CH_3CN)]BF_4 was recovered by filtration and characterized by NMR spectroscopy. The ^1H NMR spectrum in $CDCl_3$ shows the presence of exactly one equivalent of CH_3CN per silver atom, as demonstrated by the presence of a single CH_3 signal of acetonitrile, located at δ = 2.08 ppm, shifted by only a small amount from its position in the uncoordinated molecule (δ = 2.10 ppm). The X-ray crystallographic structure of this complex confirmed the tendency of these species to bind an additional ligand and showed that the metal is located in a very low symmetry site (Figure 4). The structure of **2c**[1] is closer to a regular square pyramid with strong coordination to the CH_3CN molecule and again weaker coordination to N–Ts groups.

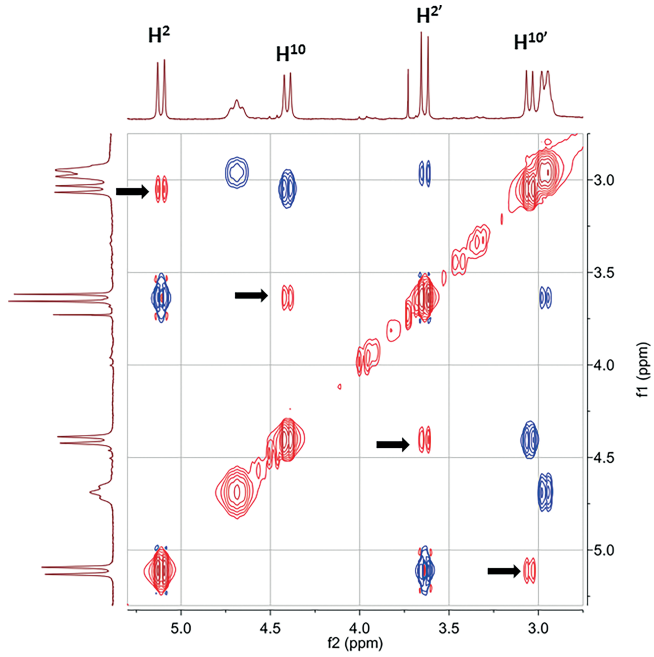


Figure 3. ^1H NMR NOESY (400 MHz) spectrum for the CH_2 region of **2d**[1] in $CDCl_3$ at T = 299.9 K. Mixing time (τ_m) was 250 ms. Exchange cross peaks marked with black arrows. Negative cross peaks arise from NOE interactions.

In this complex, no special intermolecular interaction with the anion or with the clathrated solvent is distorting the molecular geometry; therefore, the SO_2 groups of Ts are not induced to coordinate the metal (the Ag···O distances

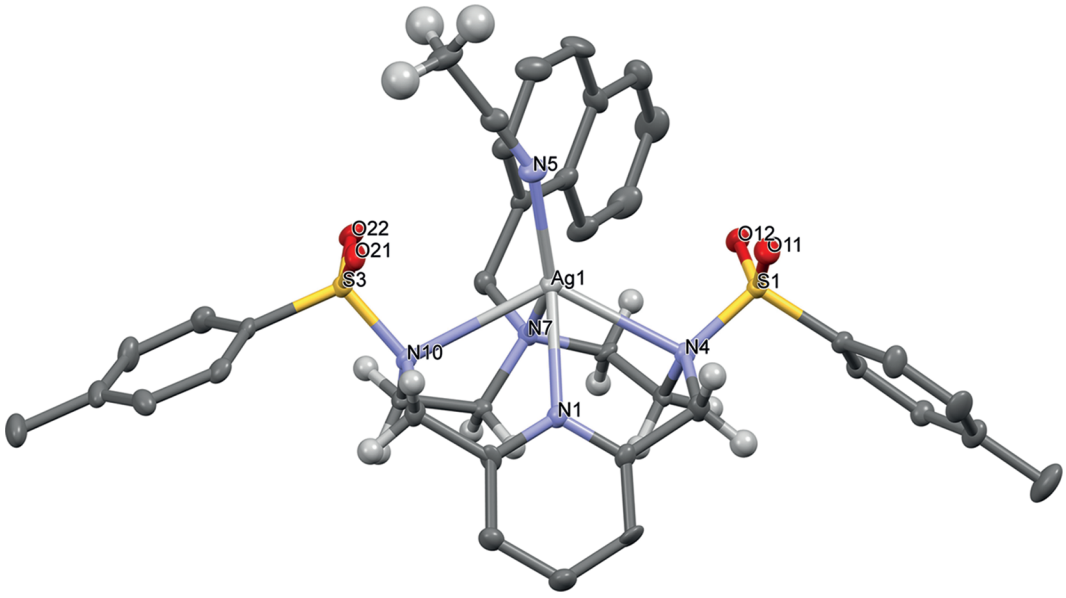


Figure 4. Structure of [(**2c**)(CH_3CN)]BF_4 with a molecule of CH_3CN coordinated to the metal center. H atoms of aryl groups are omitted for clarity. Atomic ellipsoids drawn at 30% probability level. Principal bond lengths [Å]: Ag(1)–N(5) 2.194(5); Ag(1)–N(7) 2.378(5); Ag(1)–N(1) 2.424(5); Ag(1)–N(4) 2.624(5); Ag(1)–N(10) 2.758(5).

are rather long at 3.6–3.8 Å). Figure 4 reports the main bond lengths.

