

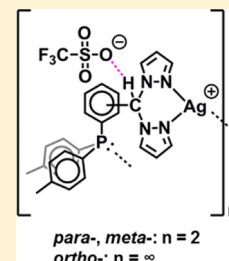
Isomer Dependence in the Assembly and Lability of Silver(I) Trifluoromethanesulfonate Complexes of the Heteroditopic Ligands, 2-, 3-, and 4-[Di(1*H*-pyrazolyl)methyl]phenyl(di-*p*-tolyl)phosphine

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Supporting Information

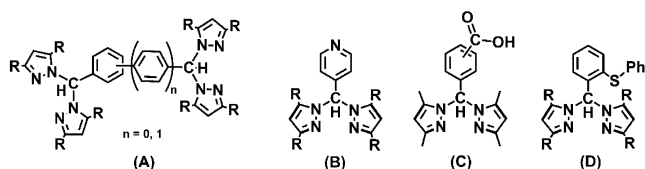
ABSTRACT: Three isomers of a new heteroditopic ligand that contains a di(1*H*-pyrazolyl)methyl (–CHpz₂) moiety connected to a di(*p*-tolyl)phosphine group via a *para*-, *meta*-, or *ortho*-phenylene spacer (*pL*, *mL*, and *oL*, respectively) have been synthesized by using a palladium(0)-catalyzed coupling reaction between HP(*p*-tolyl)₂ and the appropriate isomer of (IC₆H₄)CHpz₂. The 1:1 complexes of silver(I) trifluoromethanesulfonate, Ag(OTf), were prepared to examine the nature of ligand coordination and the type of supramolecular isomer (monomeric, cyclic oligomeric, or polymeric) that would be obtained. The single crystal X-ray diffraction studies showed that [Ag(*pL*)](OTf), **1**, and [Ag(*mL*)](OTf), **2**, possessed cyclic dimeric dication, whereas [Ag(*oL*)](OTf), **3**, was a coordination polymer. The polymeric chain in **3** could be disrupted by reaction with triphenylphosphine, and the resulting complex, [Ag(*oL*)(PPh₃)](OTf), **4**, possessed a monometallic cation where the ligand was bound to silver in a chelating κ²P,*N*- coordination mode. The solution structures of **1–4** were probed via a combination of IR, variable-temperature multinuclear (¹H, ¹³C, ³¹P) NMR spectroscopy, as well as by electron spray ionization (ESI)(+) mass spectrometry. A related complex [Ag(*m*-IC₆H₄CHpz₂)₂](OTf), **5**, was also prepared, and its solid-state and solution spectroscopic properties were studied for comparison purposes. These studies suggest that the cyclic structures of **1** and **2** are likely preserved but are dynamic in solution at room temperature. Moreover, both **3** and **4** have dynamic solution structures where **3** is likely extensively dissociated in CH₃CN or acetone rather than being polymeric as in the solid state.



INTRODUCTION

There is great interest in the development of coordination polymers because of their myriad possible uses in gas separation and storage,¹ in optical² and electronic materials,³ and even in biological/biomedical⁴ applications. Further interest is generated because the ability to modify the organic linker that bridges metal centers offers design opportunities to incorporate new functionality into a coordination polymer⁵ or to either probe fundamental or discover new principles of crystal engineering.⁶ Multitopic di(pyrazolyl)methane derivatives such as those in Chart 1^{7–11} and others^{12–16} have proven to

Chart 1. Representative Homo- and Hetero-Ditopic Aryldi(pyrazol-1-yl)methane Ligands (R = H, Me)



be ideal candidates for such studies. Pioneering work by the Reger group on homoditopic α,α,α'-tetra(pyrazol-1-yl)-(p- or m-)xylene ligands, p- or m-pz₄xyl (Chart 1A, where n = 0), showed that the reactions between AgBF₄ and the homoditopic ligands in a 1:1 ratio resulted in a coordination polymer with p-pz₄xyl but a cyclic bimetallic dication, [Ag₂L₂]²⁺, with m-

pz₄xyl.^{7a} The three-dimensional assembly of the coordination polymer or the derivative with a cyclic dication was governed by ion pairing and directional noncovalent interactions such as the quadruple pyrazolyl embrace,^{12d} a concerted set of CH⋯π and π⋯π interactions that has been found to be common in structures of metal complexes of poly(pyrazolyl)methane and borate ligands. For other metal complexes of m-pz₄xyl, the cyclic bimetallic supramolecular isomer is predominant, persists in solution, and allows for fundamental studies in electronic interactions between two metal centers.¹² Our group recently examined the silver(I) trifluoromethanesulfonate complexes of the six isomers of homoditopic α,α,α'-tetra(pyrazol-1-yl)-(X,Y-)dimethylbiphenyl ligands (X,Y = 2, 3, or 4, Chart 1A, n = 1, R = H), which showed a similar isomer dependence; cyclic supramolecular isomers were obtained for two of the six possible isomers (2,2- and 3,4-), whereas all other structurally characterized isomers were coordination polymers.^{8a} Moreover CH⋯O interactions between triflate anion and the acidic methine and 5-pyrazolyl hydrogens dominated the supramolecular structures. Concurrently, the Manzano group showed CH⋯X (X = O, F, Cl, π) noncovalent interactions involving acidic methine, aryl, and pyrazolyl hydrogen and the pyrazolyl embrace govern the solid state assembly of coordination polymers and multimetallic complexes of related biphenyl-linked ligands (Chart 1A, n = 1, R = Me, 4,4-

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isomer).^{8b} Heteroditopic ligands such as Manzano's (4-py)CHpz*₂ (pz* = 3,5-dimethylpyrazol-1-yl, Chart 1B where R = Me),⁹ Carrano's (3- or 4-CO₂HC₆H₄)CHpz*₂ (Chart 1C, R = Me),¹⁰ Marchio's (2-PhSC₆H₄)CHpz*₂ (Chart 1D),¹¹ or others^{13–16} offer an attractive increase in complexity to the design of solid state architectures because of the different manners in which the ligands could bind metal centers. Thus, Figure 1a–f displays some of the different possible supra-

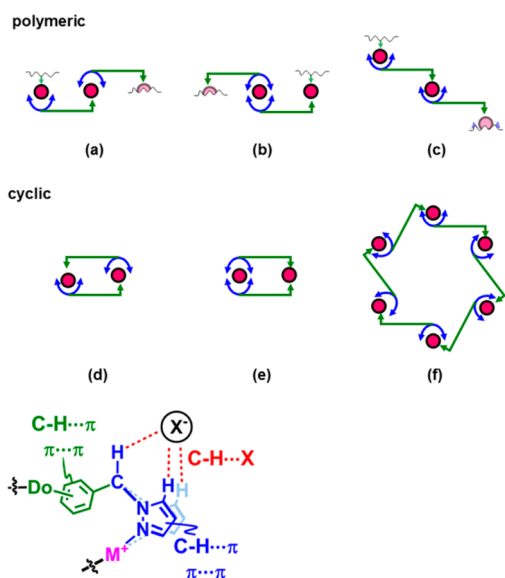


Figure 1. Representative supramolecular isomers of metal complexes of heteroditopic di(pyrazolyl)methane ligands (top and middle) and the common noncovalent interactions that organize their three-dimensional structures (bottom). Key: Di(pyrazolyl)methane unit is blue, the other donor group (Do) and its attached aryl ring is green, and the metal center is pink.

molecular isomers of 1:1 M:L complexes of heteroditopic di(pyrazolyl)methane-based ligands that have been observed. The most common structure type is the cyclic bimetallic species in Figure 1d that has different donor ends of two ligands bound to a given metal. Similarly, the most common type of coordination polymer is found in Figure 1a or 1c (the difference being the orientation of the second donor group with respect to the aryl spacer). The complexes [Ag(2-PhSC₆H₄)-CHpz*₂] (X = BF₄⁻, PF₆⁻, or O₃SCF₃⁻) showed an unusual hexameric metallacyclic structure (Figure 1f). The hexameric rings were inefficiently packed in the solid state by bridging anions and a host of other noncovalent interactions (similar to those shown in the bottom of Figure 1) to give permanent porosity to the crystalline solid and a remarkable capacity and selectivity for CO₂ gas absorption.¹¹

Among the variety of heteroditopic di(pyrazolyl)methane type ligands that have been reported, we were surprised that those with diorganophosphines as a second donor remain unknown. Thus, we set out to prepare R₂PC₆H₄CHpz₂ derivatives and explore their coordination chemistry. This contribution outlines our initial endeavors in the preparation of such ligands, specifically, of the three isomers of (*p*-tolyl)₂P-(C₆H₄)CHpz₂. We also detail an investigation into their silver(I) trifluoromethanesulfonate complexes to learn more about the coordination capabilities of the ligands and to examine what effects, if any, a change in disposition of donors

around a linking arene ring will have on supramolecular isomers and their three-dimensional crystal packing.

EXPERIMENTAL SECTION

General Considerations. Pd(PPh₃)₄ was prepared according to a literature procedure¹⁷ and stored under argon, and reactions employing this compound were performed under an argon atmosphere. *N,N'*-Dimethylethylenediamine (DMED) and all other chemicals were commercially available and were used as received. Solvents were dried by conventional methods and distilled prior to use. Di(*p*-tolyl)phosphine as a 10 wt % solution in hexanes was stored in an argon-filled drybox, and reactions employing this reagent were carried out with the exclusion of air by Schlenk techniques. The syntheses of the silver trifluoromethanesulfonate (AgOTf) complexes were carried out under an argon atmosphere using standard Schlenk techniques and in a foil-covered apparatus to protect AgOTf from light. After complex formation, no special precautions to avoid light or air were taken.

Midwest MicroLab, LLC, Indianapolis, Indiana 45250, performed all elemental analyses. IR spectra were recorded for samples as KBr pellets or as CH₃CN solutions (solution cell with KBr windows) in the 4000–500 cm⁻¹ region on a Nicolet Magna-IR 560 spectrometer. ¹H, ¹³C, ¹⁹F, and ³¹P NMR spectra were recorded on a Varian 400 MHz spectrometer. Chemical shifts were referenced to solvent resonances at δ_H 7.26 and δ_C 77.16 for CDCl₃, δ_H 2.05 for acetone-*d*₆, δ_H 1.94 and δ_C 118.26 for CD₃CN or against and external standards of CFCl₃ (δ_F 0.00 ppm) or of 85% H₃PO₄ (aq) (δ_P 0.00 ppm). The ¹H and ¹³C NMR data for 1–5 are labeled according to Figure S9, Supporting Information and 2D spectra are provided in Figures S10–S13, Supporting Information. Melting point determinations were made on samples contained in glass capillaries using an Electrothermal 9100 apparatus and are uncorrected. Mass spectrometric measurements recorded in ESI(+) mode were obtained on a Micromass Q-TOF spectrometer where formic acid (approximately 0.1% v/v) was added to the mobile phase (CH₃CN).

Syntheses. *p*-IC₆H₄CH(pz)₂. A solution of 0.967 g (14.2 mmol) of pyrazole in 10 mL of THF was added to a suspension of 0.341 g (14.2 mmol) of NaH in 10 mL of THF via cannula at a rate slow enough to control hydrogen evolution. The flask originally containing pyrazole was washed with an additional 5 mL of THF to ensure quantitative transfer. After hydrogen evolution ceased, a solution of 0.51 mL (1.638 g/mL, 7.1 mmol) of S(O)Cl₂ in 10 mL of THF was added to the solution of Na(pz) whereupon a colorless precipitate of NaCl formed. After the suspension of S(O)pz₂/NaCl had been stirred 30 min, 0.031 g (0.24 mmol) of CoCl₂ was added as a solid in one portion under an argon blanket. After the resulting blue suspension had been stirred 5 min, 1.10 g (4.74 mmol) of 4-iodobenzaldehyde was added under an argon blanket. After the suspension had been heated at reflux or 15 h, it was cooled to room temperature and 100 mL of water was added. The THF fraction was separated from the aqueous. Then the aqueous fraction was extracted with three 50 mL portions ethyl acetate. The combined organic fractions were dried over MgSO₄ and filtered, and solvent was removed by rotary evaporation to leave 1.60 g (97%) of *p*-IC₆H₄CH(pz)₂ as a white solid. Mp, 100–101 °C. ¹H NMR (400 MHz, CDCl₃) δ_H 7.70 (d, *J* = 8.5 Hz, 2 H, Ar), 7.66 (s, 1H, C_{meth}H), 7.63 (d, *J* = 1.5 Hz, 2 H, H_{3pz}), 7.53 (d, *J* = 2.3 Hz, 2 H, H_{5pz}), 6.75 (d, *J* = 8.5 Hz, 2 H, Ar), 6.35 (pst, *J*_{app} = 2 Hz, H_{4pz}) ppm. ¹³C NMR (100.5 MHz, CDCl₃) δ_C 141.1, 138.0, 136.1, 129.9, 128.9, 107.0, 95.6, 77.4 ppm.

