

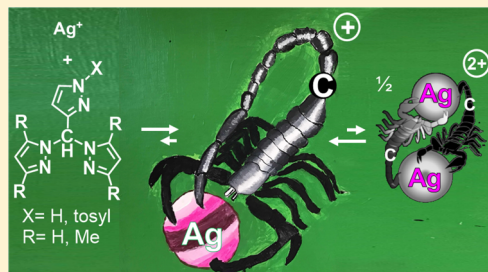
Reaction Chemistry of Silver(I) Trifluoromethanesulfonate Complexes of Nitrogen-Confused C-Scorpionates

James R. Gardinier,^{*,†} Kristin J. Meise, Fathiya Jahan, and Sergey V. Lindeman

Department of Chemistry, Marquette University, Milwaukee, Wisconsin 53201-1881, United States

S Supporting Information

ABSTRACT: Two new C-scorpionate ligands with a bis(3,5-dimethylpyrazol-1-yl)methyl group bound to the 3 position of either an *N*-tosyl (^{Ts}L*) or an *N*-H pyrazole (^{HL}*) ring have been prepared. The silver(I) complexes of these new ligands and the two previously reported analogous ligands with unsubstituted bis(pyrazol-1-yl)methyl groups (^{Ts}L and ^{HL}L) in both 1:1 and 2:1 ligand/metal ratios were investigated to explore the effects of ligand sterics on their physical and chemical properties. The structurally characterized derivatives of the type [Ag(L)₂](OTf) are four-coordinate, where the confused pyrazolyl is not bound to the metal. On the other hand, three 1:1 complexes [Ag(L)](OTf) had all pyrazolyls bound, while the $\mu\text{-}\kappa^1, \kappa^1\text{-TsL}$ derivative had an unbound confused pyrazolyl. The molecularity of the latter four ranged from polymeric to dimeric to monomeric in the solid with increasing steric bulk of the ligand. The utility of these complexes in stoichiometric ligand-transfer reactions and in styrene aziridination was demonstrated. Thus, tricarbonylmanganese(I) complexes were prepared as kinetically inert models for comparative solution diffusion NMR studies. Also, [Fe(^{HL}L)₂](OTf)₂ was prepared for similar reasons and to compare the effects of anion on spin-crossover properties.



INTRODUCTION

Scorpionate ligands, which originally referred to Trofimenko's tris(pyrazolyl)borates, Tp^x ,¹ are ubiquitous in modern coordination chemistry. The "scorpionate" moniker is also used to classify other facial trichelating ligands^{1b} such as Reglinski's tris(thioimidazolyl)borate, Tm^R (aka "soft" scorpionates),² and C-scorpionate counterparts such as tris(pyrazolyl)methane, Tpm^x ,³ and tris(pyrazolyl)methanesulfonate, Tpms^x .⁴ The chemistry of silver(I) scorpionates has seen tremendous growth in the last 15 years, ever since the subject was first reviewed.^{5,6} At the time of the 2004 review, the chemistry of these derivatives was still in its infancy because first-generation scorpionates with B–H bonds had a proclivity for reducing silver(I) to the metal. It was learned in the late 1990s that silver reduction could be slowed by increasing the steric bulk on the pyrazolyls, by removing B–H bonds, and/or by introducing electron-withdrawing groups on the pyrazolyl rings.⁶ Intensified interest in silver(I) scorpionates began with early reports from the Dias group that showed that the fluorinated scorpionate complex, $\text{AgTp}^{(\text{CF}_3)_2}$, was a competent catalyst for carbene insertion into C–halogen bonds,⁷ aromatic C=C bonds (Büchner reaction),⁸ and aliphatic C–H bonds.⁹ Further inciting interest were reports from the Pérez group that showed that AgTp^x complexes catalyzed a variety of transformations⁶ such as carbene insertion into alkane C–H bonds,¹⁰ Si–H bonds,¹¹ and C–X (X = Cl, Br) bonds¹² or were used for the cross-coupling of diazo compounds.¹³ Moreover, diverse AgTp^x -catalyzed nitrene-transfer reactions have been discovered such as aziridination of alkenes¹⁴ and dienes,¹⁵ amination of alkanes,¹⁶ and unexpected N–N bond

formations.¹⁷ More recently, other silver scorpionates, such as Huang's $\text{Ag}(\text{PPh}_3)(\text{PhTm})$ ¹⁸ and Pérez's $\text{Ag}[\text{Ph}(\text{CH}_2\text{PPh}_2)_3](\text{PPh}_3)$,¹⁹ were also found to catalyze the aziridination of styrene, albeit in much lower yields than the analogous copper complexes.

In contrast to the AgTp^x and other anionic B-scorpionates, the reaction and catalytic chemistry of AgTpms^{20} or $[\text{Ag}_n(\text{Tpm}^x)_m]^+$ ^{21,22} remains largely unreported. The chemistry of $[\text{Ag}_n(\text{Tpm}^x)_m]^+$ compounds lagged behind the Tp^x derivatives in part because of difficulties in the original ligand synthesis,²³ which were only resolved in 1984 by Elguero and co-workers.²⁴ Large-scale syntheses and subsequent functionalization chemistry of tris(pyrazolyl)methanes were then introduced in 2000.²⁵ These breakthroughs opened the door for countless new variations including Tpms .⁴ Given the remarkable achievements reported by various groups in the use of silver complexes of charge-neutral nitrogen donors to effect both aziridination and amination reactions,^{24–29} similar chemistry might be expected for tris(pyrazolyl)methanes but, surprisingly, has not yet been reported for this metal.³⁰

Our group has recently introduced a new class of tris(pyrazolyl)methanes, the nitrogen-confused C-scorpionates,³¹ where one of the three pyrazolyl rings is bound to the central methine carbon atom via a pyrazolyl ring carbon atom rather than the more usual nitrogen atom (Figure 1). With this mode of linkage, easy access to variable steric and electronic properties of the ligands can be gained by any variety

Received: November 16, 2017



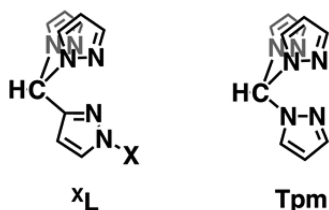


Figure 1. Depiction of “nitrogen-confused” C-scorpionates [left; X = H, Bz = CH₂C₆H₅, Ts = SO₂(*p*-tolyl)] versus the “normal” C-scorpionate, tris(pyrazolyl)methane, Tpm (right).

of simple nitrogen protection and deprotection reactions. Importantly, by a suitable choice of the confused pyrazolyl's X group, it should be possible to promote favorable supramolecular interactions in the second coordination sphere of a complex to either guide crystallization or facilitate reactions. In this contribution, the preparation of new nitrogen-confused C-scorpionate ligands with two “normal” pz* groups (=3,5-dimethylpyrazol-1-yl) and a “confused” pyrazolyl with either N-H, ^HL*, or N-Tosyl (Tosyl = *p*-toluenesulfonyl), ^{Ts}L*, bound to a central methine carbon atom is described. These bulky ligands complement those previously described, ^HL and ^{Ts}L, which had less bulky, unsubstituted, “normal” pyrazol-1-yls. For these four related nitrogen-confused scorpionate ligands, the 2:1 and 1:1 ligand/silver complexes are prepared and characterized both structurally and spectroscopically. The complexes' stoichiometric reactivity and catalytic activity for aziridination of styrene are also reported.

EXPERIMENTAL SECTION

General Considerations. The compounds (*p*-CH₃C₆H₄SO₂=Ts)pzC(O)H, ^{Ts}pzCHpz₂ (^{Ts}L), and ^HpzCHpz₂ (^HL) were prepared as described previously.³¹ The compound O=C(pz*)₂ was prepared by the literature method.³² Anhydrous CoCl₂, AgOTf (OTf = trifluoromethanesulfonate), Mn(CO)₅Br, Fe, Fe(OTf)₂, FeCl₂, PhI(OAc)₂, H₂NtS, and styrene were purchased from commercial sources and used as received. Anhydrous Fe(OTf)₂, CoCl₂, and AgOTf were stored under argon in a drybox. Commercial solvents were dried by conventional means and distilled under a nitrogen atmosphere prior to use. The silver(I), manganese(I), and iron(II) complexes were prepared under argon using Schlenk-line techniques, however, after isolation, were stored and manipulated under normal laboratory atmospheric conditions, unless otherwise specified (see the **Nitrene-Transfer Catalysis** section).

Instrumentation. Midwest MicroLab, LLC (Indianapolis, IN), performed all elemental analyses. Melting point determinations were made on samples contained in glass capillaries using an Electrothermal 9100 apparatus and are uncorrected. IR spectra were recorded for samples as KBr pellets or as either solutions or Nujol mulls between KBr plates in the 4000–500 cm⁻¹ region on a Nicolet Magna-IR 560 spectrometer or on solid samples using a Thermo Scientific Nicolet iS5 IR spectrometer equipped with an iD3 attenuated-total-reflection (ATR) accessory. ¹H, ¹³C, and ¹⁹F 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 77.23 for CDCl₃ or δ_H 1.94 and δ_C 118.26 for CD₃CN. Details regarding the diffusion-oriented NMR experiments are found in the **Supporting Information**. Abbreviations for NMR and UV-vis: br (broad), sh (shoulder), m (multiplet), ps (pseudo-), s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), sept (septet). The solution magnetic moment was measured by Evan's method.³³ Magnetic susceptibility data were collected on a Quantum Design MPMS3 SQUID magnetometer. Raw moment data were corrected for the sample shape and radial offset corrections using the MPMS 3 Sample Geometry Simulator.³⁴ Diamagnetic corrections of -218 × 10⁻⁶ emu/mol for 9, calculated from tabulated Pascal's constants,³⁵ were applied to the measured susceptibility data, as

appropriate. Electronic absorption (UV-vis/near-IR) measurements were made on a Cary 5000 instrument. Powder X-ray diffraction patterns were collected with a Rigaku MiniFlex II instrument using Cu Kα (1.54178 Å) radiation. Positive-mode electrospray ionization mass spectrometry [ESI(+) MS] measurements were obtained on a Micromass Q-TOF spectrometer where formic acid (ca. 0.1% v/v) was added to the mobile phase (CH₃CN).