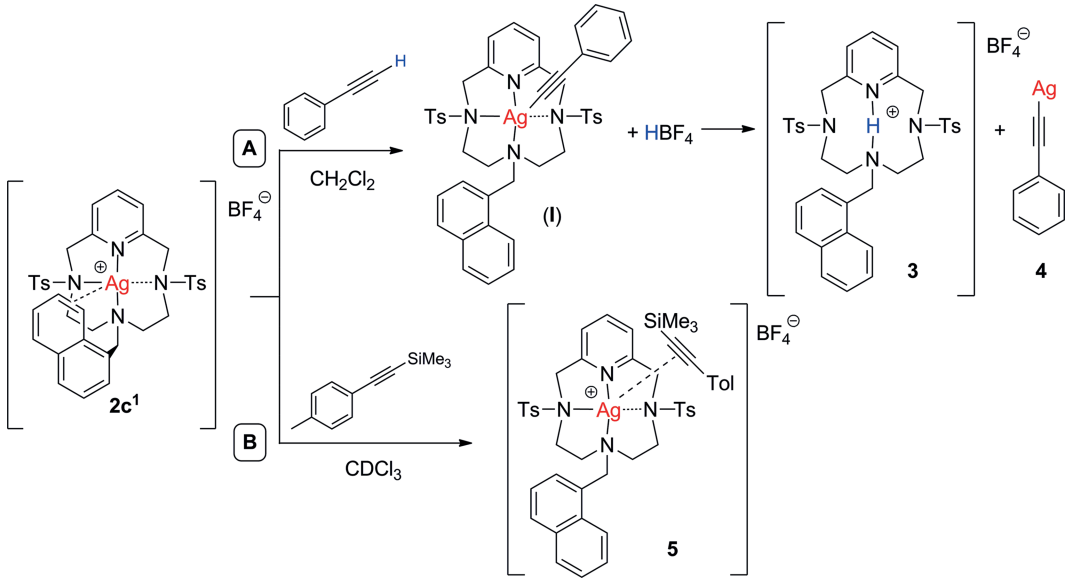
The coordination of acetonitrile to the silver(I) complexes in solution was monitored by IR spectroscopy. After the addition of two equivalents of CH_3CN to a DCE solution of **2c**^{1}, four absorption bands were observed between 2400–2200 cm^{-1} (Figure S6). The bands at 2256 and 2294 cm^{-1} correspond to the vibration modes of free acetonitrile, specifically the C≡N triple bond stretching for the former and a combination of C–H bending and C–C stretching for the latter. The two new bands at 2279 and 2308 cm^{-1} are related to the coordinated nitrile. Their shift to higher energies is a common occurrence in metal–acetonitrile complexes because the lone pair of the nitrogen lies in an orbital with partial antibonding character. As a consequence, the electron donation to the metal increases the strength of the C≡N bond, together with the force constant of its vibrational mode.[22]

The silver complexes **2** are also capable of coordinating carbon monoxide, albeit in a weak manner. The IR spectrum of a dichloromethane solution of **2c**^{1} exposed for 2 h to a 1 bar CO atmosphere displayed an absorption band at 2156 cm^{-1} (Figure S7), which is located at a higher frequency than the band of free CO (2143 cm^{-1}). This indicates that the CO adduct of **2c**^{1} is a non-classical metal carbonyl,[23] meaning that back-donation from the metal to the antibonding CO orbital is scarce or null. This behavior is not unexpected for a d^{10} closed-shell ion.[24] Brief exposure to alternating vacuum and nitrogen flushing resulted in the disappearance of the CO band from the IR spectrum.

We prepared the analogous CO complex of **2c**^{2} in deuterated chloroform with isotopically enriched carbon monoxide to easily detect the signal of the species [(**2c**)(^{13}CO)]-OTf. The CO resonance was found at δ = 177.3 ppm (Figure S8), which is shifted to a lower frequency than non-coordinated CO (δ = 181.3 ppm).[25] Nevertheless, the latter was not detected, despite the presence of a ^{13}CO atmosphere in the sample tube and, consequently, of some carbon monoxide in the $CDCl_3$ solution. This can be justified by the existence of a fast equilibrium on the NMR spectroscopic timescale between dissolved CO and metal-coordinated CO. As a consequence, the observed signal could be due to the averaged environment of the CO molecules.[26] This is in contrast with what was observed for the analogous copper complexes, which, under the same conditions, exhibit two different signals for CO,[13] thus suggesting a stronger coordination mode.

Concerning the catalytic applications we previously reported for these compounds,[17,18] the interactions with alkynes are those of greatest interest. We found that **2c**^{1} reacted with a terminal alkyne, such as phenylacetylene, to give silver phenylacetylide **4** and the protonated ligand **3**, which partially precipitated as the tetrafluoroborate salt. This behavior suggests that in the absence of a proton scavenger, phenylacetylene reacts with **2c**^{1} to give the corresponding acetylide complex (**I**) and HBF_4, which is able to undermine the silver phenylacetylide, causing the decomplexation and the protonation of the ligand **1c** (Scheme 3, path A). Conversely, when an internal alkyne such as trimethyl(*p*-tolylethynyl)silane was used, η^2 coordination occurred to give the complex **5**, without any undesired decomposition reaction (Scheme 3, path B).