The following two compounds were prepared in a similar manner. *m*-IC₆H₄CH(pz)₂. A mixture of 5.8 mmol of S(O)pz₂ [from 0.279 g (11.6 mmol) of NaH, 0.792 g (11.6 mmol) of pyrazole, and 0.42 mL (1.638 g/mL, 5.8 mmol) of S(O)Cl₂], 0.025 g (0.19 mmol) CoCl₂, and 0.900 g (3.88 mmol) of 3-iodobenzaldehyde gave 0.998 g (73%) of *m*-IC₆H₄CH(pz)₂ as a colorless solid after column chromatography (*R*_f = 0.59, 3:1 hexanes:ethyl acetate, SiO₂) and drying under a vacuum. Mp, 90–91 °C. ¹H NMR (400 MHz, CDCl₃) δ_H 7.72 (d, *J* = 7.8 Hz, 1 H, Ar), 7.66 (s, 1 H, C_{meth}H), 7.64 (d, *J* = 1.6 Hz, 2 H, H_{3pz}), 7.54 (d, *J* = 2.3 Hz, 2 H, H_{5pz}), 7.36 (s, 1 H, Ar), 7.10 (pst, *J*_{app}

= 7.8 Hz, 1 H, Ar), 6.98 (d, $J = 7.8$ Hz, 1 H, Ar), 6.36 (pst, $J_{\text{app}} = 2$ Hz, 2 H, $H_{4\text{pz}}$) ppm. ^{13}C NMR (100.5 MHz, CDCl_3) δ_{C} 141.2, 138.6, 138.5, 136.0, 130.6, 129.9, 126.4, 107.1, 94.7, 76.9 ppm.

o- $\text{IC}_6\text{H}_4\text{CH}(\text{pz})_2$. A mixture of 15.0 mmol of $\text{S}(\text{O})\text{pz}_2$ [from 0.721 g (30.0 mmol) of NaH , 2.04 g (30.0 mmol) of pyrazole, and 1.09 mL (1.638 g/mL, 15.0 mmol) of $\text{S}(\text{O})\text{Cl}_2$], 0.130 g (1.00 mmol) of CoCl_2 , and 2.32 g (10.0 mmol) of 2-iodobenzaldehyde gave a yellow oily mixture after aqueous workup. The organic fraction was passed through a short (50 g) plug of silica gel with the aid of a 3:1 (v:v) ethyl acetate/hexane solution (R_f 0.9) to separate from two pyrazolyl-containing impurities. After solvent was removed, the resulting pale yellow oil crystallized with the aid of scratching the glass to give 3.32 g (95%) of *o*- $\text{IC}_6\text{H}_4\text{CH}(\text{pz})_2$ as a colorless solid. Mp, 81–82 °C. ^1H NMR (400 MHz, CDCl_3) δ_{H} 7.90 (dd, $J = 7.9$, 1.1 Hz, 1 H, Ar), 7.80 (s, 1 H, $C_{\text{meth}}\text{H}$), 7.66 (dd, $J = 1.8$, 0.5 Hz, 2 H, $H_{3\text{pz}}$), 7.35 (td, $J = 7.3$, 1.2 Hz, 1 H, Ar), 7.32 (d, $J = 2.5$ Hz, 2 H, $H_{3\text{pz}}$), 7.09 (td, $J = 7.8$, 1.6 Hz, 1 H, Ar), 6.73 (dd, $J = 7.9$, 1.5 Hz, 1 H, Ar), 6.35 (pst, $J_{\text{app}} = 1.9$ Hz, 2 H, $H_{4\text{pz}}$) ppm. ^{13}C NMR (100.5 MHz, CDCl_3) δ_{C} 141.3, 140.3, 138.2, 131.1, 130.0, 128.8, 128.7, 106.8, 98.3, 81.3 ppm.

p-(*p*-tolyl) $_2\text{PC}_6\text{H}_4\text{CH}(\text{pz})_2$, **pL**. A solution of 1.009 g (2.88 mmol) of *p*- $\text{IC}_6\text{H}_4\text{CH}(\text{pz})_2$, 0.10 mL (0.82 g/mL, 1.0 mmol) of DMED, and 20 mL of toluene was purged with argon 15 min and then was transferred via cannula to an argon-purged flask that contained 1.877 g (5.76 mmol) of Cs_2CO_3 , 0.017 g (0.0015 mmol) of $\text{Pd}(\text{PPh}_3)_4$, and 10.0 mL (0.72 g/mL, 10 wt % in hexanes, 3.36 mmol) of $\text{HP}(\text{p-tolyl})_2$. After the resulting suspension was heated at reflux under argon 15 h, toluene was removed by vacuum distillation to leave a black solid. The black solid was dissolved in a biphasic mixture of 100 mL of H_2O and 50 mL of ethyl acetate. The layers were separated, and the aqueous portion was extracted with two 50 mL portions ethyl acetate. The combined organic fractions were dried over MgSO_4 and filtered, and then solvent was removed by vacuum distillation. The resulting oily residue was purified by column chromatography in silica gel. Elution with 4:1 hexanes/ethyl acetate gave 0.987 g (79%) of **pL** as a viscous syrup after solvent was removed from the second band ($R_f = 0.38$). ^1H NMR (400 MHz, CDCl_3) δ_{H} 7.72 (s, 1 H, $C_{\text{meth}}\text{H}$), 7.62 (d, $J = 1.3$ Hz, 2 H, $H_{3\text{pz}}$), 7.52 (d, $J = 2.2$ Hz, 2 H, $H_{3\text{pz}}$), 7.25 (d, $J = 7.5$ Hz, 2 H, Ar), 7.18 (d, $J = 7.6$ Hz, 4 H, Ar), 7.13 (d, $J = 7.6$ Hz, 4 H, Ar), 6.93 (d, $J = 7.5$ Hz, 2 H, Ar), 6.32 (dd, $J = 2$, 1 Hz, 2 H, $H_{4\text{pz}}$), 2.33 (s, 6 H, CH_3) ppm. ^{13}C NMR (100.5 MHz, CDCl_3) δ_{C} 140.8, 140.0 (d, $J_{\text{CP}} = 12.8$ Hz), 139.0, 136.2, 133.9 (d, $J_{\text{CP}} = 20.1$ Hz), 133.6 (d, $J_{\text{CP}} = 18.9$ Hz), 133.1 (d, $J_{\text{CP}} = 9.0$ Hz), 129.8, 129.4 (d, $J_{\text{CP}} = 7.4$ Hz), 126.9 (d, $J_{\text{CP}} = 6.4$ Hz), 106.7, 77.6, 21.3 ppm. ^{31}P NMR (161.8 MHz, CDCl_3) $\delta_{\text{P}} -7.6$ ppm.

The following two compounds were prepared similarly.

m-(*p*-tolyl) $_2\text{PC}_6\text{H}_4\text{CH}(\text{pz})_2$, **mL**. A mixture of 0.931 g (2.86 mmol) of Cs_2CO_3 , 5.10 mL (0.72 g/mL, 10 wt % in hexanes, 1.71 mmol) of $\text{HP}(\text{p-tolyl})_2$, 0.0083 g (7.2 μmol) of $\text{Pd}(\text{PPh}_3)_4$, 0.500 g (1.43 mmol) of *m*- $\text{IC}_6\text{H}_4\text{CH}(\text{pz})_2$, 0.10 mL (0.82 g/mL, 0.86 mmol) of DMED and 15 mL of toluene gave 0.229 g (37%) **mL** as a colorless oil after solvent was removed from the second band obtained from column chromatography ($R_f = 0.69$, 3:1 hexanes: ethyl acetate, SiO_2). ^1H NMR (400 MHz, CDCl_3) δ_{H} 7.65 (s, 1 H, $C_{\text{meth}}\text{H}$), 7.55 (d, $J = 1.3$ Hz, 2 H, $H_{3\text{pz}}$), 7.42 (d, $J = 2.4$ Hz, 2 H, $H_{3\text{pz}}$), 7.29 (m, $J = 7.6$ Hz, 3 H, Ar), 7.10 (br m, 9 H, Ar), 6.91 (d, $J = 6.5$ Hz, 1 H, Ar), 6.85 (d, $J = 7.2$ Hz, 1 H, Ar), 6.25 (dd, $J = 2$, 1 Hz, 2 H, $H_{4\text{pz}}$), 2.32 (s, 6 H, CH_3) ppm. ^{13}C NMR (100.5 MHz, CDCl_3) δ_{C} 140.8, 139.4 (d, $J_{\text{CP}} = 13.3$ Hz), 139.0, 136.4 (d, $J_{\text{CP}} = 6.2$ Hz), 134.3 (d, $J_{\text{CP}} = 18.4$ Hz), 133.8 (d, $J_{\text{CP}} = 19.6$ Hz), 133.1 (d, $J_{\text{CP}} = 9.5$ Hz), 131.9 (d, $J_{\text{CP}} = 19.8$ Hz), 129.7, 129.5 (d, $J_{\text{CP}} = 7.3$ Hz), 128.8 (d, $J_{\text{CP}} = 6.3$ Hz), 129.9, 106.6, 77.7, 21.4 ppm. ^{31}P NMR (161.8 MHz, CDCl_3) $\delta_{\text{P}} -7.1$ ppm.

o-(*p*-tolyl) $_2\text{PC}_6\text{H}_4\text{CH}(\text{pz})_2$, **oL**. A mixture of 0.972 g (2.98 mmol) of Cs_2CO_3 , 5.30 mL (0.72 g/mL, 10 wt % soln in hexanes, 1.79 mmol) of $\text{HP}(\text{p-tolyl})_2$, 0.0086 g (7.8 μmol) of $\text{Pd}(\text{PPh}_3)_4$, 0.523 g (1.49 mmol) of *o*- $\text{IC}_6\text{H}_4\text{CH}(\text{pz})_2$, 0.05 mL (0.82 g/mL, 0.48 mmol) of DMED and 15 mL of toluene gave 0.594 g (91%) **oL** as a colorless solid after solvent was removed from the second band obtained from column chromatography ($R_f = 0.46$, 4:1 hexanes: ethyl acetate, SiO_2). Mp, 116–117 °C. ^1H NMR (400 MHz, CDCl_3) δ_{H} 8.55 (d, $J = 7.6$ Hz, 1 H, Ar), 7.49 (d, $J = 1.3$ Hz, 2 H, $H_{3\text{pz}}$), 7.36 (t, $J = 7.3$ Hz, 1 H, Ar),

7.29 (t, $J = 7.3$ Hz, 1 H, Ar), 7.18 (d, $J = 2.4$ Hz, 2 H, $H_{3\text{pz}}$), 7.04 (br m, 10 H, Ar), 6.10 (dd, $J = 2$, 1 Hz, 2 H, $H_{4\text{pz}}$), 2.31 (s, 6 H, CH_3) ppm. ^{13}C NMR (100.5 MHz, CDCl_3) δ_{C} 140.9, 140.4 (d, $J_{\text{CP}} = 23.4$ Hz), 138.8, 137.0 (d, $J_{\text{CP}} = 18.5$ Hz), 134.7, 133.9 (d, $J_{\text{CP}} = 19.9$ Hz), 132.0 (d, $J_{\text{CP}} = 6.9$ Hz), 129.9, 129.5 (d, $J_{\text{CP}} = 3.8$ Hz), 129.3 (d, $J_{\text{CP}} = 7.0$ Hz), 127.5 (d, $J_{\text{CP}} = 4.0$ Hz), 106.2, 77.4, 75.5 (d, $J_{\text{CP}} = 28.0$ Hz), 21.4 ppm. ^{31}P NMR (161.8 MHz, CDCl_3) $\delta_{\text{P}} -20.1$ ppm.