Ligands. ^{Ts}pzCHpz*₂ (^{Ts}L*). A mixture of 2.132 g (8.511 mmol) of ^{Ts}pzC(O)H, 2.092 g (9.585 mmol) of O=C(pz*)₂, and 0.055 g (0.43 mmol) of CoCl₂ in 50 mL of toluene was heated at reflux for 16 h. The resulting blue mixture was cooled to room temperature, and the solvent was removed by vacuum distillation. The residue was partitioned between 100 mL of water (H₂O) and 100 mL of ethyl acetate (EtOAc). The layers were separated, and the aqueous layer was extracted with two 50 mL portions of CH₂Cl₂. The organic fractions were combined, dried over MgSO₄, and filtered. Solvents were removed by vacuum distillation to leave 3.29 g (91%) of ^{Ts}L* as a pale-yellow solid. Recrystallization by cooling a boiling supersaturated solution in methanol (MeOH) to room temperature gave crystalline ivory-tinted blocks (ca. 25 mg/mL) after filtration and drying under vacuum. Mp: 181–182 °C. IR (CH₂Cl₂, KBr): ν_{CH} 3141, 2971, 2856. IR (ATR, cm⁻¹): ν_{CH} 3195, 3163, 3146, 3051, 2973, 2923, ν_{SO} 1374 (asym), 1179 (sym). ¹H NMR (CD₃CN): δ_H 8.19 (d, *J* = 2.8 Hz, 1 H, H_{5cpz}), 7.81 (d, *J* = 8.4 Hz, 2 H, Ts), 7.48 (s, 1 H, H_{methine}), 7.41 (d, *J* = 8.4 Hz, 2 H, Ts), 6.35 (d, *J* = 2.8 Hz, 1 H, H_{4cpz}), 5.83 (s, 2 H, H_{4pz*}), 2.42 (s, 3 H, TsCH₃), 2.07 (s, 6 H, pz*CH₃), 2.05 (s, 6 H, pz*CH₃). ¹³C NMR (CD₃CN): δ_C 155.42, 149.14, 147.85, 141.71, 134.64, 133.72, 131.23, 128.84, 110.98 (C_{4cpz}), 107.56 (C_{4pz*}), 69.44 (C_{methine}), 21.71 (TsMe), 13.61 (pz*Me), 11.44 (pz*Me).

^HpzCHpz*₂ (^HL*). A solution of 15.0 mL of 5.00 M NaOH(aq) (75.0 mmol), 3.29 g (7.75 mmol) of ^{Ts}L*, and 20 mL of tetrahydrofuran (THF) was heated at reflux for 1.25 h. The solution was allowed to cool to room temperature and then extracted with two 50 mL portions of EtOAc. The organic fractions were dried over MgSO₄ and filtered. The organic solvent was removed by vacuum distillation, and the residue was triturated with diethyl ether (Et₂O) to leave 1.61 g (77%) of ^HL* as a colorless solid. Mp: 146–147 °C. IR (CH₂Cl₂, KBr): ν_{NH} 3450, ν_{CH} 3054 2986, 2857. IR (ATR, cm⁻¹): ν_{CH} 3141, 3051, 2971, 2956, 2914. ¹H NMR (CD₃CN): δ_H 11.25 (br s, 1 H, N-H), 7.56 (d, *J* = 2.3 Hz, 1 H, H_{5cpz}), 7.55 (s, 1 H, H_{methine}), 6.15 (d, *J* = 2.3 Hz, 1 H, H_{4cpz}), 5.86 (s, 2 H, H_{4pz*}), 2.21 (s, 6 H, pz*CH₃), 2.07 (s, 6 H, pz*CH₃). ¹³C NMR (CDCl₃): δ_C 148.95, 141.59, 107.19 (C_{4pz*}), 106.11 (C_{4cpz}), 69.20 (C_{methine}), 13.65 (pz*Me), 11.52 (pz*Me); two resonances presumably for quaternary pyrazolyl carbon atoms are not observed.

Silver Complexes. General Procedure. A solution of a given ligand (ca. 0.5–2.0 mmol) in 10 mL of THF was added to a solution of AgOTf (1 or 0.5 equiv) in 10 mL of THF by cannula transfer. The flask originally containing the ligand was washed twice with 2 mL of THF, and the washings were transferred to the reaction medium to ensure quantitative transfer of the reagent. After the mixture had been stirred overnight for 14 h, the colorless precipitate was collected after cannula filtration, washing the solid with two 2 mL portions of Et₂O and drying under vacuum for 30 min. The quantities of the reagents used and of the products obtained and characterization data for each of the eight new compounds are given below. An alternative workup in the case where no precipitate was observed (complex **4b**) is also described.

[Ag(^{Ts}L*)](OTf) (**1a**). A mixture of 0.306 g (0.721 mmol) of ^{Ts}L* and 0.185 g (0.720 mmol) of AgOTf gave 0.333 g (68%) of **1a** as a colorless solid after drying under vacuum at 100 °C for 4 h. Mp: 183–185 °C (dec). Anal. Calcd (found) for C₂₂H₂₄N₆AgF₃O₃S₂: C, 38.78 (39.05); H, 3.55 (3.73); N, 12.33 (12.15). IR (ATR, cm⁻¹): tosyl, 1393 (ν_{as}, SO₂), 911 (ν_{S-N}); triflate (s to vs), 1260 (ν_{as}, SO₃), 1223 (ν_s, CF₃), 1162 (ν_{as}, CF₃), 1029 (ν_s, SO₃), 638 (δ_s, SO₃). ¹H NMR (CD₃CN): δ_H 8.20 (d, *J* = 2.8 Hz, 1 H, H_{5cpz}), 7.78 (d, *J* = 8.5 Hz, 2 H, Ts), 7.46 (s, 1 H, H_{methine}), 7.41 (d, *J* = 8.5 Hz, 2 H, Ts), 6.11 (d, *J* = 2.8 Hz, 1 H, H_{4cpz}), 6.04 (s, 2 H, H_{4pz*}), 2.42 (s, 3 H, TsCH₃), 2.41 (s, 6 H, pz*CH₃), 1.94 (s, 6 H, pz*CH₃). ¹³C NMR (CD₃CN): δ_C 154.56, 151.93, 147.93, 143.85, 134.55, 134.10, 131.27, 128.87, 110.48

(C_{4cpz}), 107.32 (C_{4pz}*), 65.11 (C_{methine}), 21.75 (TsMe), 14.06 (pz*Me), 11.36 (pz*Me). ¹⁹F NMR (CD₃CN): δ_F −79.32 (s). ESI(+) MS (relative intensity) assignment: *m/z* 957 (73) [Ag(¹⁸L*)]₂⁺, 531 (36) [Ag(¹⁸L*)]⁺, 447 (7) [Na(¹⁸L*)]⁺, 425 (5) [H(¹⁸L*)]⁺, 329 (100) [¹⁸L* − Hpz*]⁺. A sample that was dried under vacuum for 30 min without heating analyzed as **3b**·THF. Anal. Calcd (found) for C₂₆H₃₂N₆AgF₃O₄S: C, 41.49 (41.39); H, 4.28 (4.19); N, 11.15 (11.23). X-ray-quality single crystals of mostly **1a** and some larger plates of **1b**·MeOH were grown by vapor diffusion of Et₂O into a MeOH solution (1.3 mL, 0.005 M).

[Ag(¹⁸L*)₂](OTf) (**1b**). A mixture of 0.250 g (0.589 mmol) of ¹⁸L* and 0.0757 g (0.295 mmol) of Ag(OTf) gave 0.289 g (89%) of **1b** as a colorless solid. Mp: 201–203 °C (dec). Anal. Calcd (found) for C₄₃H₄₈N₁₂AgF₃O₇S₃: C, 46.70 (46.81); H, 4.37 (4.72); N, 15.20 (15.31). IR (ATR, cm^{−1}): ν_{NH} 3154; triflate (s to vs), 1268 (ν_{as} SO₃), 1224 (ν_s CF₃), 1172 (ν_{as} CF₃), 1032 (ν_s SO₃), 637 (δ_s SO₃). ¹H NMR (CD₃CN): δ_H 8.19 (d, *J* = 2.8 Hz, 1 H, H_{5cpz}), 7.80 (d, *J* = 8.4 Hz, 2 H, Ts), 7.46 (s, 1 H, H_{methine}), 7.40 (d, *J* = 8.4 Hz, 2 H, Ts), 6.12 (d, *J* = 2.8 Hz, 1 H, H_{4cpz}), 5.98 (s, 2 H, H_{4pz}*), 2.38 (s, 3H, TsMe), 2.35 (s, 6 H, pz*Me), 1.65 (s, 6H, pz*Me). ¹³C NMR (CD₃CN): δ_C 154.81, 151.82, 147.89, 143.63, 134.59, 134.08, 131.35, 128.83, 110.53 (C_{4cpz}), 107.31 (C_{4pz}*), 65.66 (C_{methine}), 21.73 (TsMe), 13.63 (pz*Me), 11.36 (pz*Me). ¹⁹F NMR (CD₃CN): δ_F −79.29 (s). ESI(+) MS (relative intensity) assignment: *m/z* 957 (6) [Ag(¹⁸L*)]₂⁺, 531 (7) [Ag(¹⁸L*)]⁺, 425 (9) [Ag(¹⁸L*) − pz*]⁺, 329 (100) [¹⁸L* − pz]. X-ray-quality single crystals of **1b**·1.5CH₃CN were grown by vapor diffusion of Et₂O into a CH₃CN solution (1.3 mL, 0.02 M). Single crystals of **1b**·MeOH were grown by vapor diffusion of Et₂O into a MeOH solution (1.3 mL, 0.04 M).