The complex **5** was fully characterized by NMR spectroscopy. Evidence of the complexation, upon addition of 3 equiv.[27] of trimethyl(*p*-tolylethynyl)silane to **2c**^{1}, was gathered from the ^{1}H, ^{13}C, and ^{29}Si spectra (Table 1). The differences in chemical shift between the signals of free versus coordinated alkyne are fairly small: δ = –17.08 versus –17.29 ppm for the ^{29}Si signal, δ = 2.36 versus 2.33 ppm for the ^{1}H signal of the methyl group, and δ = 91.3/105.5 versus 93.2/105.4 ppm for the two C_{sp} carbon atoms (see the Supporting Information for details). These small differences are

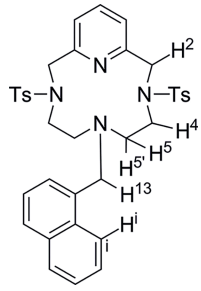


Scheme 3. Reaction of **2c**^{1} with phenylacetylene (path A) and trimethyl(*p*-tolylethynyl)silane (path B).

likely due to the presence of an excess of uncoordinated alkyne in equilibrium with the complex, and the remoteness of the methyl groups from the coordination center. On the other hand, the effects on the ligand are quite evident, with the signal of H^i down-field shifted to δ = 7.93 ppm, (a more significant shift than those observed with any other species), and the signals of H^5 and $H^{5'}$ diverging to δ = 3.09 and 1.91 ppm, respectively (see Table 1 for numbering scheme).

The down-field shift of the H^i signal of complex **2c**[1], towards the position observed in the free ligand **1c**, is a common feature for complexes **2c**–**e**, characterized by the presence of a naphthyl pendant able to coordinate to the silver as an additional ligand. Upon interaction with an external nucleophile, the displacement of the η^2-coordinated naphthyl group from the metal is responsible of a geometrical rearrangement of the ligand, causing the difference in chemical shifts. Smaller chemical shifts were observed for the corresponding ^{13}C signals, as well as for other protons (Table 1). The entity of these shifts varies with the nature of the external ligand, and could in principle be taken as a measure of the strength of coordination of weak ligands, which are in equilibrium with the free ligand in solution. The larger the fraction of complex that is bound to an auxiliary ligand, the larger the shift value. The η^2 alkyne coordinated complex **5** shows the biggest effects, with H^i at δ = 7.93 ppm, which is even lower than that of the free ligand **1c**; this probably depends on the different conformations that are accessible to the naphthyl moiety in the free ligand to relieve steric crowding.

Table 1. Chemical shifts for some selected signals in $CDCl_3$ and the numbering scheme adopted.



Compound	H^i	C^i	H^2	H^4	$H^5/H^{5'}$	H^{13}
1c	8.13	125.1	4.30	3.07	2.34	3.92
2c	9.16	111.8	4.87/ 3.59	3.54/ 2.73	2.85/ 2.25	4.36
2c(L), L =						
CO	8.94	114.4	4.93/ 3.59	3.49/ 2.63	2.88/ 2.17	4.36
CH_3CN	8.71	117.5	4.99/ 3.57	3.45/ 2.59	2.89/ 2.16	4.38
TolC≡$CSiMe_3$	7.93	124.9	4.93/ 3.59	3.45/ 2.59	3.09/ 1.91	4.31

Alcohols have been demonstrated to be suitable reagents in the domino synthesis of isochromenes catalyzed by silver complexes **2b**,[17] but in some cases we observed a quite prolonged induction time. Thus, we were intrigued to study the coordination of 2-propanol to silver complex **2b**[1]. We have

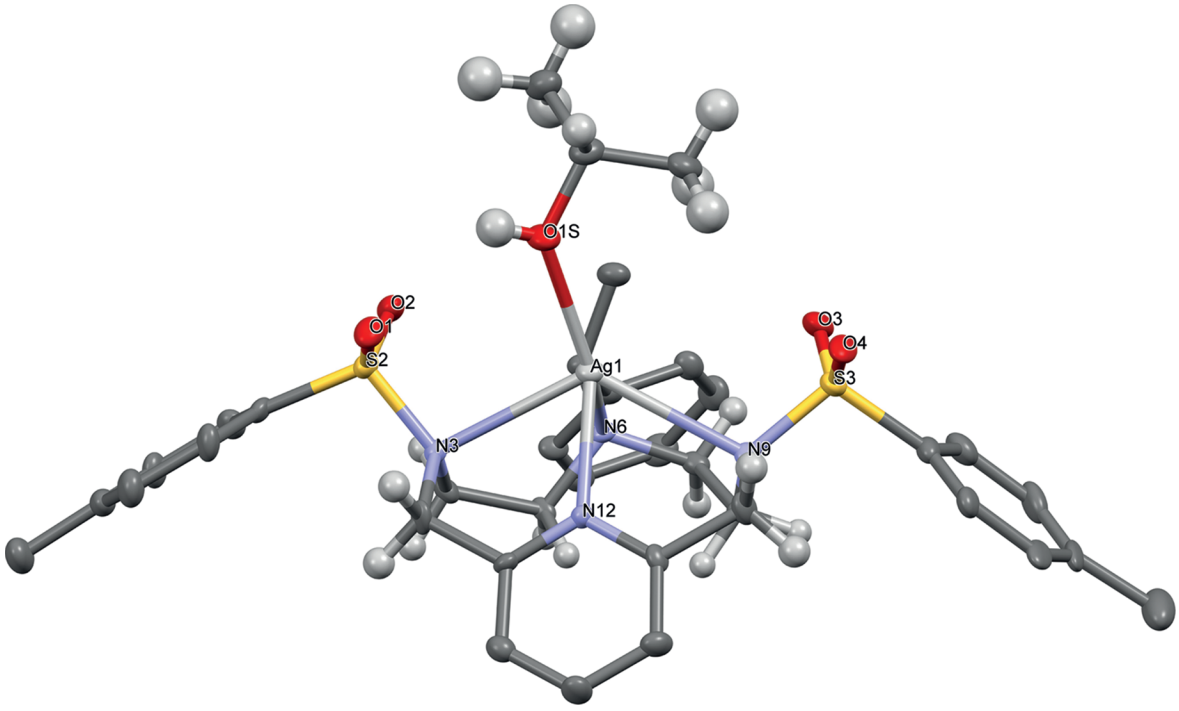


Figure 5. Structure of [(**2b**)(*i*PrOH)]BF_4 with a molecule of 2-propanol coordinated to the metal center. H atoms of aryl groups are omitted for clarity. Atomic ellipsoids drawn at 30% probability level. Principal bond lengths [Å]: Ag(1)–N(3) 2.674(5); Ag(1)–N(6) 2.435(7); Ag(1)–N(9) 2.424(5); Ag(1)–N(12) 2.661(6); Ag(1)–O(1S) 2.283(8).