[Ag(pL)](OTf), **1**. A solution of 0.241 g (0.553 mmol) of **pL** in 10 mL of THF was added via cannula to a solution of 0.142 g (0.553 mmol) of AgOTf in 10 mL of THF. The flask originally containing **pL** was washed with 5 mL of THF, and the washings were transferred to the reaction mixture to ensure quantitative transfer. After the resulting solution had been stirred 4 h, solvent was removed under a vacuum. The residue was washed with two 5 mL portions Et_2O and was dried under a vacuum to leave 0.328 g (86%) of **1** as a colorless solid. Mp, 258–259 °C dec Anal. Calcd (Found) for $\text{C}_{28}\text{H}_{25}\text{F}_3\text{N}_4\text{O}_3\text{PSAg}$: C, 48.50 (48.47); H, 3.63 (3.72); N, 8.08 (8.08). ^1H NMR (400 MHz, CD_3CN) δ_{H} 8.25 (d, $J = 2.5$ Hz, 2 H, $H_{3\text{pz}}$), 8.06 (s, 1 H, $C_{\text{meth}}\text{H}$), 7.84 (d, $J = 1.7$ Hz, 2 H, $H_{3\text{pz}}$), 7.16 (dd, $J = 11.5$, 8.1 Hz, 2 H, $H_2\text{Ar}$), 7.08 (dd, $J = 8$, 2 Hz, 4 H, $H_3\text{Tol}$), 7.00 (dd, $J = 11.7$, 7.0 Hz, 4 H, $H_2\text{Tol}$), 6.64 (d, $J = 8.0$ Hz, 2 H, $H_3\text{Ar}$), 6.57 (dd, $J = 2$, 1 Hz, 2 H, $H_{4\text{pz}}$), 2.31 (s, 6 H, CH_3) ppm. ^{13}C NMR (100.5 MHz, CD_3CN) δ_{C} 144.5 (C_3pz), 142.2 (C_4^{tol}), 139.6 (C_4^{Ar}), 135.5 (d, $J_{\text{CP}} = 18.4$ Hz, C_2^{Ar}), 135.0 (C_5pz), 134.2 (d, $J_{\text{CP}} = 16.8$ Hz, C_2^{tol}), 133.2 (d, $J_{\text{CP}} = 35.8$ Hz, $\text{C}_1^{\text{tol or Ar}}$), 130.6 (d, $J_{\text{CP}} = 10.3$ Hz, C_3^{tol}), 128.5 (d, $J_{\text{CP}} = 36.7$ Hz, $\text{C}_1^{\text{Ar or tol}}$), 128.0 (d, $J_{\text{CP}} = 11.3$ Hz, C_3^{Ar}), 107.7 (C_4pz), 75.2 (C_{meth}), 21.4 (CH_3) ppm. ^{19}F NMR (376.1 MHz, CD_3CN , 295 K) δ_{F} -79.3 (s, 3F) ppm. ^{31}P NMR (161.8 MHz, CD_3CN) δ_{P} 11.3 (d, $J_{109\text{AgP}} = 736$ Hz, $J_{107\text{AgP}} = 638$ Hz) ppm. LRMS [ESI(+), m/z] (Int.) [assign.]: 1417 (1) [AgL_3] $^+$, 1237 (2) [$\text{Ag}_2\text{L}_2(\text{OTf})$] $^+$, 981 (12) [AgL_2] $^+$, 762 (39) [Ag_2L_3] $^{2+}$, 544 (100) [Ag_2L_2] $^{2+}$. Crystals suitable for X-ray diffraction were grown by layering an acetone solution of **1** with hexanes and allowing solvents to slowly diffuse over 20 h.

[Ag(mL)](OTf), **2**. A solution of 0.161 g (0.368 mmol) of **mL** in 10 mL of THF was transferred quantitatively (by washing the flask with additional 5 mL of THF and transferring the washings) via cannula to a solution of 0.095 g (0.368 mmol) of AgOTf in 10 mL of THF. A colorless precipitate formed immediately. After the suspension had been stirred 4 h, the insoluble portion was collected by filtration, washed with two 5 mL portions Et_2O , and dried under a vacuum for 2 h to give 0.231 g (91%) of **2** as a colorless solid. Mp, 295–297 °C dec Anal. Calcd (Found) for $\text{C}_{28}\text{H}_{25}\text{F}_3\text{N}_4\text{O}_3\text{PSAg}$: C, 48.50 (48.49); H, 3.63 (3.75); N, 8.08 (7.90). ^1H NMR (400 MHz, CD_3CN) δ_{H} 8.13 (d, $J = 2.4$ Hz, 2 H, $H_{3\text{pz}}$), 7.93 (s, 1H, $C_{\text{meth}}\text{H}$), 7.67 (d, $J = 1.4$ Hz, 2 H, $H_{3\text{pz}}$), 7.63 (td, $J = 7.9$, 2.4 Hz, 1 H, C_5^{Ar}), 7.49 (dd, $J = 12.9$, 7.4 Hz, 1 H, C_6^{Ar}), 7.25 (d, $J = 7.1$ Hz, 4 H, H_3^{tol}), 6.89 (dd, $J = 12.2$, 8.0 Hz, 4 H, H_2^{tol}), 6.74 (d, $J = 8$ Hz, 1 H, H_4^{Ar}), 6.43 (dd, $J = 2$, 1 Hz, 2 H, $H_{4\text{pz}}$), 5.61 (d, $J = 9.5$ Hz, 1 H, C_2^{Ar}), 2.40 (s, 6 H, CH_3) ppm. ^{13}C NMR (100.5 MHz, CD_3CN) δ_{C} 144.6 (C_5pz), 143.2 (C_4^{tol}), 137.5 (d, $J_{\text{CP}} = 7.0$ Hz, C_3^{Ar}), 135.6 (d, $J_{\text{CP}} = 25.4$ Hz, $\text{C}_1^{\text{Ar or tol}}$), 135.0 (d, $J_{\text{CP}} = 27$ Hz, C_6^{Ar}), 134.7 (C_5pz), 134.3 (d, $J_{\text{CP}} = 34.6$ Hz, C_2^{tol}), 131.1 (d, $J_{\text{CP}} = 10.7$ Hz, C_2^{Ar}), 130.9 (C_5Ar), 130.5 (C_3^{tol}), 129.6 (C_4^{Ar}), 127.2 (d, $J_{\text{CP}} = 38.9$ Hz, $\text{C}_1^{\text{tol or Ar}}$), 107.3 (C_4pz), 75.4 (C_{meth}), 21.3 (CH_3) ppm. ^{19}F NMR (376.1 MHz, CD_3CN , 295 K) δ_{F} -79.3 (s, 3F) ppm. ^{31}P NMR (161.8 MHz, CD_3CN) δ_{P} 11.1 (d, $J_{109\text{AgP}} = 740$ Hz; $J_{107\text{AgP}} = 644$ Hz) ppm. LRMS [ESI(+), m/z] (Int.) [assign.]: 1417 (1) [AgL_3] $^+$, 1237 (3) [$\text{Ag}_2\text{L}_2(\text{OTf})$] $^+$, 981 (21) [AgL_2] $^+$, 762 (25) [Ag_2L_3] $^{2+}$, 544 (100) [Ag_2L_2] $^{2+}$. Crystals suitable for X-ray diffraction were grown over the course of 12 h by vapor diffusion of Et_2O into an acetonitrile solution of **2**.

[Ag(oL)](OTf), **3**. A solution of 0.178 g (0.407 mmol) of **oL** in 10 mL of THF was transferred quantitatively (by washing the flask with additional 5 mL of THF and transferring the washings) via cannula to a solution of 0.105 g (0.407 mmol) of AgOTf in 10 mL of THF. A colorless precipitate formed immediately. After the suspension had been stirred 4 h, the insoluble portion was collected by filtration, washed with two 5 mL portions Et_2O , and dried under a vacuum for 2 h to give 0.238 g (84%) of **3** as a colorless solid. Mp, 225–227 °C, dec Anal. Calcd (Found) for $\text{C}_{28}\text{H}_{25}\text{F}_3\text{N}_4\text{O}_3\text{PSAg}$: C, 48.50 (48.59); H, 3.63 (3.55); N, 8.08 (7.96). ^1H NMR (400 MHz, CD_3CN , 295 K) δ_{H}

Table 1. Crystallographic Data Collection and Structure Refinement for 1·0.5 acetone, 2·CH₃CN, 3, and 5

compound	1·0.5 acetone	2·CH ₃ CN	3	4	5
formula	C ₅₉ H ₅₆ Ag ₂ F ₆ N ₈ O ₇ P ₂ S ₂	C ₆₀ H ₅₆ Ag ₂ F ₆ N ₁₀ O ₆ P ₂ S ₂	C ₂₈ H ₂₅ AgF ₃ N ₄ O ₃ PS	C ₄₆ H ₄₀ AgF ₃ N ₄ O ₃ P ₂ S	C ₂₇ H ₂₂ AgF ₃ I ₂ N ₈ O ₃ S
formula weight	1444.92	1468.95	693.42	955.69	957.26
crystal system	monoclinic	monoclinic	orthorhombic	monoclinic	triclinic
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>Pbca</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$
temperature [K]	100.0(1)	100.0(1)	100.0(1)	100.0(1)	100.0(1)
<i>a</i> [Å]	22.6768(3)	11.8539(2)	21.8299(3)	9.34515(15)	9.4676(3)
<i>b</i> [Å]	11.79225(13)	15.5905(3)	13.12475(11)	13.8176(3)	11.6230(3)
<i>c</i> [Å]	23.7381(3)	17.6390(4)	22.6416(3)	33.1325(6)	15.5967(4)
α [°]	90.00	90.00	90.00	90.00	70.706(2)
β [°]	99.9683(13)	109.318(2)	90.00	90.3273(15)	86.720(2)
γ [°]	90.00	90.00	90.00	90.00	85.857(2)
<i>V</i> [Å ³]	6251.99(14)	3076.30(11)	6487.09(14)	4278.26(13)	1614.65(8)
<i>Z</i>	4	2	8	4	2
<i>D</i> _{calcd} [g cm ⁻³]	1.535	1.586	1.420	1.484	1.969
λ [Å] (Cu or Mo <i>K</i> α)	0.7107	0.7107	1.54178	0.7107	0.7107
μ [mm ⁻¹]	0.820	0.834	6.497	0.654	2.661
abs correction	numerical	numerical	numerical	numerical	numerical
<i>F</i> (000)	2928	1488	2800.0	1952	920.0
θ range [°]	2.76–29.50	2.27–29.49	3.9–73.6	2.85–29.52	2.78–29.52
reflections collected	72140	31390	33869	48712	36367
independent reflns	15868 (<i>R</i> _{int} = 0.0326)	7707 (<i>R</i> _{int} = 0.0343)	6431 (<i>R</i> _{int} = 0.0473)	10814 (<i>R</i> _{int} = 0.0324)	8114 (<i>R</i> _{int} = 0.0371)
<i>T</i> _{min/max}	0.727/0.827	0.911/0.940	0.173/0.703	0.904/0.947	0.523/0.723
data/restr/param	15868/0/781	7707/0/400	6431/0/372	10814/107/617	8114/0/406
goodness-of-fit on <i>F</i> ²	1.030	1.033	1.070	1.085	1.073
<i>R</i> 1 ^a / <i>wR</i> 2 ^b [<i>I</i> > 2 σ (<i>I</i>)]	0.0301/0.0665	0.0330/0.0712	0.0331/0.0887	0.0408/0.0916	0.0317/0.0624
<i>R</i> 1/ <i>wR</i> 2 (all data)	0.0384/0.0707	0.0451/0.0777	0.0378/0.0922	0.0493/0.0958	0.0448/0.0698
largest diff peak/hole/e Å ⁻³	0.59/–0.53	0.53/–0.49	0.70/–0.76	1.24/–0.80	1.48/–1.53

^a*R*1 = $\sum ||F_o| - |F_c|| / \sum |F_o|$. ^b*wR*2 = $[\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|]^2 / 2$.

8.35 (d, *J* = 5.0 Hz, 1 H, C_{meth}H), 7.84 (dd, *J* = 7.8, 4.1 Hz, 1 H, H₃^{Ar}), 7.58 (t, *J* = 7.6 Hz, 1 H, H₄^{Ar}), 7.44–7.42 (br m, 3 H, H₅Ar and H₅pz), 7.30 (d, *J* = 2 Hz, 2H, H₃pz) 7.27 (br m, 4 H, H₂^{tol}), 7.26 (br m, 4 H, H₃^{tol}), 6.93 (t, *J* = 8.3 Hz, 1 H, H₆^{Ar}), 6.21 (dd, *J* = 2, 1 Hz, 2 H, H₄pz), 2.37 (s, 6 H, CH₃) ppm. ¹³C NMR (100.5 MHz, CD₃CN, 295 K) δ_C 143.4 (C₃pz), 142.2 (C₄^{tol}), 139.4 (d, *J*_{CP} = 14.1 Hz, C₂^{Ar}), 135.3 (d, *J*_{CP} = 17.7 Hz, C₂^{tol}), 135.1 (C₅pz), 134.1 (d, *J*_{CP} = 2.7 Hz, C₆^{Ar}), 132.3 (C₄^{Ar}), 132.1 (d, *J*_{CP} = 26 Hz, C₁^{Ar} or ^{tol}), 131.4 (C₃^{tol}), 131.3 (d, *J*_{CP} = 4.8 Hz, C₅^{Ar}), 130.6 (d, *J*_{CP} = 6.0 Hz, C₃^{Ar}), 126.6 (d, *J*_{CP} = 34.7 Hz, C₁^{tol} or ^{Ar}), 107.8 (C₄pz), 75.0 (d, *J*_{CP} = 20.2 Hz, C_{meth}), 21.4 ppm. ¹⁹F NMR (376.1 MHz, CD₃CN, 295 K) δ_F –79.3 (s, 3F) ppm. ³¹P NMR (161.8 MHz, CD₃CN, 295 K) δ_P –1.1 (br s, LWHM = 245 Hz) ppm; (233 K) δ_P –1.6 (d, *J*_{109Ag-P} = 660 Hz; *J*_{107Ag-P} = 582 Hz) ppm. LRMS [ESI(+), *m/z*, CH₃CN/MeOH] (Int.) [assign.]: 1703 (8) [Ag₂L₃(OTf)(MeOH)]⁺, 1237 (2) [Ag₂L₂(OTf)]⁺, 1123 (10) [Ag₃L₄(OTf)(MeOH)]²⁺, 979 (100) [AgL₂]⁺, 687 (21) [Ag₃L₂(OTf)(MeOH)]²⁺, 584 (25) [AgL(CH₃CN)]⁺, 543 (5) [AgL]⁺. Crystals suitable for X-ray diffraction were grown over the course of 12 h by vapor diffusion of Et₂O into an acetonitrile solution of 3.