[Ag(¹⁸L)](OTf) (**2a**). A mixture of 0.605 g (1.64 mmol) of ¹⁸L and 0.422 g (1.64 mmol) of AgOTf gave 0.847 g (82%) of **2a** as a colorless solid. Mp: 141–146 °C (dec). Anal. Calcd (found) for C₁₈H₁₆N₆AgF₃O₃S₂: C, 34.57 (34.47); H, 2.54 (2.56); N, 13.44 (13.49). IR (ATR, cm^{−1}): tosyl, 1389 (ν_{as} SO₂), 904 (ν_{S–N}); triflate (s to vs), 1283 (ν_{as} SO₃), 1237 (ν_s CF₃), 1223 (ν_s CF₃), 1163 (ν_{as} CF₃), 1148 (ν_{as} CF₃), 1025 (ν_s SO₃), 634 (δ_s SO₃). ¹H NMR (CD₃CN): δ_H 8.23 (d, *J* = 2.8 Hz, 1 H, H_{5cpz}), 7.89 (d, *J* = 2.4 Hz, 2 H, H_{5pz}), 7.82 (s, 1 H, H_{methine}), 7.81 (d, *J* = 8.4 Hz, 2 H, Ts), 7.59 (d, *J* = 1.6 Hz, 2 H, H_{3pz}), 7.41 (d, *J* = 8.4 Hz, 2 H, Ts), 6.39 (dd, *J* = 2.4, 1.6 Hz, 2 H, H_{4pz}), 6.31 (d, *J* = 2.8 Hz, 1 H, H_{4cpz}), 2.41 (s, 3 H, TsCH₃). ¹³C NMR (CD₃CN): δ_C 153.79, 148.10, 142.99, 134.29, 134.27, 132.68, 131.32, 128.91, 110.24 (C_{4cpz}), 107.71 (C_{4pz}), 72.03 (C_{methine}), 21.72 (TsMe). ¹⁹F NMR (CD₃CN): δ_F −79.33 (s). ESI(+) MS (relative intensity) assignment: *m/z* 1101 (11) [Ag(¹⁸L)₂(OTf)]⁺, 845 (100) [Ag(¹⁸L)₂]⁺, 475 (87) [Ag(¹⁸L)]⁺, 301 (18) [¹⁸L − Hpz]⁺. X-ray-quality single-crystalline needles of **2a** were grown by vapor diffusion of Et₂O into a CH₃CN solution (1.25 mL, 0.03 M) over the course of 2 days. In certain cases, when vapor diffusion of more concentrated solutions (1.25 mL, 0.06 M) was prolonged over a period of 1 week, large block crystals of **2b** also formed amidst the majority of needles of **2a**.

[Ag(¹⁸L)₂](OTf) (**2b**). A mixture of 0.250 g (0.679 mmol) of ¹⁸L and 0.0872 g (0.339 mmol) of AgOTf gave 0.251 g (77%) of **2b** as a colorless solid. Mp: 150–151 °C (dec). Anal. Calcd (found) for C₃₅H₃₂N₁₂AgF₃O₇S₃: C, 42.30 (41.99); H, 3.25 (3.31); N, 16.91 (16.54). IR (ATR, cm^{−1}): tosyl, 1365 (ν_{as} SO₂), 902 (ν_{S–N}); triflate (s to vs), 1290 (ν_{as} SO₃), 1260 (ν_s CF₃), 1220 (ν_s CF₃), 1174 (ν_{as} CF₃), 1131 (ν_{as} CF₃), 1022 (ν_s SO₃), 638 (δ_s SO₃). ¹H NMR (CD₃CN): δ_H 8.23 (d, *J* = 2.8 Hz, 1 H, H_{5cpz}), 7.82 (br s, 3 H, overlapping H_{5pz} + H_{methine}), 7.79 (d, *J* = 8.4 Hz, 2 H, Ts), 7.56 (br s, 2 H, H_{3pz}), 7.40 (d, *J* = 8.4 Hz, 2 H, Ts), 6.36 (dd, *J* = 2.4, 1.6 Hz, 2 H, H_{4pz}), 6.35 (d, *J* = 2.8 Hz, 1 H, H_{4cpz}), 2.40 (s, 3 H, TsCH₃). ¹³C NMR (CD₃CN): δ_C 154.04, 148.08, 142.50, 134.29, 134.25, 132.05, 131.32, 128.92, 110.18 (C_{4cpz}), 107.67 (C_{4pz}), 72.40 (C_{methine}), 21.73 (TsMe). ¹⁹F NMR (CD₃CN): δ_F −79.32 (s). ESI(+) MS (relative intensity) [assignment: *m/z* 845 (7) [Ag(¹⁸L)₂]⁺, 475 (16) [Ag(¹⁸L)]⁺, 391 (13) [Na(¹⁸L)]⁺, 369 (4) [H(¹⁸L)]⁺, 301 (100) [¹⁸L − Hpz]⁺. X-ray-quality single crystals were grown by vapor diffusion of Et₂O into a CH₃OH solution (1.25 mL, 0.022 M).

[Ag(⁴L*)](OTf) (**3a**). A mixture of 0.200 g (0.740 mmol) of ⁴L* and 0.190 g (0.740 mmol) of AgOTf gave 0.337 g (86%) of **3a** as a colorless solid. Mp: 186–188 °C (dec). Anal. Calcd (found) for C₁₅H₁₈N₆AgF₃O₃S: C, 34.17 (34.20); H, 3.44 (3.37); N, 15.94 (15.81). IR (ATR, cm^{−1}): ν_{NH} 3157; triflate (s to vs), 1286 (ν_{as} SO₃), 1222 (ν_s CF₃), 1168 (ν_{as} CF₃), 1028 (ν_s SO₃), 638 (δ_s SO₃). ¹H NMR (CD₃CN): δ_H 11.47 (br s, 1 H, NH), 7.63 (d, *J* = 2.3 Hz, 1 H, H_{5cpz}), 7.49 (s, 1 H, H_{methine}), 6.17 (d, *J* = 2.3 Hz, 1 H, H_{4cpz}), 6.01 (s, 2 H, H_{4pz}*), 2.45 (s, 6 H, CH₃Pz*), 2.06 (s, 6 H, CH₃Pz*). ¹³C NMR (CD₃CN): δ_C 151.23 (br), 151.11, 143.03, 107.05 (C_{4pz}*), 106.12 (C_{4cpz}), 64.78 (C_{methine}), 14.03 (pz*Me), 11.38 (pz*Me). ¹⁹F NMR (CD₃CN): δ_F −79.34 (s). ESI(+) MS (relative intensity) assignment: *m/z* 905 (29) [Ag₂(⁴L*)₂(OTf)]⁺, 809 (12) [Ag₂(⁴L*)₂OTf − Hpz*], 755 (9) [Ag₂(⁴L*)(⁴L* − H)]⁺, 649 (100) [Ag(⁴L*)]₂⁺, 551 (10) [Ag(⁴L*)₂ − Hpz*]⁺, 418 (27) [Ag(⁴L*)(CH₃CN)]⁺, 377 (73) [Ag(⁴L*)]⁺. X-ray-quality single crystals were grown by vapor diffusion of Et₂O into a CH₃CN solution (1.4 mL, 0.04 M).

[Ag(⁴L*)₂](OTf) (**3b**). A mixture of 0.150 g (0.550 mmol) of ⁴L* and 0.0713 g (0.277 mmol) of AgOTf gave 0.170 g (77%) of **3b** as a colorless solid after drying at 100 °C for 4 h under vacuum. Mp: 181–183 °C (dec). Anal. Calcd (found) for C₂₉H₃₆N₁₂AgF₃O₃S: C, 43.67 (44.01); H, 4.55 (4.64); N, 21.07 (21.28). IR (ATR, cm^{−1}): ν_{NH} 3375; triflate (s to vs), 1283 (ν_{as} SO₃), 1223 (ν_s CF₃), 1151 (ν_{as} CF₃), 1028 (ν_s SO₃), 636 (δ_s SO₃). ¹H NMR (CD₃CN): δ_H 11.38 (br s, 1 H, NH), 7.61 (d, *J* = 2.3 Hz, 1 H, H_{5cpz}), 7.50 (s, 1 H, H_{methine}), 6.14 (d, *J* = 2.3 Hz, 1 H, H_{4cpz}), 6.00 (s, 2 H, H_{4pz}*), 2.45 (s, 6 H, CH₃Pz*), 1.98 (s, 6 H, CH₃Pz*). ¹³C NMR (CD₃CN): δ_C 150.98, 142.74, 106.92 (C_{4pz}*), 106.00 (C_{4cpz}), 65.50 (C_{methine}), 13.66 (pz*Me), 11.40 (pz*Me). ¹⁹F NMR (CD₃CN): δ_F −79.32 (s). ESI(+) MS (relative intensity) assignment: *m/z* 647 (100) [Ag(⁴L*)]₂⁺, 418 (2) [Ag(⁴L*)(CH₃CN)]⁺, 377 (23) [Ag(⁴L*)]⁺, 175 (44) [L − pz*]. A sample that was dried under vacuum but without heating analyzed as **3b**·0.5THF·0.5H₂O. Anal. Calcd (found) for C₃₁H₄₁N₁₂AgF₃O₄S: C, 44.19 (44.04); H, 4.90 (4.75); N, 19.95 (20.08). X-ray-quality single crystals were grown by vapor diffusion of Et₂O into a CH₃OH solution (1.3 mL, 0.02 M).