chosen a secondary alcohol, as they have been used with success as nucleophiles in the above-mentioned reaction. We were, in fact, confident that their coordination to silver(I) could protect the metal complex from adsorbing atmospheric moisture, especially in complexes **2a**,**b** in which the ligands do not possess the pendant naphthyl moiety. The presence of an alcoholic ligand can slow down the reaction without killing the catalytic activity. The silver complex **2b**^{1} is only slightly soluble in 2-propanol and after two hours of heating at reflux a white solid was collected and characterized by NMR spectroscopic experiments as [(**2b**)-(*i*PrOH)]BF_4 (see the Supporting Information). Crystals suitable for X-ray crystallography were grown from a saturated solution of **2b**^{1} in propanol by layering *n*-hexane (Figure 5).

The structure of **2b**^{1} is also a square pyramid with coordination of 2-propoanol in the apical position, as for **2c**^{1} and **2a**^{1}, the Ag–O coordination is the shortest bond. The two N–tosyl groups are symmetrically coordinated and the O atoms of the SO_2 groups are quite distant from the metal (in the range 3.4–3.9 Å). No solvent molecule is clathratred in this crystal; therefore, the intermolecular interactions are weak and do not perturb the molecular geometry too much, demonstrating that the square pyramid is the preferred stereochemistry. The apical ligand, however, is somewhat distorted from the ideal site, as a result of a medium–weak intramolecular hydrogen bond occurring with O1, which moves O1S away from the vertical axis of the pyramid, as visible from Figure 5.

Conclusion

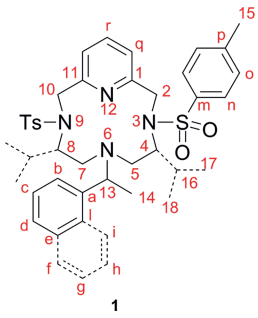
The silver(I) complexes with pyridine-containing ligands, [Ag^{I}(Pc-L)], have already been demonstrated as active catalysts for some domino and multicomponent reactions, such as the synthesis of 1-alkoxyisochromenes[17] and the A^3-coupling.[18] We have reported here their rich coordination chemistry with special emphasis on their behavior with reagents commonly employed in the above-mentioned reactions. Both the π-philic (alkyne coordination) and the σ-philic (alcohol and nitrile coordination) nature of silver(I) has been clearly demonstrated. The weak and reversible coordination of CO to the silver atom has been monitored experimentally to show that the interaction has mainly σ-donor character from the ligand to the metal, as expected. The hygroscopic nature of the complexes has been highlighted, also demonstrated by a structural determination of a water-containing complex that was obtained after exposure to atmospheric moisture (non-distilled solvents). Moreover, the silver complexes of the chiral ligands **1b** and **1d**–**e** have been prepared and fully characterized. All these data shed some light on the in-depth understanding of the catalytic reactions under study. Current efforts in our laboratory are devoted to finding new interesting reactivities of the silver complexes to scrutinize new potential nucleophiles for the silver(I) catalyzed synthesis of isochromenes, and to explore the capability of the chiral complexes to induce stereoselectivity in these transformations.

Experimental Section

General Experimental Details: All of the reactions that involved the use of reagents sensitive to oxygen or moisture were carried out under an inert atmosphere. The syntheses of the silver complexes were carried out under a nitrogen atmosphere by employing standard Schlenk techniques. All chemicals and solvents were commercially available and were used after distillation or treatment with drying agents. ^{1}H NMR spectroscopic analyses were performed with 300 or 400 MHz spectrometers at room temperature. Deuterated solvents were passed over basic alumina, degassed, and stored under nitrogen over molecular sieves. Samples were degassed prior to acquisition with three freeze–pump–thaw cycles. The coupling constants (*J*) are expressed in Hertz (Hz), and the chemical shifts (δ) in ppm. ^{13}C NMR spectroscopic analyses were performed with the same instruments at 75.5 and 100 MHz, and an attached proton test (APT) sequence was used to distinguish the methine and methyl carbon signals from those arising from methylene and quaternary carbon atoms. All ^{13}C NMR spectra were recorded with complete proton decoupling. The ^{1}H NMR signals of the ligand described in the following have been attributed by correlation spectroscopy (COSY) and nuclear Overhauser effect spectroscopy (NOESY) techniques. Assignments of the resonance in ^{13}C NMR spectra were made using the APT pulse sequence and heteronuclear single quantum correlation (HSQC) and heteronuclear multiple bond correlation (HMBC) techniques. The ^{15}N and ^{109}Ag NMR signals of the compounds described have been attributed by the HMBC technique and were referenced to external NH_3 at δ = 0.00 ppm and 1 M $AgNO_3$ in $CDCl_3$ at δ = 41.52 ppm, respectively. The chemical shifts of the ^{11}B and ^{19}F NMR signals of the compounds described have been attributed employing $BF_3{\cdot}Et_2O$ and $CFCl_3$, respectively, as references. 2D NOESY or EXSY experiments were recorded by using the *noesygpph* pulse program and were recorded at τ_m = 5, 40, 60, 90, 250, and 900 ms and with a recycle delay d_1 = 2 s, adjusting the temperature at *T* = 299.88 K (calibrated). Low resolution MS spectra were recorded with instruments equipped with electron ionization (EI), ESI/ion trap (using a syringe pump device to directly inject sample solutions), or fast atom bombardment (FAB) (for Pc-L and metal complexes) sources. The values are expressed as mass–charge ratios and the relative intensities of the most significant peaks are shown in brackets. High resolution MS spectra were recorded with an instrument equipped with an electrospray source and an ion cyclotron resonance–Fourier transform mass spectroscopy (ICRFTMS) analyzer. UV/Vis spectra of the ligands and their silver complexes were recorded in $CHCl_3$. Elemental analyses were recorded in the analytical laboratories of Università degli Studi di Milano. Data collections for the crystal structure determinations were carried out using an Agilent SuperNova Mo microsource, Al-filtered[28] and working at 50 kV and 0.8 mA. All crystal structures were solved by direct methods using SHELXS97 and refined with SHELX97,[29] within the wings suite of programs.[30] H atoms were rigidly modeled on the riding C or N atoms. Optical rotations were measured on a Perkin–Elmer instruments model 343 plus. $[\alpha]_D$ values are given in 10^{-1} deg cm^2 g^{-1}. The ligands **1a**–**e**[12–14] and the silver(I) complexes **2a**$^{1-3}$ and **2c**^{1,2} were synthesized as previously reported.[17,18]