[Ag(*oL*)(PPh₃)](OTf), 4. Upon addition of 0.0265 g (0.101 mmol) of PPh₃ as a solid to a stirred suspension of 0.0700 g (0.101 mmol) of 3 in 20 mL of CH₂Cl₂, a colorless solution formed. After the solution had been stirred 1 h at room temperature, solvent was removed under a vacuum. The residue was washed with two 5 mL portions hexane and was dried under a vacuum to leave 0.0835 g (87%) 4 as a colorless solid. Mp, 225–226 °C, dec Anal. Calcd (Found) for C₄₆H₄₀F₃N₄O₃P₂SAg: C, 57.81 (57.68); H, 4.22 (4.18); N, 5.86 (5.84). ¹H NMR (400 MHz, acetone-*d*₆, 295 K) δ_H 8.75 (br s, 1 H), 8.07 (br d, *J* = 8 Hz, 1 H), 7.71–7.43 (br m, 20 H), 7.41–7.21 (br m, 9 H), 7.06 (br m, 1 H), 6.24 (br s, 2 H, H₄pz), 2.38 (br s, 6 H, CH₃) ppm. ¹³C NMR (100.5 MHz, acetone-*d*₆, 295 K) δ_C not reported because broad resonances and low signal-to-noise gave uninformative spectrum even after reasonable acquisition period of 15 h. ¹⁹F NMR (376.1 MHz, acetone-*d*₆, 295 K) δ_F –79.1 (s, 3F) ppm. ³¹P NMR (161.8 MHz, acetone-*d*₆, 295 K) δ_P br s +11.8 (LWHM = 290 Hz, 1 P,

PPh₃), br s –2.1 (LWHM = 599 Hz, 1 P, P(*p*-tolyl)₂) ppm; (193 K) δ_P 11.6 (dd, *J*_{109Ag-P} = 558 Hz, *J*_{107Ag-P} = 484 Hz, *J*_{P-P} = 108 Hz, 1P, PPh₃), –2.4 (dd, *J*_{109Ag-P} = 457 Hz, *J*_{107Ag-P} = 396 Hz, *J*_{P-P} = 108 Hz, 1P, P(*p*-tolyl)₂) ppm. Crystals suitable for X-ray diffraction were grown over the course of 15 h by allowing a layer of hexane to diffuse into a dichloromethane solution of 4.

[Ag(*m*-IC₆H₄CH(pz)₂)](OTf), 5. A solution of 0.304 g (0.868 mmol) of *m*-IC₆H₄CH(pz)₂ in 10 mL of THF was transferred quantitatively (by washing the flask with an additional 5 mL of THF and transferring the washings) via cannula to a solution of 0.112 g (0.434 mmol) of AgOTf in 5 mL of THF. A colorless precipitate formed after several hours. After the mixture had been stirred 12 h, the insoluble portion was collected by filtration, washed with two 5 mL portions Et₂O, and dried under a vacuum for 2 h to give 0.356 g (86%) of 5 as a colorless solid. Mp, 220–221 °C dec Anal. Calcd (Found) for C₂₇H₂₂F₃I₂N₈O₃SAg: C, 33.88 (33.73); H, 2.32 (2.44); N, 11.71 (11.64). ¹H NMR (400 MHz, CD₃CN) δ_H 7.85 (d, *J* = 2.5 Hz, 2 H, H₃pz), 7.82 (s, 1 H, C_{meth}H), 7.78 (d, *J* = 7.9 Hz, 1 H, C₆^{Ar}), 7.59 (d, *J* = 1.8 Hz, 2 H, H₃pz), 7.20 (s, 1 H, H₂^{Ar}), 7.16 (t, *J* = 7.9 Hz, 1 H, H₅^{Ar}), 6.88 (d, *J* = 7.9 Hz, 1 H, H₄^{Ar}), 6.42 (dd, *J* = 3, 2 Hz, 2 H, H₄pz) ppm. ¹³C NMR (100.5 MHz, CD₃CN) δ_C 142.7 (C₃pz), 139.4 (C₆^{Ar}), 139.3 (C₃^{Ar}), 136.6 (C₂^{Ar}), 132.8 (C₅pz), 131.5 (C₅^{Ar}), 127.4 (C₄^{Ar}), 107.5 (C₄pz), 94.6 (C₁^{Ar}), 76.0 (C_{meth}) ppm. LRMS [ESI(+), *m/z*] (Int.) [assign.]: 807 (100) [AgL₂]⁺, 498 (23) [AgL(CH₃CN)]⁺, 351 (50) [HL]⁺, 283 (92) [L-pz]. Crystals suitable for X-ray diffraction were grown over the course of 12 h by vapor diffusion of Et₂O into an acetonitrile solution of 5.

Crystallography. X-ray intensity data from a colorless block of 1·acetone, a colorless prism of 2·CH₃CN, a colorless needle of 3, a colorless prism of 4, and a colorless prism of 5 were collected at 100.0(1) K with an Oxford Diffraction Ltd. Supernova diffractometer equipped with a 135 mm Atlas CCD detector using Mo(*K* α) radiation for 1·acetone, 2·CH₃CN, 4, and 5 but Cu(*K* α) for 3. Raw data frame integration and *L*_p corrections were performed with CrysAlis Pro

Scheme 1. Preparation of Ligands and Silver Complexes

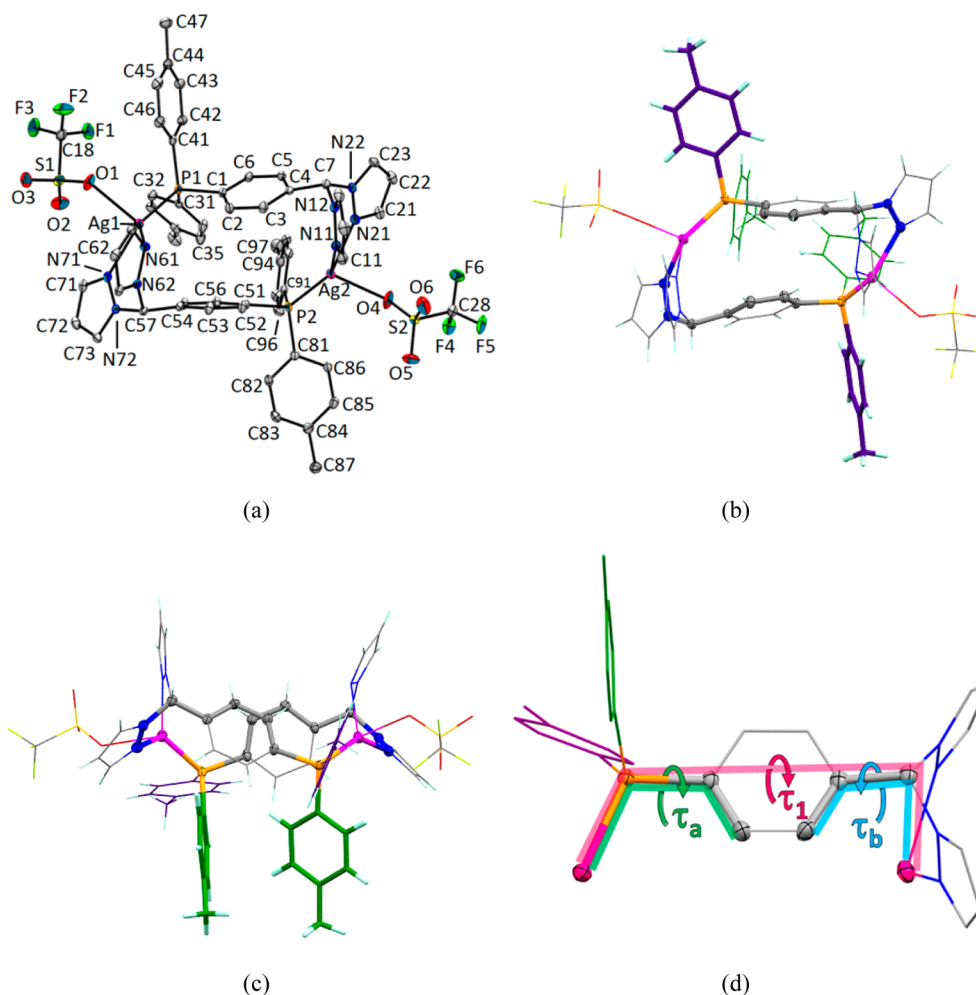
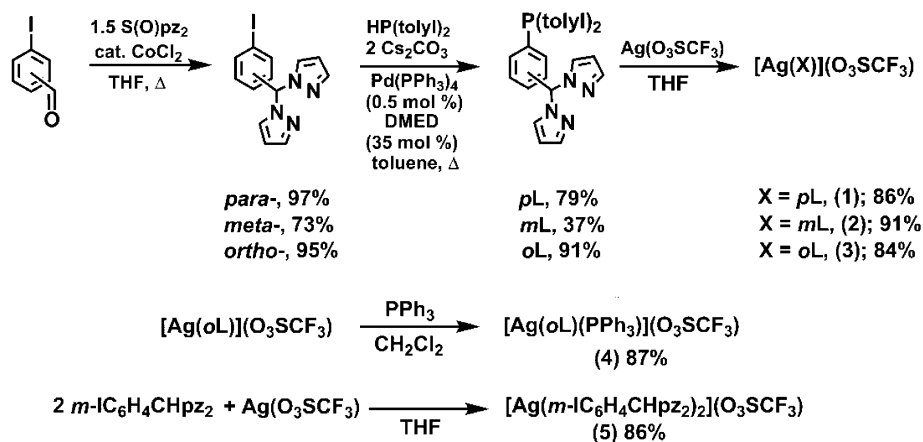


Figure 2. Views of the structure of 1:0.5 acetone with solvent removed for clarity. (a) Approximately down the b -axis; (b) 18-member metallacycle, approximately down the C_2 axis, with equatorial tolyl groups highlighted (violet capped sticks); (c) orthogonal to approximate C_2 axis with axial tolyl groups highlighted (green capped sticks). (d) Labeling scheme of various torsion angles. Selected bond distances (Å): Ag1–P1 2.3555(5), Ag1–O1 2.5125(14), Ag1–N61 2.3336(15), Ag1–N71 2.3094(15), Ag2–P2 2.3445(5), Ag2–O4 2.4734(16), Ag2–N11 2.2713(15), Ag2–N21 2.3361(16). Selected bond angles (°): P1–Ag1–O1 108.27(4), N61–Ag1–P1 127.90(4), N61–Ag1–O1 92.17(5), N71–Ag1–P1 137.84(4), N71–Ag1–O1 97.21(5), N71–Ag1–N61 82.54(5), P2–Ag2–O4 110.51(5), N11–Ag2–P2 135.10(4), N11–Ag2–O4 105.59(6), N11–Ag2–N21 82.67(5), N21–Ag2–P2 126.11(4), N21–Ag2–O4 84.20(6).

(Oxford Diffraction, Ltd.).¹⁸ Final unit cell parameters were determined by least-squares refinement of 34071, 14148, 14020, 22446, and 15970 reflections of 1-acetone, 2- CH_3CN , 3, 4, and 5,

respectively, with $I > 2\sigma(I)$ for each. Analysis of the data showed negligible crystal decay during collection in each case. Direct methods structure solutions, difference Fourier calculations, and full-matrix

least-squares refinements against F^2 were performed with Olex2¹⁹ and SHELXTL.²⁰ A numerical absorption correction based on Gaussian integration over a multifaceted crystal model were applied to the data for each crystal. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in geometrically idealized positions and included as riding atoms. For **3**, the unit cell contains four large void spaces with volumes of approximately 266 Å³ (1064/6487 or 16.4% of total cell volume). The voids are filled with heavily disordered solvent (ca. 1:1 Et₂O/CH₃CN). The solvent mask routine implemented in Olex2 was applied to the data to account for the electron density from these solvents. In the structure of **4**, the pyrazolyl group that is not bound to silver is rotationally disordered over two positions in a 1:1 ratio. The triflate anion is disordered over two positions in an 88:12 ratio. The X-ray crystallographic parameters and further details of data collection and structure refinements are given in Table 1.