[Ag(⁴L)](OTf) (**4a**). A mixture of 0.196 g (0.915 mmol) of ⁴L and 0.235 g (0.915 mmol) of AgOTf gave 0.366 g (85%) of **4a** as a colorless solid. Mp: 175–178 °C (dec). Anal. Calcd (found) for C₁₁H₁₀N₆AgF₃O₃S: C, 28.04 (28.39); H, 2.14 (2.31); N, 17.84 (17.86). IR (ATR, cm^{−1}): ν_{NH} 3154; triflate (s to vs), 1276 (ν_{as} SO₃), 1224 (ν_s CF₃), 1167 (ν_{as} CF₃), 1027 (ν_s SO₃), 632 (δ_s SO₃). ¹H NMR (CD₃CN): δ_H 11.90 (br s, 1 H, NH), 7.96 (d, *J* = 2.6 Hz, 2 H, H_{5pz}), 7.93 (s, 1 H, H_{methine}), 7.71 (d, *J* = 2.4 Hz, 1 H, H_{5cpz}), 7.62 (d, *J* = 1.8 Hz, 2 H, H_{3pz}), 6.38 (m, 3 H, overlapping H_{4pz}&4cpz). ¹³C NMR (CD₃CN): δ_C 143.42 (br), 143.09, 132.70, 131.64, 107.49 (C_{4pz}), 106.49 (C_{4cpz}), 71.70 (C_{methine}). ¹⁹F NMR (CD₃CN): δ_F −79.29 (s). ESI(+) MS (relative intensity) assignment: *m/z* 1265 (3) [Ag₃(⁴L)₃(OTf)₂]⁺, 1051 (1) [Ag₃(⁴L)₂(OTf)₂]⁺, 793 (41) [Ag₂(⁴L)₂(OTf)]⁺, 678 (3) [Ag₂(⁴L)₂Cl]⁺, 643 (32) [Ag₂(⁴L)(⁴L − H)]⁺, 579 (4) [Ag₂(⁴L)(OTf)]⁺, 535 (95) [Ag(⁴L)]₂⁺, 465 (6) [Ag₂(⁴L)(Cl)]⁺, 361 (35) [Ag(⁴L)]⁺, 323 (100) [Ag(⁴L)]⁺. X-ray-quality single crystals were grown by vapor diffusion of Et₂O into a CH₃CN solution (1.4 mL, 0.04 M).

[Ag(⁴L)₂](OTf) (**4b**). A mixture of 0.192 g (0.896 mmol) of ⁴L and 0.115 g (0.448 mmol) of AgOTf in 20 mL of THF gave a solution (no precipitate) after 1 h, so the solvent was removed by vacuum distillation. The colorless residue was washed with Et₂O and dried at 100 °C under vacuum for 4 h to give 0.218 g (71%) of **4b** as a colorless solid. Mp: 124–126 °C (dec). Anal. Calcd (found) for C₂₁H₂₀N₁₂AgF₃O₃S: C, 36.80 (36.44); H, 2.94 (3.12); N, 24.52 (24.50). IR (ATR, cm^{−1}): ν_{NH} 3126; triflate (s to vs), 1276 (ν_{as} SO₃), 1224 (ν_s CF₃), 1158 (ν_{as} CF₃), 1029 (ν_s SO₃), 637 (δ_s SO₃). ¹H NMR (CD₃CN): δ_H 11.82 (br s, 1 H, NH), 7.91 (d, *J* = 2.6 Hz, 2 H, H_{5pz}), 7.90 (s, 1 H, H_{methine}), 7.69 (d, *J* = 2.4 Hz, 1 H, H_{5cpz}), 7.58 (d, *J* = 1.8 Hz, 2 H, H_{3pz}), 6.37 (m, 3 H, overlapping H_{4pz}&4cpz). ¹³C NMR (CD₃CN): δ_C 142.62, 132.12, 131.55, 107.48 (C_{4pz}), 106.25 (C_{4cpz}), 72.45 (C_{methine}). ¹⁹F NMR (CD₃CN): δ_F −79.31 (s). ESI(+) MS (relative intensity) assignment: *m/z* 535 (57) [Ag(⁴L)₂]⁺, 362 (5) [Ag(⁴L)(CH₃CN)]⁺, 321 (100) [Ag(⁴L)]⁺, 147(60) [L − H_{pz}]. X-

ray-quality single-prismatic crystals of **4b**·acetone·H₂O were obtained by evaporation of a solution of a mixture of acetone and H₂O. The crystals analyzed as **4b**·acetone·H₂O. Anal. Calcd (found) for C₂₃H₂₆N₁₂AgF₃O_{4.5}S: C, 37.86 (37.77); H, 3.71 (3.62); N, 22.07 (22.38). Under most other conditions (1,2-dichloroethane solutions, evaporation of THF or CH₂Cl₂ solutions, vapor diffusion of pentane into THF or acetone solutions, of Et₂O into CH₃CN or MeOH solutions, layering hexane onto acetone solutions), a mixture of mainly very long (>2 mm), highly crystalline, but extremely thin needles of **4b**-solvate was obtained along with a few plates of **4a**. After drying under vacuum at room temperature (and exposure to air), these analyzed as **4b**-solvate·H₂O. Anal. Calcd (found) for **4b**·CH₃CN·H₂O, C₂₃H₂₅N₁₃AgF₃O₄S: C, 37.11 (37.44); H, 3.38 (3.12); N, 24.46 (24.50).

Reactions. General Procedure for the Preparation of Tricarbonylmanganese(II) Complexes. Under an argon atmosphere and with exclusion of light (aluminum-foil-wrapped apparatus), a mixture of Mn(CO)₅Br and [Ag(L)](OTf) (1 equiv) in 10 mL of CH₃CN was heated at reflux for 3 h, during which time a precipitate formed. The solution was filtered, CH₃CN was removed under vacuum, and the yellow residue was washed with two 2 mL portions of Et₂O and dried under vacuum. The yellow solids are slightly light-sensitive, so they are best stored in the dark (aluminum-foil-wrapped vials). The quantities of reagents used and of the products obtained and characterization data for each of the four new compounds are given below.

[*fac*-Mn(CO)₃(^tL*)](OTf) (5**).** A mixture of 0.127 g (0.186 mmol) of **1a** and 0.0512 g (0.186 mmol) of Mn(CO)₅Br gave 0.118 g (89%) of **5** as a yellow solid. Mp: >210 °C. Anal. Calcd (found) for C₂₅H₂₄N₆F₃MnO₈S₂: C, 42.14 (41.97); H, 3.39 (3.43); 11.79 (11.54). IR (ATR, cm⁻¹): ν_{CO} 2038, 1931; tosyl, 1396 (ν_{as}, SO₂), 903 (ν_{S-N}); triflate (CH₂Cl₂/KBr, s to vs), 1252 (ν_{as}, SO₃), 1203 (ν_s, CF₃), 1153 (ν_{as}, CF₃), 1026 (ν_s, SO₃), 630 (δ_s, SO₃). ¹H NMR (CD₃CN, 333 K, two species in a 5:1 ratio): major, δ_H 8.49 (br s, 1 H, H_{5cpz}), 7.78 (d, J = 7.5 Hz, 2 H, Ts), 7.61 (s, 1 H, H_{methine}), 7.43 (d, J = 7.5 Hz, 2 H, Ts), 7.17 (br s, 1 H, H_{4cpz}), 6.15 (s, 2 H, H_{4pz*}), 2.52 (s, 6 H, pz*CH₃), 2.50 (s, 6 H, pz*CH₃), 2.42 (s, 3 H, TsCH₃); minor, δ_H 7.89 (s, 1 H, H_{methine}), 6.90 (s, 1 H, H_{5cpz}), 6.12 (s, 2 H, H_{4pz*}), 5.42 (s, 1 H, H_{4cpz}); Ts and pz*CH₃ protons not observed, overlapping major resonances. ¹³C NMR (CD₃CN, only resonances for major species are given): δ_C 221.30 (CO), 220.86 (CO), 157.40, 153.84, 149.33, 145.27, 142.11, 133.84, 131.76, 128.79, 111.61 (C_{4cpz}), 110.16 (C_{4pz}), 60.86 (C_{methine}), 21.78 (TsMe), 15.15 (pz*Me), 11.45 (pz*Me); resonance for CF₃ not observed. ¹⁹F NMR (CD₃CN): δ_F -78.87 (s). ESI(+) MS (relative intensity) assignment: m/z 563 (100) [Mn(CO)₃(^tL*)]⁺, 497 (19) [Mn(H₂O)(^tL*)]⁺, 433 (5) [Mn(CO)₃(^NL*)]⁺. UV-vis [CH₃CN; λ, nm (ε, M⁻¹ cm⁻¹): 359 (2430). Twinned needle crystals were grown by heating a mixture of 50 mg of **5** in 0.5 mL of MeOH to dissolution and then cooling the solution to room temperature.

[*fac*-Mn(CO)₃(^tL*)](OTf) (6**).** A mixture of 0.200 g (0.320 mmol) of **2a** and 0.088 g (0.320 mmol) of Mn(CO)₅Br gave 0.165 g (79%) of **6** as a yellow solid. X-ray-quality single crystals were grown by diffusion of a layer of 3 mL of hexanes into a CH₂Cl₂ solution (1.5 mL, 0.014 M) or layering 5 mL of Et₂O onto a CH₃CN solution (1.4 mL, 0.03 M). Mp: 144 °C (dec). Anal. Calcd (found) for C₂₁H₁₆N₆F₃MnO₈S₂: C, 38.42 (38.46); H, 2.46 (2.61); 12.80 (12.57). IR (ATR, cm⁻¹): ν_{CO} 2045, 1933; tosyl, 1396 (ν_{as}, SO₂), 910 (ν_{S-N}); triflate (s to vs), 1250 (ν_{as}, SO₃), 1159 (ν_{as}, CF₃), 1020 (ν_s, SO₃), 625 (δ_s, SO₃). ¹H NMR (CD₃CN, 333 K; two species in a 5:1 ratio): major species, δ_H 8.44 (d, J = 3.0 Hz, 1 H, H_{5cpz}), 8.27 (d, J = 2.8 Hz, 2 H, H_{5pz}), 8.24 (s, 1 H, H_{methine}), 8.21 (d, J = 2.0 Hz, 2 H, H_{3pz}), 7.80 (d, J = 8.4 Hz, 2 H, Ts), 7.44 (d, J = 8.4 Hz, 2 H, Ts), 7.06 (d, J = 3.0 Hz, 1 H, H_{4cpz}), 6.55 (dd, J = 2.8 and 2.0 Hz, 2 H, H_{4pz}), 2.42 (s, 3 H, TsCH₃); minor species, δ_H 8.32 (d, J = 2.8 Hz, 2 H, H_{5pz}), 8.28 (s, 1 H, H_{methine}), 8.15 (d, J = 2.0 Hz, 2 H, H_{3pz}), 8.14 (d, J = 2.7 Hz, 1 H, H_{5cpz}), 7.72 (d, J = 8.5 Hz, 2 H, Ts), 7.42 (d, J = 8.5 Hz, 2 H, Ts), 6.74 (dd, J = 2.8 and 2.0 Hz, 2 H, H_{4pz}), 5.85 (d, J = 2.7 Hz, 1 H, H_{4cpz}), 2.43 (s, 3 H, TsCH₃). ¹³C NMR (CD₃CN): δ_C 221.29 (CO), 214.95 (CO), 149.39, 148.15, 141.19, 136.19, 131.77, 130.99, 129.56, 128.91, 111.55 (C_{4cpz}), 109.79 (C_{4pz}),