General Procedure for the Synthesis of Silver Complexes 2b,d,e: The silver salt and all silver-containing solutions were kept in the dark until the final isolation of the product. Ligand **1** was dissolved in 1,2-dichloroethane (≈ 2×10^{-2} M), the silver salt (weighed under a nitrogen atmosphere) was added, and the mixture was stirred for 1 h, then filtered to remove any traces of unreacted solid. The solvent was concentrated to half volume, then *n*-hexane was added.

The mixture was evaporated to dryness and *n*-hexane was added again, yielding a well-dispersed white powder. Finally, the product was recovered by filtration in open air.



1

Selected Experimental Data (See the Supporting Information for Full Details)

2b^1-(13 *S*): 1b-(13 *S*) (M_W = 618.81; 0.246 g; 0.398 mmol), $AgBF_4$ (M_W = 194.67; 0.077 g; 0.398 mmol), $C_2H_4Cl_2$ (20 mL), and *n*-hexane (≈ 40 mL) were used as described above. Yield: 0.217 g (M_W = 813.48) 67%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.82 (m, 4 H, H^n), 7.68 (t, J = 7.7 Hz, 1 H, H^r), 7.48–7.35 (m, 10 H, ArH + H^o + $H^{q'}$), 7.22 (d, J = 7.7 Hz, 2 H, H^q), 5.14 (d, J = 15.9 Hz, 1 H, CH_2^2), 4.83–4.80 (m, 2 H, CH_2^{10} and CH^{13}), 4.01 (m, 1 H, CH_2), 3.85 (d, J = 15.9 Hz, 1 H, C$H_2^{2'}$), 3.73 (m, 1 H, CH_2), 3.59 (d, J = 14.9 Hz, 1 H, C$H_2^{10'}$), 2.97 (m, 1 H, CH_2), 2.57 (m, 1 H, CH_2), 2.48 (br. s, 6 H, CH_3^{15} and C$H_3^{15'}$), 2.35 (m, 1 H, CH_2), 2.12 (m, 1 H, CH_2), 1.77 (d, J = 6.0 Hz, 3 H, CH_3^{14}) overlapping with 1.75–1.68 (m, 2 H, CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.0 (C^1), 152.6 (C^{11}), 146.1 (C), 145.8 (C), 140.4 (C^rH), 137.5 (C), 131.3 (C), 130.8 (C^oH), 130.7 ($C^{o'}$H), 129.5 (CH), 129.3 (C), 128.9 (CH), 128.2 (CH), 127.9 (C^nH), 125.5 ($C^{q'}$H), 124.8 (C^qH), 56.7 (C^2H_2), 56.6 (C^{13}H), 56.3 ($C^{10}H_2$), 49.0 (CH_2), 48.4 (CH_2), 48.0 (CH_2), 46.1 (CH_2), 21.8 ($C^{15}H_3$), 19.2 ($C^{14}H_3$) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –152.85 ($^{10}BF_4$), –152.90 ($^{11}BF_4$) ppm. MS (FAB): *m*/*z* (%) = 725/727 (91:100) [M – BF_4]$^+$, 619 (35) [MH – $AgBF_4$]$^+$. $C_{33}H_{38}AgBF_4N_4O_4S_2$ (813.48): calcd. C 48.72, H 4.71, N 6.89; found C 48.75, H 4.51, N 6.53.