RESULTS AND DISCUSSION

Synthesis. Scheme 1 summarizes the preparative routes to the ligands and silver complexes.

The di(*p*-tolyl)phosphine group was introduced to the aryldi(pyrazolyl)methane moiety by a palladium(0)-catalyzed coupling reaction between commercial di(*p*-tolyl)phosphine and the easily prepared isomers of (IC₆H₄)CHp_z. The di(*p*-tolyl)phosphine group was chosen over the less expensive diphenylphosphine for the convenience of providing relatively simple ¹H NMR spectral data (vide infra) compared to a diphenylphosphino analogue. This palladium-catalyzed coupling route proceeded smoothly for the *ortho*- and *para*-derivatives. The synthetic yield for the *meta*- derivative was consistently (significantly) lower than that for the other isomers, an observation for which we do not have a satisfactory explanation. Regardless, the current palladium-catalyzed reaction provides a clean route to the ligands. Alternative, perhaps more conventional, routes to the ligands do not proceed as expected. For instance, attempts at lithium aryl exchange between *n*-butyllithium and haloaryldi(pyrazolyl)methane followed by reaction with diarylphosphine halides or esters gave inseparable mixtures due to competitive deprotonation of the acidic methine and (5-)pyrazolyl hydrogens of the (IC₆H₄)CHp_z moiety. Also, the CoCl₂-catalyzed Peterson rearrangement²¹ of arylphosphino carboxaldehydes (obtained in low yields) with S(O)p_z did not give any detectable products perhaps due to poisoning of the metal catalyst by binding to the bulky phosphine. The ensuing reactions between THF solutions of silver(I) trifluoromethanesulfonate, Ag(OTf), and either *mL* or *oL* resulted in the immediate precipitation of the desired 1:1 complexes, [Ag(*mL*)](OTf), **2**, and [Ag(*oL*)](OTf), **3**. The analogous reaction with *pL* did not form a precipitate in THF, as [Ag(*pL*)](OTf), **1**, is surprisingly more soluble in THF than the other derivatives. All of the complexes are soluble in CH₃CN but are insoluble in Et₂O and hydrocarbon solvents. Complex **1** is significantly more soluble than either **2** or **3** (the latter is nearly insoluble) in CH₂Cl₂. In contrast to **1** and **2**, complex **3** also shows very low solubility in acetone. When 1 equiv of triphenylphosphine is added to a suspension of **3** in CH₂Cl₂, a solution is obtained immediately upon mixing since [Ag(*oL*)(PPh₃)](OTf), **4**, is formed. The complex [Ag(*m*-IC₆H₄CHp_z)₂](OTf), **5**, was isolated in good yield after collecting the precipitate from mixing THF solutions of the ligand and silver salt.

Solid State. Complex **1** crystallized as a hemisolvate, 1·0.5 acetone, by vapor diffusion of Et₂O into an acetone solution. Views of the structure of **1** are given in Figure 2. The crystal of

1·0.5 acetone shows a cyclic dimer with two AgN₂PO kernels that arises by the metal coordinating to one oxygen atom of a triflate anion, two pyrazolyl nitrogens from one bridging ligand, and a phosphorus atom from a second bridging ligand (Figure 2a). The average Ag–N_{pz} distance of 2.313 Å is at the lower limit of the 2.3–2.4 Å range previously found for four-coordinate silver bound to pyrazolyl groups.²² The average Ag–P distance of 2.349 Å is consistent with that found for other silver complexes bound to one phosphine such as (PPh₃)AgNO₃ (2.369(6) Å),²³ [(PPh₃)Ag(O₃SCF₃)₃] (avg. 2.345(5),^{24a} avg. 2.369(1) Å^{24b}), and [(PPh₃)AgCl]₄ (2.376(3), 2.388(3) Å).²⁵ The average Ag–O bond length of 2.49 Å is very close to the average value 2.48(13) Å found for other trifluoromethanesulfonate complexes of silver(I)²⁶ in a search of the Cambridge Structural Database (CSD),²⁷ as detailed in the Supporting Information. Analysis of the bond angles about each silver using Hauser's four-coordinate geometry index,²⁸ $\tau_4 = [360^\circ - (\alpha + \beta)]/141^\circ = 0.67$ for Ag1 and 0.70 for Ag2 where α and β are the largest angles about each silver (138 and 128° for Ag1; 135 and 126° for Ag2), indicates that the coordination geometry is seesaw shaped; a τ_4 value of zero would correspond to a tetrahedron, while a value of 1 would indicate square planar geometry. It is also of interest to note that the dimer formed from two bridging ligands and two silvers is characterized by an 18-member (Ag₂C₁₀N₄P₂) metallacycle ring that has a silver–silver separation of 7.65 Å and has approximate local C₂ symmetry of framework (ring) atoms (Figure 2b,c). The conformation of the metallacycle is such that there are two types of *p*-tolyl groups that can be classified as either “axial” (thicker green rings bottom part of Figure 2c) or “equatorial” (thicker violet rings in Figure 2b). The “axial” *p*-tolyl groups are on the same side of the metallacycle ring. Similarly there are two types of pyrazolyl groups, occupying either “axial” or “equatorial” positions with respect to the metallacycle. The “axial” pyrazolyls are found on the same side of the metallacycle ring but on the side opposite of the “axial” *p*-tolyl groups. The 18-member metallacycle deviates from perfect C₂ symmetry as detected by measurement of the AgP–C_{meth}Ag torsion angle, τ_1 (pink lines, Figure 2d), associated with each ligand ($\tau_1 = 71$ and 77°, for ligands A and B, respectively); an acute angle indicates the two silver atoms are on the same side of the central phenylene linker. The τ_1 torsion angle can also be decomposed into two components based on the relative disposition of the silver-bound di(*p*-tolyl)phosphine or di(pyrazolyl)methane unit with respect to the phenyl group that links the moieties. That is, one torsion angle, τ_a (green lines, Figure 2d) defined as the acute angle associated with four atoms AgP–C_{ipso}C_{ortho}, essentially describes the rotation of the Ag–P bond from the mean plane of the phenyl linker. A second torsion angle, τ_b (blue lines, Figure 2d) defined as the acute angle of four atoms, AgC_{meth}–C_{ipso}C_{ortho}, provides a measure of the rotation of the Ag–C_{meth} vector from coincidence with the mean plane of the phenyl linker (approximated by the C_{ipso}–C_{ortho} bond). Negative values for τ_a and τ_b indicate a clockwise rotation of the Ag–P or Ag–C_{meth} vector from the plane of the phenylene linker (again, approximated by the C_{ipso}–C_{ortho} bond); positive values describe a counter-clockwise rotation. The τ_1 , τ_a , and τ_b values for one ligand (“A”, containing P1) are 71.1, –12.0, and 80.6°, respectively, whereas those values for the other ligand (“B”, containing P2) are 77.2, –41.7, and –67.4°. The different τ_a (or τ_b) values found for ligands A and B of the metallacycle are sufficient to exclude any symmetry relation between ligands.

Complex **2** crystallizes as a CH_3CN solvate, $2 \cdot \text{CH}_3\text{CN}$, after vapor diffusion of Et_2O into an acetonitrile solution. In this case, a cyclic dimeric dication is formed from two ligands

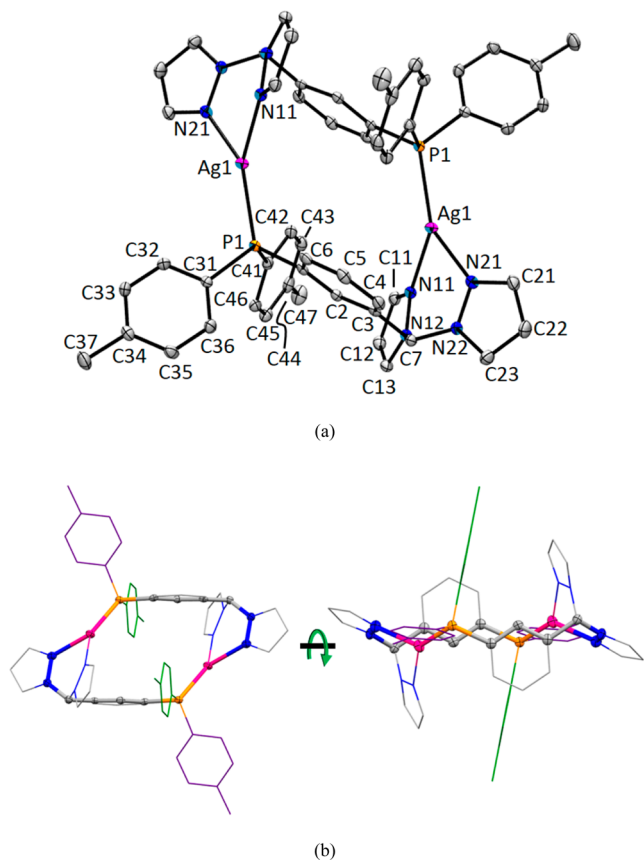


Figure 3. Structure of $2 \cdot \text{CH}_3\text{CN}$. (a) A dimeric dication with atom labeling. Hydrogen atoms, triflate anion and acetonitrile solvate molecule removed for clarity. (b) Views emphasizing 16-member metallacyclic ring and symmetrically distinct *p*-tolyl groups (green and violet). Selected bond distances (Å): Ag1–P1 2.3445(6), Ag1–N11 2.2564(18), Ag1–N21 2.3043(19). Selected bond angles (°): N11–Ag1–P1–144.04(5), N11–Ag1–N21 82.90(7), N21–Ag1–P1 132.63(5).

bridging two silver centers with an $\text{Ag} \cdots \text{Ag}$ separation of 6.003 Å (Figure 3a); the triflate anions are not bound to silver centers²⁹ as was the previous case. The dication has inversion (C_i point group) symmetry, and thus each silver has an identical planar “Y-shaped” AgN_2P coordination environment (sum of angles about Ag = 360°). The average $\text{Ag}-\text{N}_{\text{pz}}$ bond distance of 2.28 Å is at the upper limit of the 2.2–2.3 Å range found for tricoordinate silver (bound to pyrazolyl donors),²² and the $\text{Ag}-\text{P}$ bond distance of 2.3445(6) is nearly identical to the average distance found for 1–0.5 acetone, which demonstrates previous observations that the $\text{Ag}-\text{P}$ distance depends mainly on the number of phosphines bound to silver and to a lesser extent on the coordination number of silver.³⁰ The dication also possesses a 16-member $\text{Ag}_2\text{C}_8\text{N}_4\text{P}_2$ metallacyclic ring. There are two types of pyrazolyl groups, “axial” and “equatorial”, where “axial” pyrazolyls project further above and below the mean plane of the 16-member metallacycle ring than the “equatorial” pyrazolyls, right of Figure 3b. The ring can be said to be in a chair conformation where either “equatorial” or “axial” pyrazolyl nitrogens serve as the “head” and “foot” of the chair. There are also two types of *p*-tolyl groups, “axial” (green,

Figure 3b) and “equatorial” (violet, Figure 3b), but the “axial” *p*-tolyl groups are on opposite faces of the mean plane of the metallacycle. Finally, as a means of comparison with **1**, the τ_1 , τ_a , and τ_b values for each ligand of the dication in **2** are -25.2 , $+51.7$, $+79.4$ for one ligand and $+25.2$, -51.7 , -79.4 for the other. The acute τ_1 values in **2** indicate that the two silvers are on the same side of the central phenylene linker, while the identical magnitudes but opposite signs of the τ_1 , τ_a , and τ_b values indicate symmetry equivalence (by inversion) of the two ligands.