66.34 (C_{methine}), 21.78 (TsMe). ¹⁹F NMR (CD₃CN): δ_F -79.26 (s). ESI(+) MS (relative intensity) assignment: m/z 507 (100) [Mn(CO)₃(^tL*)]⁺, 441 (29) [Mn(H₂O)(^tL*)]⁺, 423 (3) [Mn(^tL*)]⁺, 418 (5) [Mn(CO)₃(^N(CH₃CN)L*)]⁺, 377 (11) [Mn(CO)₃(^NL*)]⁺, 359 (4) [Mn(CO)₃(^tL*)]⁺. UV-vis [CH₃CN; λ, nm (ε, M⁻¹ cm⁻¹): 353 (2430).

[*fac*-Mn(CO)₃(^tL*)](OTf) (7**).** A mixture of 0.158 g (0.299 mmol) of **3a** and 0.0822 g (0.299 mmol) of Mn(CO)₅Br gave 0.151 g (85%) of **7** as a yellow solid. Mp: 170 °C (dec). Anal. Calcd (found) for C₁₈H₁₈N₆F₃MnO₆S: C, 38.72 (38.59); H, 3.25 (3.62); 15.05 (15.01). IR (Nujol/KBr, cm⁻¹): ν_{NH} 3413. IR (ATR, cm⁻¹): ν_{CO} 2034, 1928; triflate (CH₂Cl₂/KBr, s to vs), 1276 (ν_{as}, SO₃), 1225 (ν_s, CF₃), 1157 (ν_{as}, CF₃), 1028 (ν_s, SO₃), 625 (δ_s, SO₃). ¹H NMR (CD₃CN): δ_H 7.89 (br s, 1 H, H_{5cpz}), 6.64 (br s, 1 H, H_{methine}), 6.89 (br s, 1 H, H_{4cpz}), 6.12 (br s, 2 H, H_{4pz*}), 2.51 (br s, CH₃), 2.49 (br s, CH₃); N-H not observed. ¹³C NMR (CD₃CN): δ_C 221.52 (CO), 215.59 (CO), 156.49, 144.58, 134.96, 109.44 (C_{4pz*}), 106.49 (C_{4cpz}), 60.87 (C_{methine}), 15.15 (pz*Me), 11.41 (pz*Me). ¹⁹F NMR (CD₃CN): δ_F -79.28 (s). ESI(+) MS (relative intensity) assignment: m/z 409 (100) [Mn(CO)₃(^tL*)]⁺, 366 (11) [Mn(CH₃CN)(^tL*)]⁺, 353 (21) [Mn(CO)(^tL*)]⁺, 325 (43) [Mn(^tL*)]⁺. UV-vis [CH₃CN; λ, nm (ε, M⁻¹ cm⁻¹): 347 (2360). Crystals can be obtained by diffusion of a layer of 5 mL of Et₂O into a CH₃CN solution (1.4 mL, 0.03 M).

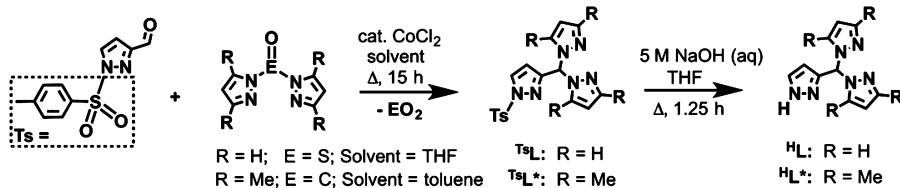
[*fac*-Mn(CO)₃(^tL*)](OTf) (8**).** A mixture of 0.200 g (0.425 mmol) of **4a** and 0.117 g (0.425 mmol) of Mn(CO)₅Br gave 0.187 g (88%) of **8** as a yellow solid. Mp: >210 °C. Anal. Calcd (found) for C₁₄H₁₀N₆F₃MnO₆S: C, 33.09 (33.31); H, 1.98 (2.03); N, 16.54 (16.44). IR (Nujol/KBr, cm⁻¹): ν_{NH} 3396. IR (ATR, cm⁻¹): ν_{CO} 2043, 1944; triflate (CH₂Cl₂/KBr, s to vs), 1288 (ν_{as}, SO₃), 1221 (ν_s, CF₃), 1145 (ν_{as}, CF₃), 1018 (ν_s, SO₃), 619 (δ_s, SO₃). ¹H NMR (CD₃CN, 333 K): δ_H 12.85 (br s, N-H), 8.22 (br s, 2 H, H_{3pz}), 8.18 (d, J = 2 Hz, 2 H, H_{5pz}), 8.14 (br s, H_{methine}), 7.87 (br s, 1 H, H_{5cpz}), 6.81 (br s, 1 H, H_{4cpz}), 6.49 (br m, 2 H, H_{4pz}). ¹³C NMR (CD₃CN, 295 K): δ_C 221.29 (CO), 213.17 (CO), 147.67, 145.38, 135.50, 134.64, 109.13 (C_{4cpz}), 106.87 (C_{4pz}), 66.71 (C_{methine}); CF₃ resonances not observed. ¹⁹F NMR (CD₃CN): δ_F -79.24 (s). ESI(+) MS (relative intensity) assignment: m/z 353 (96) [Mn(CO)₃(^tL*)]⁺, 310 (48) [Mn(CH₃CN)(^tL*)]⁺, 287 (11) [Mn(CO)₃(^tL*) - pz]⁺, 269 (100) [Mn(^tL*)]⁺. UV-vis [CH₃CN; λ, nm (ε, M⁻¹ cm⁻¹): 346 (2300). X-ray-quality single crystals were grown by diffusion of a layer of 3 mL of hexanes into a CH₂Cl₂ solution (1.9 mL, 0.04 M).

[Fe(^tL)₂](OTf)₂ (9**). Method A.** A solution of 0.250 g (1.17 mmol) of ^tL in 10 mL of THF was added to a solution of 0.207 g (0.585 mmol) of Fe(OTf)₂ in THF under argon. A yellow-orange solid initially precipitated but changed pink within 30 min. After the resulting pink suspension had been stirred for 16 h, THF was removed by cannula filtration and the solid was washed with 5 mL of Et₂O then dried in a 140 °C oven for 2 h to give 0.341 g (75%) of **9** as a pink powder. Purple single crystals suitable for X-ray diffraction were grown by vapor diffusion of Et₂O into a solution of 15 mg of **9** in 1.5 mL of MeOH. Characterization data listed below are for crystals or dissolved crystals.

Method B. A solution of 0.205 g (0.434 mmol) of **4a** in 10 mL of MeOH was added to an argon-purged solution of 0.0275 g (0.217 mmol) of FeCl₂ in 10 mL of H₂O. Upon mixing, a purple solution and colorless precipitate formed. After the mixture had been stirred for 45 min, the precipitated AgCl was removed by filtration and solvent was removed from the filtrate under vacuum to leave 0.150 g (89%) of **9** as a pink-purple powder.

Method C. A mixture of 0.0500 g (0.106 mmol) of **4a** and 0.0030 g (0.053 mmol) of Fe⁰ powder in 8 mL of CH₃CN was heated at reflux for 14 h with vigorous stirring. The resulting pink solution was separated from the metallic residue by cannula filtration. The residue was washed with two 2 mL portions of CH₃CN. After removing the solvent from the combined CH₃CN soluble fractions by vacuum distillation, a purple solid remained. The solid was dissolved in 1 mL of MeOH, and the solution was subjected to Et₂O vapor diffusion over 2 days. The mother liquor was decanted from the so-formed red-purple crystals. The crystals were washed with Et₂O and were dried under vacuum for 30 min to give 0.028 g (53%) of **9** as red-purple crystals.

Scheme 1. Preparative Routes to Nitrogen-Confused Scorpionate Ligands



Characterization Data for 9. Mp: colorless by 110 °C; did not melt below 250 °C. Anal. Calcd (found) for $\text{C}_{22}\text{H}_{20}\text{N}_{12}\text{F}_6\text{FeO}_6\text{S}_2$: C, 33.77 (34.05); H, 2.58 (2.71); 21.48 (21.40). μ_{eff} (Evan's, CD_3OD): 2.0 μ_{B} . IR (Nujol/KBr, cm^{-1}): ν_{NH} 3140; triflate ($\text{CH}_2\text{Cl}_2/\text{KBr}$, s to vs), 1265 (ν_{asf} SO_3), 1232 (ν_{sf} CF_3), 1164 (ν_{asf} CF_3), 1018 (ν_{sf} SO_3), 623 (δ_{sf} SO_3). UV-vis [CH_3CN ; λ , nm (ϵ , $\text{M}^{-1} \text{cm}^{-1}$): 214 (25700), 271 (4650), 315 (sh, 6200), 331 (7300), 520 (100), 1103 (6). ^1H NMR (CDCl_3): δ_{H} 46.21, 30.71, 23.33, 20.19, 11.56, 7.17, -9.96. ESI(+) MS (relative intensity) assignment: m/z 633 (1) [$\text{Fe}(\text{HL})_2(\text{OTf})$] $^+$, 483 (10) [$\text{Fe}(\text{HL})(\text{L})$] $^+$, 243 (8) [$\text{Fe}(\text{HL})_2$] $^{2+}$, 209 (9) [$\text{Fe}(\text{HL})(\text{HL} - \text{pz})$] $^{2+}$, 177 (15) [$\text{Fe}(\text{HL})(\text{CH}_3\text{CN})_2$] $^{2+}$, 156 (11) [$\text{Fe}(\text{HL})(\text{CH}_3\text{CN})$] $^{2+}$, 147 (100) [$\text{HL} - \text{pz}$] $^+$. If crystals were dried under vacuum for 30 min but not heated at 140 °C for 2 h, then the sample repeatedly analyzed as 9-MeOH: Anal. Calcd (found) for $\text{C}_{23}\text{H}_{24}\text{N}_{12}\text{F}_6\text{FeO}_7\text{S}_2$: C, 33.92 (33.86); H, 2.97 (2.69); 20.64 (20.65).