2d^1-(13 *R*): 1d-(13 *R*) (M_W = 668.87; 0.297 g; 0.444 mmol), $AgBF_4$ (M_W = 194.67; 0.089 g; 0.457 mmol), $C_2H_4Cl_2$ (12 mL), and *n*-hexane (≈ 20 mL) were used as described above. Yield: 0.375 g (M_W = 863.54) 98%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.42 (pst, J = 7.1 Hz, 1 H, H^i), 8.15 (d, J = 8.3 Hz, 1 H, ArH), 8.00 (m, 1 H, H^h), 7.94 (d, J = 7.5 Hz, 1 H, ArH), 7.87 (d, J = 8.2 Hz, 2 H, H^n), 7.83 (pst, J = 7.8 Hz, 1 H, H^r), 7.68–7.62 (m, 3 H, ArH), 7.52 (d, J = 8.2 Hz, 2 H, H^o), 7.38 (d, J = 8.2 Hz, 2 H, $H^{n'}$), 7.33 (d, J = 7.9 Hz, 1 H, $H^{q'}$), 7.29 (d, J = 8.2 Hz, 2 H, $H^{o'}$), 7.08 (d, J = 7.6 Hz, 1 H, H^q), 5.66 (q, J = 6.7 Hz, 1 H, CH^{13}), 5.11 (d, J = 15.4 Hz, 1 H, CH_2^2), 4.70 (m, 1 H, CH_2^4), 4.40 (d, J = 13.9 Hz, 1 H, CH_2^{10}), 3.64 (d, J = 15.4 Hz, 1 H, C$H_2^{2'}$), 3.04 (d, J = 13.9 Hz, 1 H, C$H_2^{10'}$), 2.99–2.95 (m, 2 H, CH_2), 2.63 (m, 1 H, CH_2), 2.54 (s, 3 H, CH_3^{15}), 2.49 (m, 1 H, CH_2), 2.41 (s, 3 H, C$H_3^{15'}$), 2.41–2.09 (m, 3 H, CH_2), 1.65 (d, J = 6.7 Hz, 3 H, CH_3^{14}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.3 (C^1), 152.6 (C^{11}), 145.9 (C^p), 145.7 ($C^{p'}$), 141.3 (C^rH), 137.4 (C), 135.2 (C), 133.8 (CH), 132.4 (C), 131.8 (C), 130.8 (C^oH), 130.3 ($C^{o'}$H), 129.7 (C), 129.6 (CH), 128.7 ($C^{n'}$H), 128.3 (C^nH), 127.7 (CH), 126.30 (CH), 126.26 (CH), 125.5 (CH), 125.3 (CH), 125.1 (C^hH), 104.7 (C^iH)*, 56.7 (C^2H_2), 56.4 ($C^{10}H_2$), 51.8 (C^{13}H), 49.2 (CH_2), 48.9 (CH_2), 48.8 (CH_2), 45.5 (CH_2), 21.9 ($C^{15}H_3$), 21.8 ($C^{15'}H_3$), 9.0 ($C^{14}H_3$)* ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –153.03 ($^{10}BF_4$), –153.08 ($^{11}BF_4$) ppm. ^{11}B NMR (128 MHz, $CDCl_3$): δ = –1.39 (p, J_{B-F} = 1.1 Hz) ppm. ^{15}N NMR (40 MHz, $CDCl_3$): δ = 265 (N^{12}), 101 and 97 (N^3 and N^9), 40 (N^6) ppm. ^{109}Ag NMR (19 MHz, $CDCl_3$): δ = 536 ppm. $C_{37}H_{40}AgBF_4N_4O_4S_2$ (863.54): calcd. C 51.46, H 4.67, N 6.49; found C 51.15, H 4.57, N 6.21.

2e^1-(4 *S*,8 *S*,13 *R*): 1e-(4 *S*,8 *S*,13 *R*) (M_W = 753.03; 0.143 g; 0.190 mmol), $AgBF_4$ (M_W = 194.67; 0.037 g; 0.190 mmol), $C_2H_4Cl_2$ (7 mL), and *n*-hexane (≈ 14 mL) were used as described above. Yield: 0.0943 g (M_W = 947.70) 52%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.69 (d, J = 8.4 Hz, 1 H, H^i), 8.08–7.86 (m, 6 H, ArH), 7.81 (d, J = 7.6 Hz, 1 H, ArH), 7.72 (pst, J = 7.5 Hz, 1 H, H^h), 7.59–7.44 (m, 8 H, ArH), 7.37 (d, J = 7.5 Hz, 1 H, ArH), 6.02 (q, J = 6.5 Hz, 1 H, CH^{13}), 5.38 (d, J = 17.5 Hz, 1 H, CH_2^2), 4.93 (d, J = 14.0 Hz, 1 H, CH_2^{10}), 4.59 (pst, J = 12.1 Hz, 1 H, CH_2), 4.24 (d, J = 17.5 Hz, 1 H, C$H_2^{2'}$), 4.17 (m, 1 H, CH), 4.07 (d, J = 14.0 Hz, 1 H, C$H_2^{10'}$), 2.50 (s, 3 H, CH_3^{15}), 2.47 (s, 3 H, C$H_3^{15'}$) overlapping with 2.49 (m, 1 H, CH_2), 2.30–2.20 (m, 2 H, CH^{16} and CH), 2.04 (d, 3 H, J = 6.5 Hz, CH_3^{14}), 1.62 (m, 2 H, CH_2), 1.03 (m, 1 H, C$H^{16'}$), 0.88 (m, 3 H, CH_3^{17}), 0.46 (d, 3 H, J = 5.6 Hz, CH_3^{18}), –0.01 (d, 3 H, J = 5.0 Hz, C$H_3^{17'}$), –0.32 (d, 3 H, J = 5.6 Hz, C$H_3^{18'}$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.8 (C), 152.6 (C), 145.8 (C), 145.5 (C), 141.3 (CH), 135.3 (C), 134.52 (C), 134.48 (C), 134.4 (C), 132.5 (C), 130.8 (CH), 130.6 (CH), 129.8 (CH), 128.8 (CH), 128.4 (CH), 127.2 (CH), 126.8 (C^hH), 126.5 (CH), 126.0 (CH), 125.3 (CH), 125.0 (CH), 124.2 (CH), 122.7 (C^iH), 63.6 (CH), 59.1 (CH), 57.1 ($C^{10}H_2$), 54.4 (C^{13}H), 54.1 (CH_2), 52.5 (CH_2), 49.1 (C^2H_2), 30.4 (CH), 28.4 ($C^{16'}$H), 23.9 ($C^{14}H_3$), 22.7 ($C^{18}H_3$), 21.8 ($C^{15}H_3$ and $C^{15'}H_3$), 21.1 ($C^{17}H_3$), 21.0 ($C^{18'}H_3$), 17.7 ($C^{17'}H_3$) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –153.13 ($^{10}BF_4$), –153.19 ($^{11}BF_4$) ppm. ^{15}N NMR (40 MHz, $CDCl_3$): δ = 270 (N^{12}), 45 (N^6) ppm; N^3 and N^9 were not detected. $C_{43}H_{52}AgBF_4N_4O_4S_2$ (947.70): calcd. C 54.50, H 5.53, N 5.91; found C 54.35, H 5.90, N 5.89.