Complex **3** crystallizes in the orthorhombic space group $Pbca$ after vapor diffusion of Et_2O into an acetonitrile solution. The asymmetric unit consists of one ligand, one silver, and one triflate anion, Figure 4a. The ligand again acts in a bridging manner by binding one silver center with the phosphorus atom and another silver with two nitrogens of the CHpZ_2 moiety. In contrast to the previous cases, the obtuse τ_1 torsion angle of 151.5° in **3** indicates that the silver centers are on opposite faces of the phenylene group that separates the phosphino and di(pyrazolyl)methane groups. This disposition of donor groups results in a coordination polymer instead of a cyclic species, Figure 4b. The coordination polymer propagates along the *b*-direction. Specifically, the polymer is generated by translation of the asymmetric unit along the *b*-glide plane perpendicular to the *a*-axis (i.e., with reflection through the *ac*-plane). The silver centers can be considered either three- or four-coordinate depending on one’s view of the long $\text{Ag1}-\text{O1}$ contact of 2.809(3) Å, Figure 4c. We favor tetracoordination because this distance is 0.43 Å less than the sum of the van der Waals radii (3.24 Å) and is within 3σ of the average $\text{Ag}-\text{O}$ distance of 2.48(13) Å found from the CSD (Figure S2, Supporting Information), and since the average $\text{Ag}-\text{N}_{\text{pz}}$ distance of 2.33 Å is in the 2.3–2.4 Å range found for other tetracoordinate silver complexes with pyrazolyl-ligands.²² If the silver is considered tetracoordinate, then the four-coordinate geometry index, $t_4 = 0.60$, indicates a seesaw geometry. There are two other contacts, $\text{Ag1}-\text{O2}$ 3.055(2) Å and $\text{Ag1}-\text{H7}$ 2.82, that are about 0.2 Å less than the sum of the respective van der Waals radii and, as such, can be considered secondary interactions.

The structure of **4** (Figure 5) consists of a monomeric species that has tetracoordinate silver bound to a triphenylphosphine, to *oL* in a chelating $\kappa^2\text{N},\text{P}$ -manner, and to an oxygen of the triflate anion (in a κ^1 -fashion). The structure is afflicted by disorder that allows limited discussion of the coordination environment but precludes extensive analysis of the supramolecular structure. That is, the pyrazolyl ring that is not bound to the silver is rotationally disordered about the $\text{C7}-\text{N22(a)}$ bond equivalently over two positions. The triflate anion is located in two nearby positions in an 88:12 ratio, favoring the position depicted on the left of Figure 5 with two oxygen atoms of the anion oriented toward the triphenylphosphine group. The $\text{Ag}-\text{O}$ distance of either disorder component ($\text{Ag1}-\text{O1}$ 2.461(3), $\text{Ag1}-\text{O1a}$ 2.323(17) Å) is shorter than the 2.48 Å average $\text{Ag}-\text{O}$ (triflate) distance from the above CSD database search, which permits a confident assertion of $\kappa^1\text{O}$ -coordination. The $\text{Ag}-\text{N}_{\text{pz}}$ distance of 2.408(2) Å is in line with tetracoordinate silver. The $\text{Ag1}-\text{P1}$ distance of 2.5060(6) Å is longer than those distances in **1**–**3** but is consistent with four-coordinate silver complexes of $\text{P}(p\text{-tolyl})_3$.³¹ The $\text{Ag}-\text{P2}$ (PPh_3) distance of 2.4186(6) Å is in line with the ca. 2.42 Å average $\text{Ag}-\text{P}$ distance found in other tetracoordinate silver complexes with two triarylphosphine ligands.^{30,32}

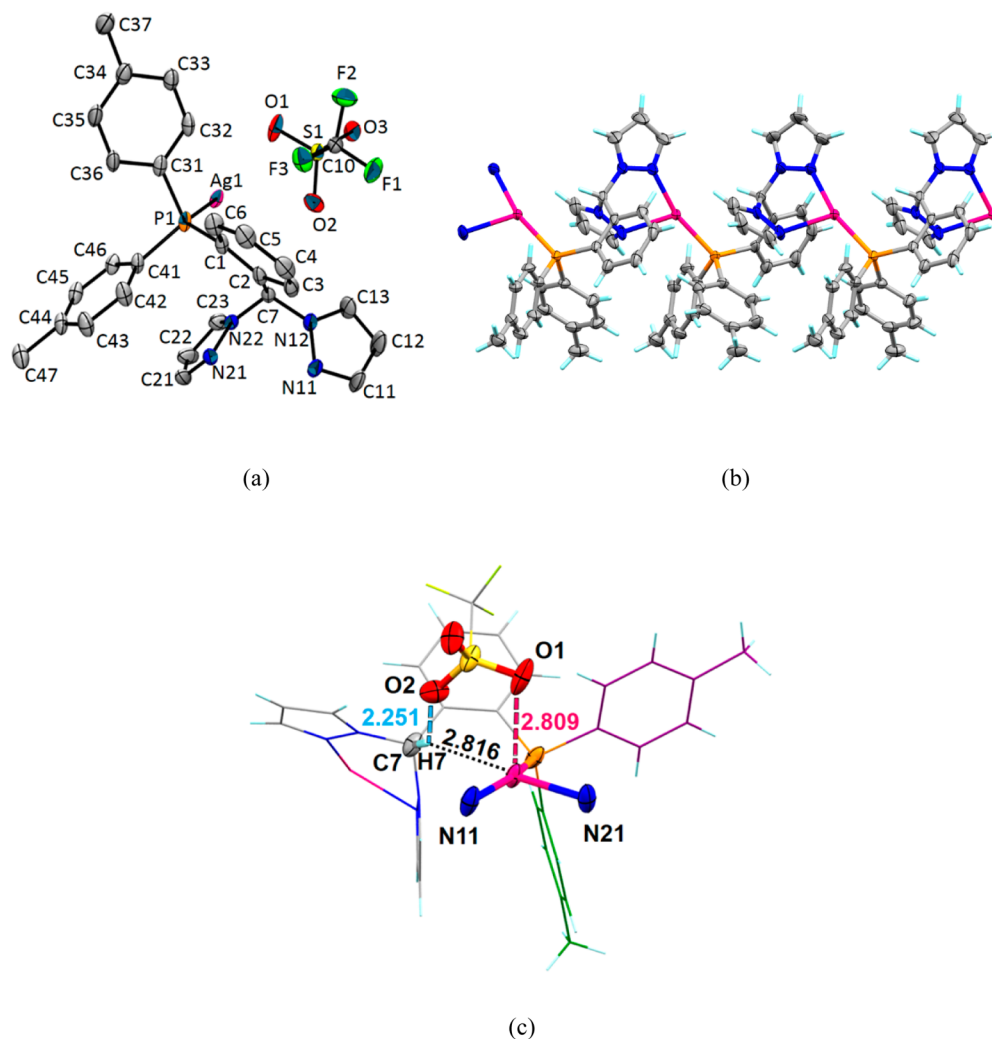


Figure 4. Structure of $[\text{Ag}(\text{oL})](\text{OTf})$, **3**. (a) Asymmetric unit with atom labeling and with hydrogen atoms removed for clarity. (b) View down the a -axis of a chain propagating along the b -direction, triflate anions removed for clarity. (c) View of primary and secondary coordination sphere around silver with interatomic distances in Å. Selected bond distances (Å): Ag1–P1 2.3839(6), Ag1–N11 2.266(2), Ag1–N21 2.394(2), Ag1–O1 2.809(3). Selected bond angles ($^\circ$): P1–Ag1–N21 113.53(6), N11–Ag1–P1 160.73(7), N11–Ag1–N21 83.37(8), P1–Ag1–O1 99.67(5), N11a–Ag1–O1 89.85(9), N21a–Ag1–O1 87.57(8).

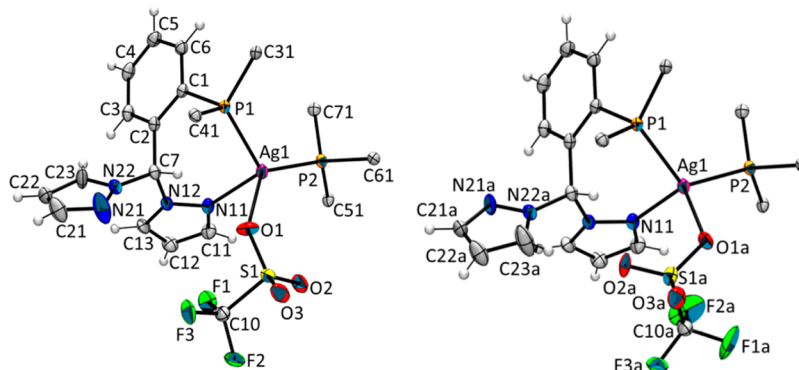


Figure 5. Views of two disorder components in the structure of $[\text{Ag}(\text{oL})(\text{PPh}_3)](\text{OTf})$, **4**, with atom labeling. Only the *ipso*-carbon atom bound to the phosphine atom on of the tolyl groups of oL and on the phenyl rings in PPh_3 are shown for clarity. Selected bond distances (Å): Ag1–P1 2.5060(6), Ag1–P2 2.4186(6), Ag1–N11 2.408(2), Ag1–O1 2.461(3), Ag1–O1a 2.323(17). Selected bond angles ($^\circ$): P2–Ag1–P1 124.13(2), P2–Ag1–O1 131.42(7), O1–Ag1–P1 92.39(6), O1a–Ag1–P1 102.0(5), O1a–Ag1–P2 106.0(4), O1a–Ag1–N11 111.8(4), N11–Ag1–P1 105.25(5), N11–Ag1–P2 107.59(5), N11–Ag1–O1 89.19(8).

Supramolecular Structures. Aside from fundamental interest, the analysis of the supramolecular structures of

complexes **1**•acetone, **2**• CH_3CN , **3**, and **5** is of importance to the interpretation of their solid state IR spectrum and

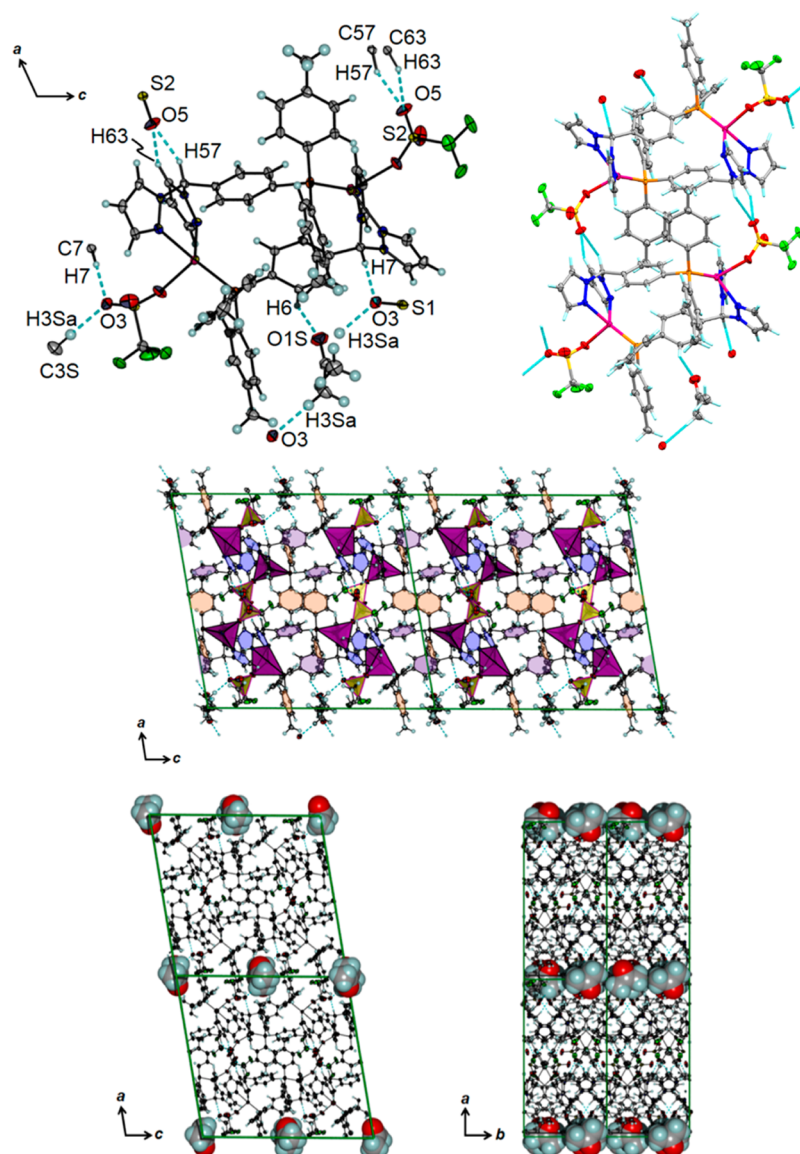


Figure 6. Supramolecular structure of **1**·0.5 acetone. Top left: View of CH...O interactions (cyan dashed lines); top right: Dimer formed by interactions involving only O5. Middle: View of *bc*-sheet bilayer structure (Ag as pink tetrahedra, triflate SO₃C unit as yellow tetrahedra, pyrazolyl rings as blue pentagons, phenylene linkers as violet hexagons; tolyl rings as orange hexagons); bottom: View of four unit cells down *b*- (left) and down *c*- (right) showing acetone filling channels along the *b*-direction.