Catalytic Aziridination. To ensure reproducibility, AgOTf and other silver(I) complexes to be used as catalysts were dried at 100 °C under vacuum for 2 h prior to use.

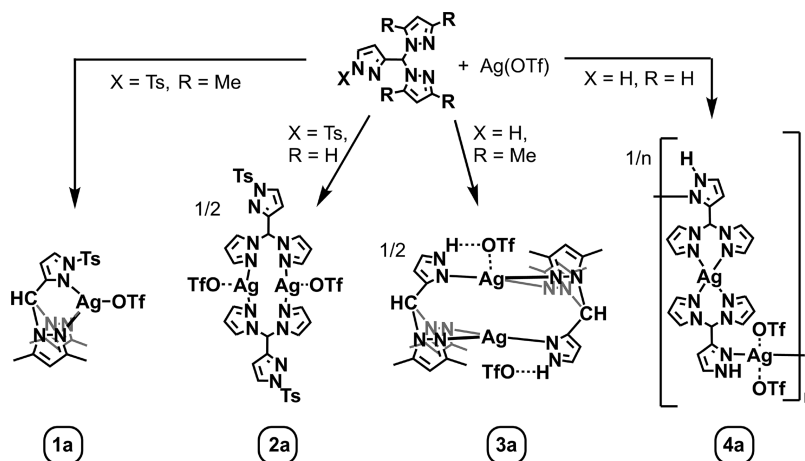
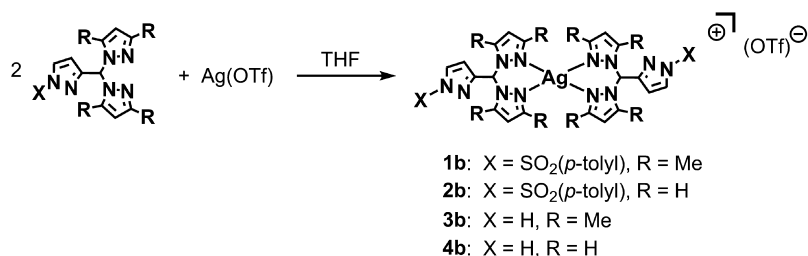
General Procedure. A 0.5 g sample of activated 4 Å molecular sieves and a Teflon-coated magnetic stir bar were added to a Schlenk flask under an argon blanket. The flask was flame-dried under vacuum, then backfilled with argon, and allowed to cool to room temperature. Next, the silver catalyst (0.020 mmol), 0.171 g (1.00 mmol) of tosylamine, and 0.322 g (1.00 mmol) of $\text{PhI}(\text{OAc})_2$ were added under an argon blanket. The reaction flask was subjected to three evacuation and argon backfill cycles. Next, 4 mL of dry distilled CH_3CN was added by syringe. The reaction flask was placed in an oil bath maintained at 80 °C and allowed to equilibrate for 15 min. Then, 0.57 mL (0.521 g, 5.00 mmol) of styrene was added by syringe, at which time the solution changed color to orange or, in some instances, orange-brown. After the reaction mixture had been stirred at 80 °C for 16 h, it was filtered through a sintered glass frit. The solid residue was washed with two 2 mL portions of CH_3CN . Next, between 25 and 30 mg of bis(trimethylsilyl)benzene was added to the solvate as a nonvolatile NMR standard, and solvent was removed by rotary evaporation to leave a brown-orange oily residue. The residue was separated by column chromatography on silica gel by first flushing with hexanes to remove the first fraction (which moves with the solvent front) that contains the NMR standard and iodobenzene. The eluent was then changed to 4:1 (v/v) hexanes/EtOAc. The next (second) fraction ($R_f = 0.7$) was a diastereomeric mixture of 2,4-diphenyl-*N*-tosylpyrrolidine,³⁶ and the third fraction ($R_f \sim 0.4$) contained the desired aziridine. The excess H_2NTs and an unidentified brown product remained in the column (but could be eluted with MeOH if desired). The yields of aziridine are the average of a minimum of three catalytic runs.

Crystallography. X-ray intensity data from a colorless needle of 1a, a colorless plate of 1b, a colorless prism of 1b-MeOH, a colorless needle of 2a, a colorless irregular block of 2b, a colorless prism of 3a, a colorless plate of 3b, a colorless plate of 4a, a yellow plate of 6, a yellow prism of 8, and a pink prism of 9 were each collected at 100.0(1) K with an Oxford Diffraction Ltd. A Supernova diffractometer equipped with a 135 mm Atlas CCD detector using Cu $K\alpha$ radiation for the data of 1a, 1b-1.5 CH_3CN , 1b- CH_3OH , 3b, 4b-acetone- H_2O , 8, and 9 was used, while Mo $K\alpha$ radiation was used for the other experiments. Raw data frame integration and Lp corrections were performed with *CrysAlisPro* (Oxford Diffraction, Ltd.).³⁷ Final unit cell parameters were determined by least-squares refinement of the 15713, 22719, 14418, 10710, 25334, 19082, 19683, 14285, 18698, 27362, 6891, and 6853 reflections of 1a, 1b-1.5 CH_3CN ,

1b-MeOH, 2a, 2b, 3a, 3b, 4a, 4b-acetone- H_2O , 6, 8, and 9, respectively, with $I > 2\sigma(I)$ for each. Analysis of the data showed negligible crystal decay during collection in each case. Direct-method structure solutions were performed with *Olex2.solve*,³⁸ while difference Fourier calculations and full-matrix least-squares refinements against F^2 were performed with *SHELXTL*.³⁹ Numerical absorption corrections based on Gaussian integration over a multifaceted crystal model were applied to the data for each of the complexes except for 9, which employed a multiscan empirical absorption correction using spherical harmonics, as implemented in the *SCALE3 ABSPACK* scaling algorithm. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms bond to nitrogen atoms in the structures 3a, 3b, 4a, 4b-acetone- H_2O , 8, and 9 were located and refined, whereas all other hydrogen atoms were placed in geometrically idealized positions and included as riding atoms. The X-ray crystallographic parameters and further details of data collection and structure refinements are given in Tables S1–S3. *Special details:* The crystal of 3b was a nonregular twin with a 2:1 component ratio, where component 2 was rotated by 5.441° around [0.59 0.68 0.43] in reciprocal space. The structure of 4a shows polymeric chains along z that possess strong quasi-symmetry: a 2-fold axis through ions Ag1 and Ag2 results in a higher centrosymmetric pseudosymmetry of the crystal, $P2_1/c$. However, an attempt at refinement in the centrosymmetric space group resulted in a much higher $R \sim 13\%$, whereas refinement as a racemic twin (with a 31:69 component ratio) in space group Pc gave $R = 6.8\%$ [Flack parameter, 0.00(16)]. Therefore, the noncentrosymmetric model was chosen. The crystal of 4b-acetone- H_2O was a nonregular twin with a 2:1 component ratio and a 2.38° rotation around [−0.97 0.18 0.16] (reciprocal space). The structure of 9 represents a regular quasi-merohedral (pseudoorthogonal) twin (rotation 180° around x) with a 61:39 component ratio.

RESULTS AND DISCUSSION

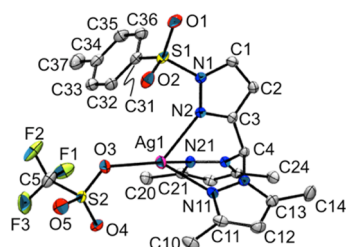
The new nitrogen-confused scorpionate ligands, TsL^* and HL^* , each with two 3,5-dimethylpyrazolyl groups and either an *N*-tosyl or a *N*-H moiety, respectively, were prepared in a manner similar to that reported³¹ for the parent ligands (with two unsubstituted pyrazol-1-yl groups), as summarized in Scheme 1. That is, the CoCl_2 -catalyzed Peterson rearrangement⁴⁰ between *N*-tosyl-3-carboxaldehydopyrazole and an excess of bis(3,5-dimethylpyrazol-1-yl)carbonyl in toluene gave the desired ligand, TsL^* , in high yield. Excess $\text{O}=\text{C}(\text{pz}^*)_2$ is required for high yield because the reaction with only 1 equiv consistently gave 63(±2)% yield after purification. The alternative use of $\text{O}=\text{S}(\text{pz}^*)_2$ in THF (like that used in the synthesis of TsL) in place of $\text{O}=\text{C}(\text{pz}^*)_2$ in toluene gave lower yields (ca. 60%), presumably due to steric issues that required higher reaction temperature. Deprotection of TsL^* by aqueous base proceeded smoothly to give HL^* but required longer reaction time than deprotection of TsL (45 min versus 10 min), as indicated by thin-layer-chromatography monitoring. In contrast to the parent deprotected ligand, HL , which required extensive extraction, HL^* is much less soluble in H_2O , so extraction and subsequent purification were uncomplicated. The *N*-tosyl ligands give characteristic IR bands near 1380 and 1180 cm^{-1} for antisymmetric and symmetric S–O stretches, respectively. The IR spectra for HL and HL^* show weak bands

Scheme 2. Summary of the Solid-State Coordination Behavior of 1:1 $^3\text{L}/\text{Ag}(\text{OTf})$ ComplexesScheme 3. Preparation and Labeling of 2:1 $^3\text{L}/\text{Ag}(\text{OTf})$ Complexes

for N–H stretches at 3430 and 3450 cm^{-1} , respectively.⁴¹ For these latter ligands in CD_3CN , the ^1H NMR resonance for the N–H group appears as a broad singlet downfield near 11.3 ppm, a region similar to that found for other pyrazoles.