Supporting Information (see footnote on the first page of this article): Detailed experimental procedures, text, figures, and tables reporting full NMR spectra for all compounds along with 2D NMR spectra for compound **2d^1** and data for naphthylidene rotation rate determination. UV and IR spectra for coordination complexes and crystallographic details.

CCDC-1413034 [for **2a^1**(H_2O)], 1413035 [for **2c^1**(CH_3CN)], and 1413036 [for **2b^1**(*i*PrOH)] contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

Financial support from the Università degli Studi di Milano (Sviluppo Unimi Bando TRANSITION GRANT – HORIZON 2020 – Linea A1_B Progetto "Italia per l'Europa. Cod.: 18499") is gratefully acknowledged.

[1] L. F. Lindoy, *The Chemistry of Macrocyclic Ligand Complexes*, Cambridge University Press, Cambridge, UK, **1992**.
[2] D. K. Cabbiness, D. W. Margerum, *J. Am. Chem. Soc.* **1969**, *91*, 6540–6541.
[3] A. E. Martell, "The Chelate Effect" in *Werner Centennial, Vol. 62*, Advances in Chemistry ACS, **1967**, pp. 272–294.
[4] R. D. Hancock, *J. Chem. Educ.* **1992**, *69*, 615–621.
[5] N. F. Curtis, *J. Chem. Soc.* **1960**, 4409–4413.
[6] B. P. Burke, S. J. Archibald, *Annu. Rep. Prog. Chem. Sect. A* **2013**, *109*, 232–253.
[7] D. E. Fenton, *Chem. Soc. Rev.* **1999**, *28*, 159–168.