Table 2. Geometries of C–H...O Weak Hydrogen-Bonding Interactions in **1·acetone**

Donor(D)–(H) ...Acceptor(A)	D–H (Å)	H...A (Å)	D...A (Å)	D–H...A (°)
C–H...O interactions				
C7–H7...O3	1.00	2.14	3.130(2)	169
C23–H23... O1	0.95	2.53	3.368(2)	147
C57–H57...O5	1.00	2.21	3.119(2)	150
C63–H63...O5	0.95	2.40	3.133(2)	134
C85–H85... O6	0.95	2.59	3.484(2)	158
C3S–H3Sa...O3	0.98	2.47	3.432(3)	169
C6–H6...O1S	0.95	2.36	3.224(3)	151

potentially to the powder X-ray diffraction (PXRD) studies described later. The supramolecular structure of **1**·acetone is shown in Figure 6 and is discussed below, while analyses of the other structures are provided in the Supporting Information. A feature common to the supramolecular structures of all the current complexes, and to most other Ag(OTf) complexes of

di(pyrazolyl)methane ligands,^{8a} is CH...O weak hydrogen bonding interactions³³ that occur between the triflate anion and the acidic methine and 5-pyrazolyl hydrogen atoms. That is, in **1**·acetone, a variety of weak CH...O hydrogen bonding interactions organize the 3D structure into stacked bilayer sheets with channels along the *b*-axis that hold solvent. Figure 6

shows only the shortest (sum of van der Waals radii ~ 0.2 Å) and presumably strongest of these “intermolecular” CH \cdots O interactions (cyan dashed lines), while Table 2 collects the metrics of these and of the longer interactions. Of the two independent triflate anions, that with S2 serves as a bridge to connect neighboring dications along the *a*-direction to form a dimer of dications (top right of Figure 6). That is, one of the oxygens (O4) interacts with Ag2 of one cation, while O5 acts as an acceptor in a bifurcated weak hydrogen bonding interaction with the methine (H57) and 5-pyrazolyl (H67) hydrogen donors of a neighboring dication with the metrics listed in Table 2. The third oxygen atom (O6) of this triflate anion participates in a long and presumably very weak noncovalent bonding interaction with a tolyl ring hydrogen (H85, *ortho*- to the methyl group). The Ag1–O1 bonds anchor two of the other independent triflate anions (that each contain S1) to the dimer of dications. The oxygen atom O3 of each “S1-containing” triflate acts as an acceptor in a bifurcated CH \cdots O interaction with the methine hydrogen (H7) of neighboring dimer of dications as well as with a methyl group hydrogen (H3Sa) of an acetone solvate molecule. A bilayer sheet structure, that is one unit cell in width along the *a*-direction but infinite in the *bc*-plane (Figure 6), is formed since each dimer of dications contains two hydrogen donors and two acceptors of four C7H7 \cdots O3 interactions. The *bc*-sheets are further connected along the *a*-direction by two types of CH \cdots O interactions involving the acetone solvate molecule. The first interaction, C3SH3Sa \cdots O3, described previously, holds the acetone molecule to one sheet, while the oxygen atom of acetone (O1S) acts as an acceptor to a phenylene hydrogen (H6) that is *ortho*- to the ditolylphosphine group (top left of Figure 6) of an adjacent bilayer sheet. As a result of the sheet stacking, there are channels along the *b*-direction that contain acetone molecules as shown in the two views in the bottom of Figure 6.

It is important to note that each oxygen of both types of triflate ion in 1·acetone (or of the anions in 2·CH₃CN, 3, 4, or 5, see Supporting Information) experiences a distinct (weak hydrogen-bonding) environment in the solid state. If the C–H \cdots O interactions are significant, the local symmetry around either S1 or S2 in 1·acetone could be effectively lowered to C₁ and give rise to an increase in the number and/or broadness of S–O stretches in the solid state IR spectrum (*vide infra*) compared to the idealized case where the local symmetry about sulfur in the CF₃SO₃ group is C_{3v}.

PXRD. Powder X-ray diffraction data were collected for the solid samples of 1–3 and 5 obtained immediately after their initial isolation (as-prepared samples are precipitated from THF and/or washed with Et₂O and dried under a vacuum), and after recrystallization from various solvents followed by drying under a vacuum. The PXRD patterns obtained for as-prepared samples of 5 match those calculated from single-crystal X-ray diffraction data (Figure S6, Supporting Information) which is expected since this compound crystallized without solvent in the lattice. This contrasts the situation for 2 where the diffraction pattern of the solvent-free (combustion analysis) powder does not match that calculated for the single crystal of 2·CH₃CN (Figure S6), as might be expected. While X-ray diffraction quality crystalline blocks of 1·0.5 acetone were obtained after allowing a layer of hexanes to diffuse into an acetone solution of 1, vapor diffusion of Et₂O into an acetonitrile solution of 1 produces microcrystalline, ultrathin needles that are unsuitable for single crystal X-ray diffraction.

Simply air drying these ultrathin needles is sufficient to give a solvent-free sample of 1 as determined by combustion analysis.

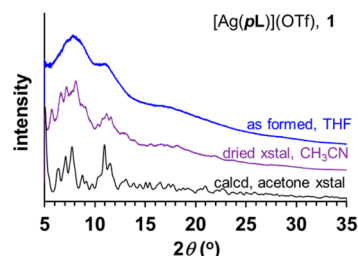


Figure 7. PXRD patterns obtained for samples of 1 obtained under various conditions compared to data (bottom) calculated from the single crystal diffraction data for 1·0.5 acetone.

Samples of air-dried needles of 1 (from CH₃CN) and those as-prepared samples of 1 from THF showed variable levels of crystallinity (middle and top of Figure 7, respectively). Given the supramolecular structure of 1·0.5 acetone that showed solvent partly occupying channels, the ease of solvent removal, and the similarity of PXRD patterns, it is likely that the structures of the crystalline samples obtained from other solvent systems (i.e., especially the microcrystalline needles from CH₃CN) are closely related to that of 1·0.5 acetone. Similarly, the crystal of 3 had heavily disordered solvent (Et₂O:CH₃CN) in large voids in the crystal (Supporting Information). Yet, the calculated PXRD pattern matched that of the as-isolated, solvent-free (combustion analysis) powder indicating that the overall structural features remain intact regardless of the presence or absence of solvent.

IR Spectra. The IR spectra of 1–4 and 5 in CH₃CN show characteristic bands for “unbound” or “ionic” triflate anions at 1271, 1157, 1093, and 966 cm^{−1}, for SO₃ and CF₃ stretching modes and combination bands,³⁴ but the solid state spectra are much more complicated than expected (Figure S7) presumably due to the various different weak CH \cdots O interactions and, in the case of 1, to the two crystallographically distinct types of triflate anions in the unit cell. For instance, single crystal X-ray diffraction of 5 shows tetracoordinate silver ($\tau_4 = 0.73$, seesaw AgN₄ geometry, see Figure S1) due to binding only to pyrazolyl nitrogen donors. In this case, the triflate anion is not bound to the metal center, yet the solid-state IR spectrum is complicated. Examination of the supramolecular structure reveals that each of the three oxygens of the triflate participates in a different type of CH \cdots O interaction (Figure S5) which may effectively lower the local symmetry of the SO₃ moiety and give rise to a greater than expected number of S–O stretches. The IR spectra of as-isolated powders of 1–4 and 5 are identical to those obtained for air-dried crystals; combustion analyses indicate that the powders or air-dried crystals are solvent-free.

Solution. NMR. The variable temperature multinuclear NMR and ESI(+) MS data (*vide infra*) indicate that, in solution at room temperature, compounds 1 and 2 likely maintain cyclic structures similar to the solid state, whereas the solution structures of 3 and 4 are different than their solid-state structures. The ³¹P NMR spectral data of triarylphosphine silver(I) complexes are particularly useful for characterization as they can be diagnostic of the number and type of phosphine ligands bound to silver.^{30,35} Silver has two naturally occurring NMR-active (*I* = 1/2) nuclei, ¹⁰⁷Ag (52% abundance) and ¹⁰⁹Ag (48% abundance). When silver is bound to one phosphorus atom, a characteristic set of doublet resonances

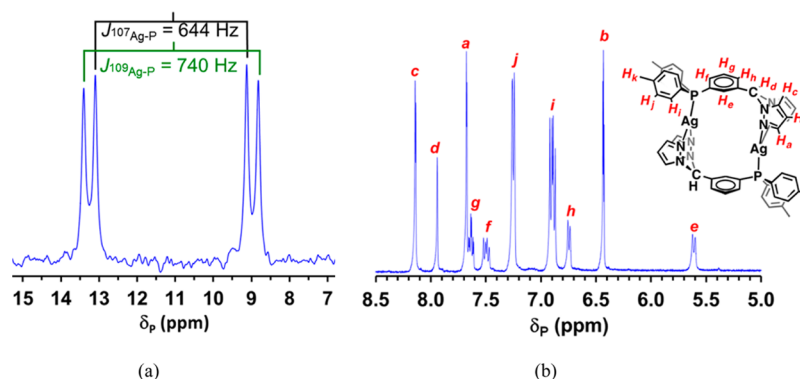


Figure 8. (a) ^{31}P NMR spectrum of $[\text{Ag}(\text{mL})](\text{OTf})$, **2**, in CD_3CN at 295 K and (b) downfield portion of the ^1H NMR spectrum of **2** with atom labeling scheme.

such as shown in Figure 8a is expected. In the absence of exchange, the nearly overlapping doublets are resolved, and the ratio of one-bond coupling constants $^1J_{^{109}\text{Ag}-\text{P}}/^1J_{^{107}\text{Ag}-\text{P}}$ should be 1.15, corresponding to the ratio of the nuclear magnetic moments (μ_N in nuclear magneton units, μ_N) $\mu_N(^{109}\text{Ag}) = -0.13056 \mu_N$; $\mu_N(^{107}\text{Ag}) = -0.11357 \mu_N$.³⁶ Typically, however, in complexes such as $[\text{Ag}(\text{PPh}_3)_n]^+$ ($n = 1-4$) the solution exchange is rapid at room temperature so the doublet resonances are not resolved; they only become resolved at low temperature (below 203 K).^{35b} The ^{31}P NMR spectra of **1** and **2** in CD_3CN are remarkable in that the doublet resonances are resolved at room temperature, indicative of slow exchange on the NMR time scale. In fact, resolution of the two doublets for $^{109}/^{107}\text{Ag}-\text{P}$ coupling is lost due to exchange broadening only after heating CD_3CN solutions of **1** to 60 °C or of **2** to 40 °C. At room temperature, the $^1J_{^{107}\text{Ag}-\text{P}}$ coupling constant of 638 Hz for **1** and 644 Hz for **2**, is comparable to other silver complexes with only one phosphine bound to silver such as $(\text{Ph}_3\text{P})\text{Ag}(\text{NO}_3)$ (780 Hz),^{30a} $(\text{Ph}_3\text{P})\text{Ag}(\text{PF}_6)$ (755 Hz),^{35b} and $(\text{tBu}_3\text{P})\text{Ag}(\text{NO}_3)$ (683 Hz),^{35d} or to other complexes binding one phosphine and pyrazolyl donors such as $[(\text{Ph}_3\text{P})\text{Ag}(\text{pz}_6\text{C}_6)](\text{SbF}_6)$ (648 Hz),³⁷ $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\text{pz}_3\text{Ag}(\text{PPh}_3))] (565 \text{ Hz})$,³⁸ or $[\text{HB}(\text{pz}_3)\text{Ag}(\text{PPh}_3)] (607 \text{ Hz})$.³⁹ Silver complexes bound to two phosphines have much smaller $^1J_{^{107}\text{Ag}-\text{P}}$ coupling constants in the 400–500 Hz range such as 496 Hz for $[(p\text{-tolyl}_3\text{P})_2\text{Ag}]\text{PF}_6$,^{35b} 507 Hz for $[(\text{Ph}_3\text{P})_2\text{Ag}](\text{PF}_6)$,^{35b} and 432 Hz for $[(\text{tBu}_3\text{P})_2\text{Ag}](\text{NO}_3)$.^{35d} Thus, neither **1** nor **2** isomerize in solution to give a species where one silver is bound to two phosphines and the other silver is only bound to pyrazolyls (like Figure 1e). A second line of evidence that a cyclic structure is preserved in solution at room temperature comes from the ^1H NMR data of **2**. The downfield portion of the spectrum and labeling scheme are shown on the right of Figure 8. Although we verified assignments of hydrogen resonances in **mL** and **2** by 2D NMR (NOESY, COSY) experiments, the aryl hydrogen resonances (both the tolyl and central phenylene) of **2** can be assigned by simple inspection by considering relative integration, the asymmetric nature of the ligand that gives different distinctive multiplicities to the central phenylene resonances (H_{e-h} , Figure 8), and by the different magnitudes of the hydrogen–phosphorus coupling constants. The doublet resonance at 5.6 ppm ($^3J_{\text{H}-\text{P}} = 9.5 \text{ Hz}$) for the single hydrogen atom, H_e , situated between the phosphorus and the methine carbon, is highly shielded compared to other resonances or to that of the free ligand at 6.8 ppm ($^3J_{\text{H}-\text{P}} = 7.1 \text{ Hz}$) in the same solvent. Inspection of the solid state structure