With the four ligands in hand, their 1:1 (Scheme 2) and 2:1 (Scheme 3) $\text{L}/\text{Ag}(\text{OTf})$ complexes were prepared in high yields by mixing THF solutions of the appropriate ligand (1 or 2 mol equiv) and 1 equiv of the silver salt and collecting the precipitate by filtration. All of the silver complexes are light-stable colorless solids. Most are air-stable, but **3b** and **4b** readily absorb adventitious H_2O , so care must be taken if one wants anhydrous complexes. Each complex is soluble in many Lewis basic organic solvents, with the exception of Et_2O (insoluble) or THF (slightly soluble), and has modest solubility in CHCl_3 or CH_2Cl_2 . Vapor diffusion of Et_2O into either CH_3CN or CH_3OH solutions of the various complexes afforded X-ray-quality single crystals in most cases except for **4b**, for which evaporation from acetone/ H_2O mixtures gave the mixed solvate.

Solid State. Views of the structures of the various silver complexes are provided in Figures 2–7 and S1–S12. More

Figure 2. Structure of **1a** with hydrogen atoms removed for clarity.

complete details of the supramolecular structures that show three-dimensional organization by weak charge-assisted hydrogen bonding between the triflate anion and acidic hydrogen atoms of the cations in each compound are given in the Supporting Information.

As illustrated in Figure 2, **1a** features four-coordinate silver as a result of binding to the tridentate, $\kappa^3\text{N}$, ligand and a triflate oxygen. Noteworthy is the fact that while the Ag–N bond of tosylpyrazolyl is nearly 0.1 Å longer than those of the other pyrazolyls (Table 1), the average Ag–N_{pz} distance of 2.37 Å is firmly in the 2.3–2.4 Å range for other four-coordinate silver pyrazolyl complexes⁴² including $\{[\kappa^3\text{-(3-tBupz)}_3\text{CH}]\text{Ag}\}(\text{OTf})$ (avg 2.38 Å)^{22a} and $\{[\kappa^3\text{-(3-Phpz)}_3\text{CH}]\text{Ag}(\text{CH}_3\text{CN})\}\text{BF}_4$ (2.36 Å).^{22b} The three pyrazolyls are also disparately twisted, as quantified by either the Ag–N–C–C_{meth} torsion angle of the “confused” pyrazolyl (4°, here) or the Ag–N–N–C_{methine} torsion angles of the “normal” pyrazolyls (6 and 18° for rings containing N11 and N21, respectively). The Ag–O distance [Ag–O3 2.224(2) Å] is among the shortest known for silver triflate complexes; it is shorter than relatives such as $\{\text{Ag}[\text{C}_6\text{H}_5\text{CH}_2\text{OCH}_2\text{Cpz}_3]\}\text{OTf}$ (2.343 Å),⁴³ $\{\text{Ag}[\text{4-MeO-2,6-pz}^*_2\text{-triazine}]\}\text{OTf}$ (2.292 Å),⁴⁴ and $\text{Ag}[\text{HC}(\text{pz}^{3\text{tBu}})_3]\text{OTf}$ (2.264 Å)^{22a} and is between the distances found in $\{\text{Ag}_2(\mu_2\text{-4,13-dibenzyl-4,13-diaza-18-crown-6})\}(\text{OTf})_2$ [2.252(3) and 2.215(3) Å].⁴⁵ The bond angles about silver in **1a** give a τ_8 parameter⁴⁶ of 0.61 near the border of a distorted sawhorse coordination geometry ($\tau_8 = 0.63\text{--}0.45$) and a distorted tetrahedral geometry ($\tau_8 = \sim 0.9\text{--}0.63$).

Complex **2a** exists as a dimer with inversion symmetry as a result of two ligands that sandwich two closely spaced silver centers [Ag...Ag separation 3.0588(4) Å; Figure 3]. The $\mu\text{-}\kappa^1, \kappa^1$ ligands act in a manner where the two “normal” pyrazolyls on each ligand bind to two different silver centers

Table 1. Selected Bond Distances (Å) and Angles (deg) in 1a, 2a, and 3a

1a		2a		3a			
Bond Distances (Å)							
Ag1–N2	2.4273(17)	Ag1–N11	2.182(2)	Ag1–O1	2.724(3)	Ag2–N32	2.173 (2)
Ag1–N11	2.3391(18)	Ag1–N21	2.232(2)	Ag1–N2	2.196(2)	Ag2–N11	2.316(3)
Ag1–N21	2.3434(18)	Ag1–O3	2.5864(18)	Ag1–N41	2.307(3)	Ag2–N21	2.274(3)
Ag1–O3	2.2235(16)	Ag1⋯Ag1′	3.0588(4)	Ag1–N51	2.331(2)	Ag1⋯Ag2	2.8271(4)
Bond Angles (deg)							
O3–Ag1–N11	131.19(6)	N11–Ag1–O3	95.24(7)	O1–Ag1–N41	100.53(8)	N11–Ag2–N32	136.66(9)
O3–Ag1–N21	138.16(7)	N21–Ag1–O3	85.92(7)	O1–Ag1–N51	85.39(9)	N21–Ag2–N32	138.86(9)
N2–Ag1–N11	80.90(6)			N2–Ag1–N41	135.99(9)		
N2–Ag1–N21	77.27(6)			N2–Ag1–N51	141.51(9)		
O3–Ag1–N2	127.21(6)	N11–Ag1–N21	154.09(8)	O1–Ag1–N2	96.08(9)	N11–Ag2–N21	82.83(9)
N11–Ag1–N21	80.61(6)			N41–Ag1–N51	80.63(9)		

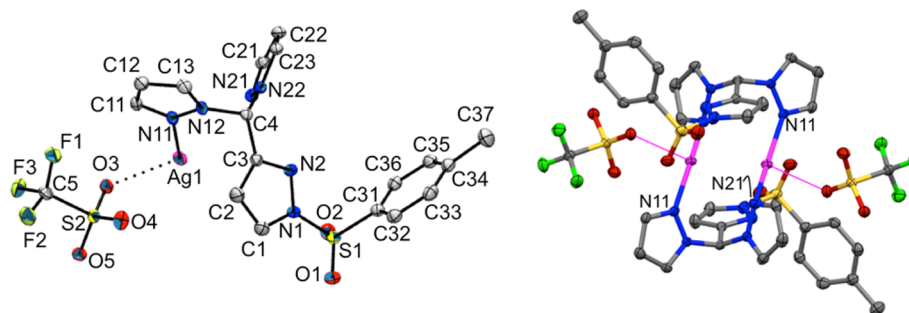


Figure 3. Views of the structure of 2a with hydrogen atoms removed for clarity: (left) asymmetric unit with atom labeling; (right) dimeric unit.

with Ag–N11 of 2.182(2) Å and Ag–N21 of 2.232(2) Å. The average Ag–N distance of 2.207 Å is much longer than the 2.10–2.14 Å range found for two-coordinate silver bound to pyrazolyls⁴² and is at the lower end of the 2.2–2.3 Å range for three-coordinate silver. The tosyl-protected “confused” pyrazolyl is highly twisted (“pz twist” = 76°) such that the very long Ag–N2 distance of 2.672 Å is probably better described as an Ag– π secondary interaction rather than a σ -bonding interaction. As a comparison, the “pz twists” of the “normal” pyrazolyls (here, with shorter Ag–N bonds) are 19° for the ring with N21 and 55° for the ring with N11. Instead, the coordination sphere about each silver center is completed by interaction with an oxygen atom of a triflate anion, Ag...O3 = 2.586(2) Å, which is within the ca. 2.07–2.75 Å range (average Ag...O distance = 2.48 \pm 0.13 Å) found for other complexes of silver triflate.⁴⁷

Figure 4 shows the dimeric structure of 3a, while Table 1 gives selected interatomic distances and angles. As opposed to dimeric 2a, which had μ - κ^1, κ^1 ligands with an unbound

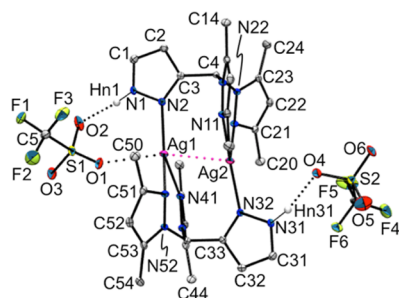


Figure 4. Structure of 3a with partial atom labeling. Most of the hydrogen atoms are omitted for clarity.

“confused” pyrazolyl, the dimer in 3a is constructed of two bridging μ - κ^2, κ^1 ligands sandwiching two silver atoms. Here, the two dimethylpyrazolyl rings chelate one silver center, while the confused pyrazolyl binds the second proximal silver to give a short Ag...Ag separation of 2.8271(4) Å (compared to twice the van der Waals radii of silver = 3.44 Å). The ligands are arranged such that each silver is bound to one “confused” pz nitrogen and to two pz* nitrogen atoms.

Two triflate anions are also affixed to the dimer by short hydrogen bonds involving the confused pyrazolyl’s N–H groups (N1–H1n...O2 = 1.935 Å; N31–H31n...O4 = 1.897 Å). The triflate anion with O1 also forms a long bond with silver (Ag1–O1 = 2.724 Å), but the other triflate is not bound; the closest contact to Ag2 is with O4 at 3.632 Å. The disparity in the anion binding sites is responsible for the longer average Ag–N distance involving Ag1 (2.278 Å) than Ag2 (2.254 Å), distances that straddle the borderline demarcating three- or four-coordinate silver pyrazolyl complexes.