[8] a) S. Hong, B. Wang, M. S. Seo, Y.-M. Lee, M. J. Kim, H. R. Kim, T. Ogura, R. Garcia-Serres, M. Clémancey, J.-M. Latour, W. Nam, *Angew. Chem. Int. Ed.* **2014**, *53*, 6388–6392; *Angew. Chem.* **2014**, *126*, 6506; b) W. Ye, D. M. Ho, S. Friedle, T. D. Palluccio, E. V. Rybak-Akimova, *Inorg. Chem.* **2012**, *51*, 5006–5021; c) T. A. Jackson, J.-U. Rohde, M. S. Seo, C. V. Sastri, R. DeHont, A. Stubna, T. Ohta, T. Kitagawa, E. Münck, W. Nam, L. Que, *J. Am. Chem. Soc.* **2008**, *130*, 12394–12407.
[9] a) C. V. Esteves, J. Madureira, L. M. P. Lima, P. Mateus, I. Bento, R. Delgado, *Inorg. Chem.* **2014**, *53*, 4371–4386; b) J. Y.-C. Chang, G.-L. Lu, R. J. Stevenson, P. J. Brothers, G. R. Clark, K. J. Botting, D. M. Ferry, M. Tercel, W. R. Wilson, W. A. Denny, D. C. Ware, *Inorg. Chem.* **2013**, *52*, 7688–7698; c) L. M. P. Lima, D. Esteban-Gomez, R. Delgado, C. Platas-Iglesias, R. Tripier, *Inorg. Chem.* **2012**, *51*, 6916–6927; d) S. J. Archibald, *Annu. Rep. Prog. Chem. Sect. A* **2012**, *108*, 271–291; e) S. J. Archibald, *Annu. Rep. Prog. Chem. Sect. A* **2009**, *105*, 297–322; f) R. Delgado, V. Felix, L. M. P. Lima, D. W. Price, *Dalton Trans.* **2007**, 2734–2745; g) B. M. Kim, S. M. So, H. J. Choi, *Org. Lett.* **2002**, *4*, 949–952.
[10] a) M. Rezaeivala, H. Keypour, *Coord. Chem. Rev.* **2014**, *280*, 203–253; b) K. M. Lincoln, M. E. Offutt, T. D. Hayden, R. E. Saunders, K. N. Green, *Inorg. Chem.* **2014**, *53*, 1406–1416; c) F. Dioury, S. Sambou, E. Guene, M. Sabatou, C. Ferroud, A. Guy, M. Port, *Tetrahedron* **2007**, *63*, 204–214; d) R. M. Nunes, R. Delgado, M. F. Cabral, J. Costa, P. Brandao, V. Felix, B. J. Goodfellow, *Dalton Trans.* **2007**, 4536–4545; e) S. Taktak, W. H. Ye, A. M. Herrera, E. V. Rybak-Akimova, *Inorg. Chem.* **2007**, *46*, 2929–2942; f) K. P. Guerra, R. Delgado, M. G. B. Drew, V. Felix, *Dalton Trans.* **2006**, 4124–4133; g) K. P. Guerra, R. Delgado, L. M. P. Lima, M. G. B. Drew, V. Felix, *Dalton Trans.* **2004**, 1812–1822; h) V. Felix, J. Costa, R. Delgado, M. G. B. Drew, M. T. Duarte, C. Resende, *J. Chem. Soc., Dalton Trans.* **2001**, 1462–1471; i) S. Aime, M. Botta, L. Frullano, S. G. Crich, G. Giovenzana, R. Pagliarin, G. Palmisano, F. R. Sirtori, M. Sisti, *J. Med. Chem.* **2000**, *43*, 4017–4024.
[11] S. Aime, E. Gianolio, D. Corpillo, C. Cavallotti, G. Palmisano, M. Sisti, G. B. Giovenzana, R. Pagliarin, *Helv. Chim. Acta* **2003**, *86*, 615–632.
[12] A. Caselli, F. Cesana, E. Gallo, N. Casati, P. Macchi, M. Sisti, G. Celentano, S. Cenini, *Dalton Trans.* **2008**, 4202–4205.
[13] B. Castano, S. Guidone, E. Gallo, F. Ragaini, N. Casati, P. Macchi, M. Sisti, A. Caselli, *Dalton Trans.* **2013**, *42*, 2451–2462.
[14] B. Castano, T. Pedrazzini, M. Sisti, E. Gallo, F. Ragaini, N. Casati, A. Caselli, *Appl. Organomet. Chem.* **2011**, *25*, 824–829.
[15] a) B. Castano, E. Gallo, D. J. Cole-Hamilton, V. Dal Santo, R. Psaro, A. Caselli, *Green Chem.* **2014**, *16*, 3202–3209; b) B. Castano, P. Zardi, Y. C. Honemann, A. Galarneau, E. Gallo, R. Psaro, A. Caselli, V. Dal Santo, *RSC Adv.* **2013**, *3*, 22199–22205.
[16] a) V. K.-Y. Lo, A. O.-Y. Chan, C.-M. Che, *Org. Biomol. Chem.* **2015**, *13*, 6667–6680; b) G. Abbiati, E. Rossi, *Beilstein J. Org. Chem.* **2014**, *10*, 481–513; c) R. J. Scamp, J. W. Rigoli, J. M. Schomaker, *Pure Appl. Chem.* **2014**, *86*, 381–393; d) M. Harmata, (Ed.), *Silver In Organic Chemistry*, John Wiley & Sons, Inc., Hoboken, USA, **2010**; e) M. Alvarez-Corral, M. Munoz-Dorado, I. Rodriguez-Garcia, *Chem. Rev.* **2008**, *108*, 3174–3198; f) M. Naodovic, H. Yamamoto, *Chem. Rev.* **2008**, *108*, 3132–3148; g) Y. Yamamoto, *Chem. Rev.* **2008**, *108*, 3199–3222.
[17] M. Dell'Acqua, B. Castano, C. Cecchini, T. Pedrazzini, V. Pirovano, E. Rossi, A. Caselli, G. Abbiati, *J. Org. Chem.* **2014**, *79*, 3494–3505.
[18] M. Trose, M. Dell'Acqua, T. Pedrazzini, V. Pirovano, E. Gallo, E. Rossi, A. Caselli, G. Abbiati, *J. Org. Chem.* **2014**, *79*, 7311–7320.
[19] R. Eujen, B. Hoge, D. J. Brauer, *Inorg. Chem.* **1997**, *36*, 1464–1475.
[20] C. Martín, J. M. a. Muñoz-Molina, A. Locati, E. Alvarez, F. Maseras, T. s. R. Belderrain, P. J. Pérez, *Organometallics* **2010**, *29*, 3481–3489.
[21] a) E. Caytan, S. Roland, *Organometallics* **2014**, *33*, 2115–2118; b) B. K. Keitz, R. H. Grubbs, *Organometallics* **2010**, *29*, 403–408; c) D. Schott, C. J. Sleigh, J. P. Lowe, S. B. Duckett, R. J. Mawby, M. G. Partridge, *Inorg. Chem.* **2002**, *41*, 2960–2970; d) L. Cronin, C. L. Higgitt, R. N. Perutz, *Organometallics* **2000**, *19*, 672–683; e) C. L. Perrin, T. J. Dwyer, *Chem. Rev.* **1990**, *90*, 935–967.
[22] D. Jamróz, M. Wójcik, J. Lindgren, *Spectrochim. Acta Part A* **2000**, *56*, 1939–1948.
[23] D. F. McIntosh, G. A. Ozin, R. P. Messmer, *Inorg. Chem.* **1981**, *20*, 3640–3650.
[24] J. Schaefer, A. Kraft, S. Reininger, G. Santiso-Quinones, D. Himmel, N. Trapp, U. Gellrich, B. Breit, I. Krossing, *Chem. Eur. J.* **2013**, *19*, 12468–12485.
[25] H. V. R. Dias, C. J. Lovely, *Chem. Rev.* **2008**, *108*, 3223–3238.
[26] P. S. Pregosin, *NMR in Organometallic Chemistry*, Wiley-VCH, Weinheim, Germany, **2012**.
[27] The addition of only one equivalent did not result in any change of the observed ^{1}H NMR spectrum.
[28] P. Macchi, H.-B. Buergi, A. S. Chimpri, J. Hauser, Z. Gal, *J. Appl. Crystallogr.* **2011**, *44*, 763–771.
[29] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112–122.
[30] L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837–838.

Received: July 13, 2015
Published Online: October 1, 2015