of **2** (Figure 3b) shows that this H_e hydrogen is sandwiched between the π -clouds of both a tolyl group and a pyrazolyl ring. Upon warming the solution to 60 °C, the doublet resonance for H_e becomes deshielded and exhibits the greatest downfield shift (of 0.2 ppm) compared with other resonances. The resonance for the tolyl hydrogens, H_i , close to the phosphorus atom, experiences the next greatest shift of 0.1 ppm downfield, followed by the resonance for H_f (the other phenylene hydrogen *ortho*- to P) which shifts upfield by 0.06 ppm. The resonances for pyrazolyl hydrogens only shift by 0.01 ppm over the same temperature range. Thus, the environment around the phosphorus atom exhibits the greatest change with temperature, perhaps being indicative of dissociation at high temperature. Interestingly, there is only one set of resonances for each pyrazolyl and tolyl group in the ^1H NMR spectrum of either **1** or **2**, even at low temperature (233 K for CD_3CN , 193 K in acetone- d_6). Two sets of resonances for tolyl group hydrogens and two sets of resonances for pyrazolyl hydrogens were expected based on the solid state structures of the complexes that showed distinct “axial” and “equatorial” rings of each type. Thus, while the low temperature ^{31}P NMR data (and ^1H NMR data for **2**) indicate that the metallacycles are intact, the 18- and 16-member metallacycles of **1** and **2**, respectively, must have low barriers to inversion that would allow facile exchange axial and equatorial pyrazolyl or tolyl rings. Reger and co-workers have recently demonstrated similar dynamic behavior in metallacycles supported by related *m*- pz_4xy .^{7b,e}

In contrast to the above, the ^{31}P NMR spectrum of **3** in CD_3CN shows only a broad singlet at room temperature due to (intermediate) exchange. Upon lowering the temperature to 273 K, the coalescence temperature is reached, and the resonance appears as a broad doublet. Two doublet resonances for $^{109}\text{Ag}-\text{P}$ and $^{107}\text{Ag}-\text{P}$ coupling are only partially resolved at 233 K, near the freezing point of the solvent, where the $^1J_{^{107}\text{Ag}-\text{P}}$ coupling constant of ca. 580 Hz is in line with other complexes with one phosphine bound to silver, as described above. It is of interest that the energy barrier to exchange (indicated by loss of $\text{Ag}-\text{P}$ coupling) decreases with increasing steric bulk around the phosphorus atom of the ligand in the complexes in the order: $3 < 2 < 1$. Such a trend further implicates that exchange occurs by dissociation of the phosphine.

Finally, the ^{31}P NMR spectrum of **4** in acetone- d_6 (Figure 9) at room temperature consists of two broad singlet resonances near $\delta_p + 11 \text{ ppm}$ and -3 ppm , for the phosphorus nuclei of the PPh_3 ligand and the $\text{P}(p\text{-tolyl})_2$ moiety, respectively. Such an

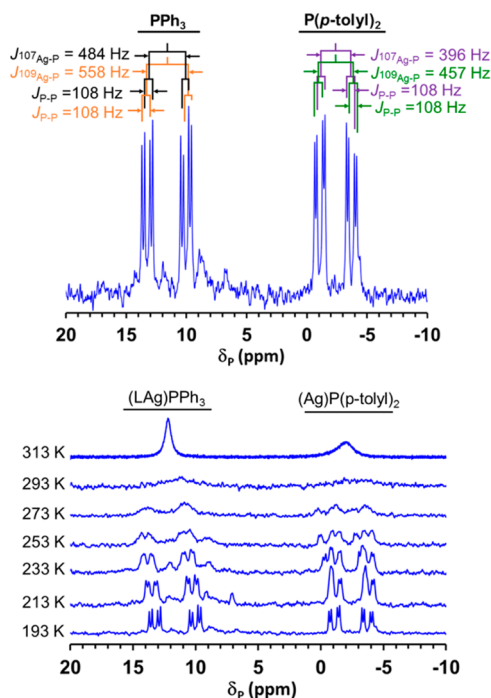


Figure 9. Top: ^{31}P NMR spectrum of $[\text{Ag}(\text{oL})(\text{PPh}_3)](\text{OTf})$, **4**, in acetone- d_6 at 193 K. Bottom: overlay of spectra of **4** in acetone- d_6 acquired at different temperatures.

assignment is based on the observation that the difference between the chemical shift of the resonance for a silver(I) triarylphosphine complex and that for the free triarylphosphine ligand, $\Delta\delta_{\text{p}} = \delta_{\text{p}}(\text{complex}) - \delta_{\text{p}}(\text{ligand})$, is typically on the order of +20 ppm.³⁹ In this case, free PPh_3 and the free ligand resonate at δ_{p} -6 and -20 ppm, respectively, giving $\Delta\delta_{\text{p}}$ of 17 ppm for each type of phosphine. For reference, the $\Delta\delta_{\text{p}}$ for **1–3** were 19, 18, and 19 ppm, respectively. At low temperature, each singlet resonance of **4** resolves into two overlapping doublet of doublet resonances due to $^{109}\text{Ag-P}$, $^{107}\text{Ag-P}$, and P–P coupling as illustrated in the top of Figure 9. The $^1J_{^{107}\text{Ag-P}}$

coupling constant of 484 Hz for the PPh_3 moiety and of 396 Hz for the $\text{P}(p\text{-tolyl})_2$ moiety are in the expected 400–500 Hz range for bis(triaryl)phosphine complexes, as outlined earlier. Moreover, the two different types of phosphorus lead to a $^2J_{\text{P-P}}$ coupling of 108 Hz, which is larger than 26 Hz found in $[\text{PhB}(\text{CH}_2\text{PPh}_2)_3]\text{Ag}(\text{PEt}_3)^{40}$ but is on par with 134 Hz found for $\{[\mu-(\eta^5\text{-C}_5\text{H}_4)\text{PPh}_2]\text{Ag}(\text{PPh}_3)\}_2$.⁴¹ At intermediary temperatures (213 K to ca. 253 K) other resonances are observed in the baseline of the ^{31}P NMR spectrum (between 10 to 5 ppm and near 0 ppm), but their low intensity and the low signal-to-noise ratio prevented definitive assignment of these presumed intermediates or equilibrium species.

ESI(+) Mass Spectrometry. Complexes **1–3** as CH_3CN solutions were characterized by ESI(+) mass spectrometry. The parent (100%) peak for **1** occurred at $m/z = 544$ for the $[\text{Ag}_2\text{L}_2]^{2+}$ dication. The identity of the dication versus an $[\text{AgL}]^+$ cation is easily determined by examination of the isotope pattern, especially since the former shows half-integer peaks, as in the right of Figure 10. Careful inspection of the intensities of the experimental data for the peaks near $m/z = 544$ of **2** (most notably by the peaks at $m/z = 543$ and 547, right of Figure 10) reveals that they deviate slightly from the theoretical values for $[\text{Ag}_2\text{L}_2]^{2+}$ because about 5–10% of the total signal in this region is for $[\text{Ag}(\text{mL})]^+$. The spectra of **1** and **2** also show a low abundance peak (1–2%) at $m/z = 1237$ for $[\text{Ag}_2\text{L}_2(\text{OTf})]^+$, providing further evidence for the persistence of the metallacycles under these conditions. In the spectrum of **3**, the parent peak is at $m/z = 979$ for $[\text{AgL}_2]^+$. The second most abundant peak occurs at $m/z = 584$ for $[(\text{oL})\text{Ag}(\text{CH}_3\text{CN})]^+$. A low abundance (5%) peak found at $m/z = 543$ is for the monocation $[\text{AgL}]^+$. Collectively, the data indicate that **3** is extensively dissociated under these conditions rather than being polymeric akin to the complexes' solid state structure.

SUMMARY AND CONCLUSIONS

Silver(I) trifluoromethanesulfonate complexes of the newly prepared heteroditopic ligands containing di(*p*-tolyl)phosphine and di(pyrazolyl)methane groups bound to a phenylene spacer

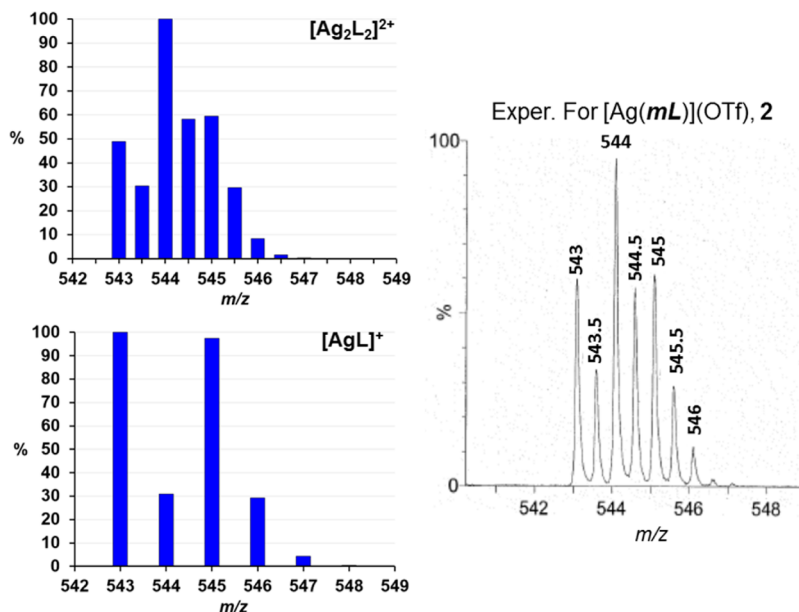


Figure 10. Comparison of theoretical isotope pattern for $[\text{AgL}]^+$, $[\text{Ag}_2\text{L}_2]^{2+}$, and the experimental pattern for **2**.

give different solid state and solution structures depending on the juxtaposition of the donor moieties. A coordination polymer, **3**, is formed in the solid state if the donors are situated *ortho*- to one another on the phenylene ring. However, when the groups are disposed either *para*- (as in **1**) or *meta*- (as in **2**), the resultant silver complexes have cyclic bimetallic dications with 18- and 16-membered metallacyclic rings, respectively. In crystals of 1·0.5 acetone, 2·CH₃CN, and **3**, the supramolecular structure was organized mainly by CH··O interactions involving the triflate oxygen and the acidic methine and 5-pyrazolyl hydrogens. The persistence of the cyclic structures of each **1** and **2** in CH₃CN is evident by the ~640 Hz one-bond Ag–P coupling in the room-temperature ³¹P NMR spectrum, the variable temperature ¹H NMR spectrum of **2**, and the ESI(+) mass spectrum of **1** and **2**. The ³¹P NMR data for **1** and **2** are particularly remarkable because one-bond Ag–P coupling is not observed in the room temperature spectrum of **3**, [Ag(PR₃)_n]⁺ (*n* = 1–4), or most other heteroleptic [LAgP]ⁿ⁺ complexes due to the lability of the Ag–P bond or bonds between other donors and silver. Evidently cyclic structures slow the rate of exchange, an observation that may have use in the future design of shape-persistent supramolecular assemblies of silver(I). The combination of NMR and ESI(+) mass spectral data for **3** suggests that the coordination polymer is likely extensively dissociated in CH₃CN. Insight into the possible solution structure of **3** in CH₃CN was gleaned by exploring the reaction between **3** and the strong Lewis donor PPh₃, which gave a monomeric Lewis adduct **4** that showed a chelating κ²-P,N ligand in the solid state. The solution structure of **4** was dynamic where exchange involving phosphine could only be stopped at very low temperature (193 K in acetone-*d*₆). Future studies on the reactivity of these ligands and their silver(I) complexes toward transition metal salts is underway in our laboratory.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Structure of $\{(m\text{-IC}_6\text{H}_4\text{CHpz}_2)_2\text{Ag}\}(\text{OTf})$, **5**. Details and results of CSD Query of Ag–O(triflate) distances. Supramolecular structure of 2·CH₃CN. Supramolecular structure of [Ag(oL)](OTf), **3**. Supramolecular structure of $[(m\text{-IC}_6\text{H}_4\text{CHpz}_2)_2\text{Ag}](\text{OTf})$, **5**. Powder X-ray diffraction patterns for **2**, **3**, and **5**. IR spectra of **1**–**4** and **5**. Figures for NMR assignments and 2D NMR spectra. References. Crystallographic information files. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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