Complex 4a crystallizes as a one-dimensional coordination polymer that propagates along the *c* axis as a result of bridging ligands that bind neighboring silver centers (Figure 5). The ligands show a μ - κ^2, κ^1 binding mode, where the chelating portion of the ligand is composed of the “normal” pyrazolyls, while the unidentate portion involves the “confused” pyrazolyl. These ligands are arranged so as to alternate AgN₄ and AgN₂ kernels (i.e., one silver is bound to the chelating portions of two ligands, while the other silver is bound to two κ^1 “confused” pyrazolyl nitrogen atoms). Selected bond distances and angles are given in Table 2. The average Ag–N distances of 2.299 and 2.321 Å for Ag3 and Ag4, respectively, are clearly indicative of four-coordinate silver, whereas those of 2.153 Å for Ag1 and 2.162 Å for Ag2 are between the ranges usually found for two- and three-coordinate silver pyrazolyls. Inspection of the coordination sphere about silver reveals two long Ag–O

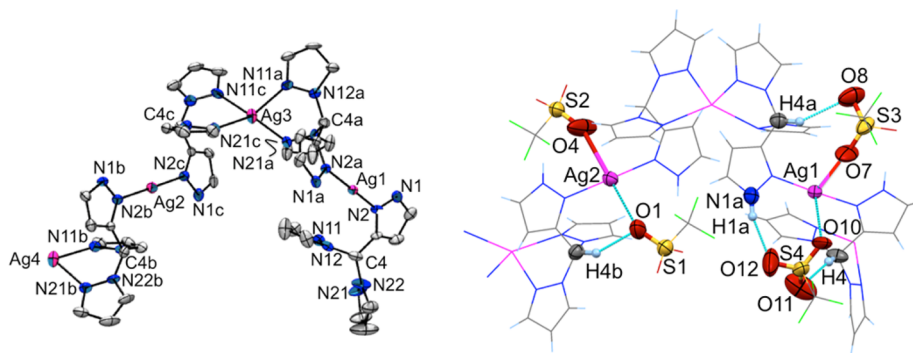


Figure 5. Portion of the structure of **4a** with partial atom labeling. Most hydrogen atoms are removed for clarity, and thermal ellipsoids are shown at 30% probability.

Table 2. Selected Bond Distances (Å) and Angles (deg) in **4a**

Bond Distances (Å)			
Ag1–N2	2.158(8)	Ag2–N2b	2.176(8)
Ag1–N2a	2.150(8)	Ag2–N2c	2.148(8)
Ag3–N11a	2.322(10)	Ag4–N11	2.266(10)
Ag3–N11c	2.339(10)	Ag4–N21	2.365(12)
Ag3–N21a	2.275(9)	Ag4–N11b	2.282(8)
Ag3–N21c	2.258(9)	Ag4–N21b	2.370(9)
Bond Angles (deg)			
N2–Ag1–N2a	175.3(3)	N2b–Ag2–N2c	179.0(3)
N11a–Ag3–N11c	113.0(3)	N11–Ag4–N11b	138.3(4)
N11a–Ag3–N21a	86.6(4)	N11–Ag4–N21	84.5(4)
N11a–Ag3–N21c	121.7(4)	N11–Ag4–N21b	124.3(4)
N11c–Ag3–N21a	123.7(4)	N11b–Ag4–N21	120.2(4)
N11c–Ag3–N21c	83.9(4)	N11b–Ag4–N21b	81.7(3)
N21a–Ag3–N21c	130.9(3)	N21–Ag4–N21b	109.1(4)

interactions on each silver center: one that is below the 2.75 Å Ag–O bonding limit (Ag1–O7 = 2.734 Å and Ag2–O4 = 2.719 Å) and one that is just above the limit (Ag1–O10 = 2.756 Å and Ag2–O1 = 2.767 Å). If the longer Ag–O distance were considered a secondary contact, then Ag1 and Ag2 would both be three-coordinate. Then, because Ag1 sits 0.084 Å out of the O7–N2–N2a plane, the four atoms form an acute triclinic pyramid (based on a 3% folded T), while the planar Ag2–N2b–N2c–O4 unit represents a slightly distorted T-shape (or, more specifically, a γ -constricted near-closed Y).⁴⁸ The “confused” pyrazolyl’s N–H group serves as a hydrogen-bond donor to triflate oxygen atoms to further secure triflate ions to

the chain and between chains to assemble the supramolecular structure (Figure S8).

The structures of the diligated $[\text{Ag}^{\text{rL}}_2](\text{OTf}) \cdot n(\text{solvate})$ complexes, **1b**·1.5CH₃CN, **1b**·CH₃OH, **2b**, **3b**, and **4b**·acetone·H₂O (Scheme 3), were determined, and those of the latter two complexes are given in Figures 6 and 7, while the others are provided in the Supporting Information. Selected bond distances and angles in four of the five complexes are summarized in Table 3; the data for **1b**·CH₃OH are nearly identical with those of the acetonitrile solvate, so they are given in the Supporting Information. Each has four-coordinate silver as a result of the metal binding to the nitrogen atoms of the “normal” pyrazolyl rings; the “confused” pyrazolyl ring of each ligand is not bound to the metal center. The average Ag–N distances are quite similar across the series and are in the expected range for four-coordinate silver(I) pyrazolyl complexes: 2.33 Å in each solvate of **1b**, 2.31 Å in **2b**, 2.34 Å in **3b**, 2.35 (Ag1) and 2.36 Å (Ag1a) in the two symmetry-independent units of **4b**·acetone·H₂O. The shapes of the AgN₄ coordination polyhedra are also similar, as can be gleaned from examination of their bond angles and associated τ_8 values: τ_8 = 0.56 for both solvates of **1b** and for **3b**, τ_8 = 0.71 for **2b**, and τ_8 = 0.63 (Ag1) or 0.59 (Ag1a) for the independent units in **4b**·acetone·H₂O. All of these values are within the ranges for either a distorted tetrahedral (τ_8 = ~0.90–0.63) or a distorted sawhorse (τ_8 = ~0.63–0.45) geometry.⁴⁶ The unbound “confused” pyrazolyls in each complex involve disparate noncovalent interactions that help to differentiate the supramolecular structures. The SO groups of the tosyl unit in each solvate of **1b** (rather than of the triflate) are hydrogen-bonded to the methine hydrogen atoms of the neighboring cations to

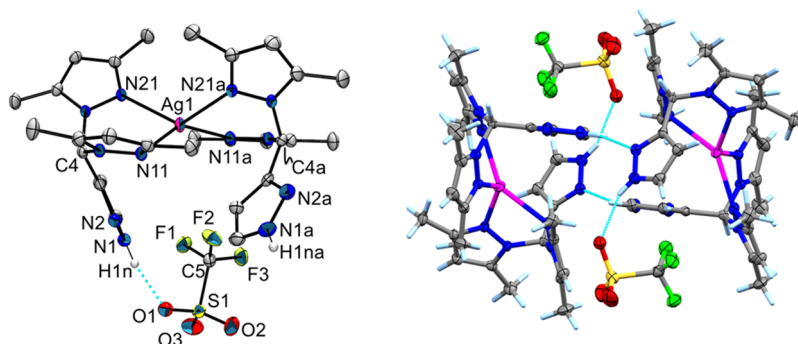


Figure 6. Views of **3b** with most of the hydrogen atoms removed for clarity and with partial atom labeling: (left) asymmetric unit; (right) hydrogen-bonded (cyan lines) dimer.

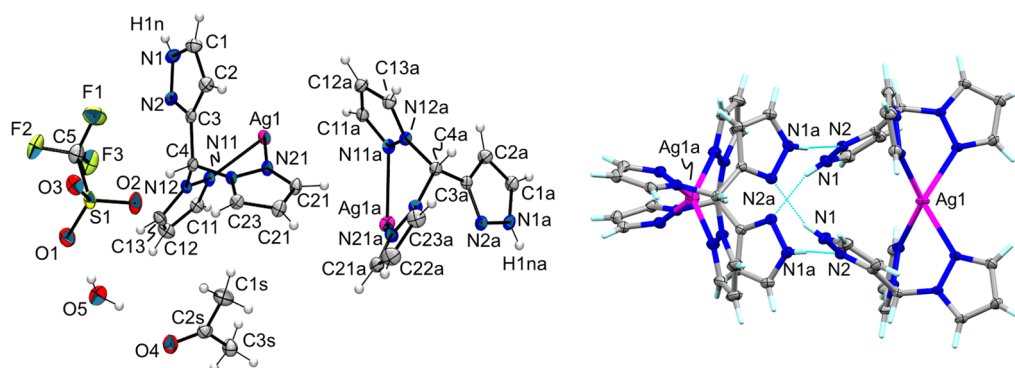
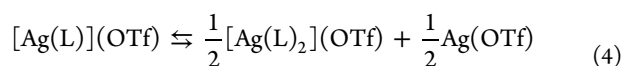
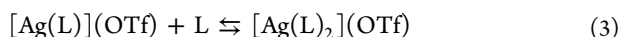
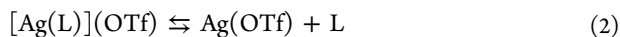
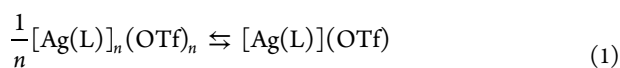


Figure 7. Structure of **4b**·acetone·H₂O: (left) asymmetric unit with atom labeling; (right) hydrogen-bonded (cyan lines) dimer of cations.

help to organize the three-dimensional extended structure (Figures S2 and S3). In contrast, the low steric profile of the normal pyrazolyls in **2b** allows contact between the triflate anion and the acidic methine hydrogen atom and relegates the tosyl SO groups to associate with acidic pyrazolyl ring hydrogen atoms in the assembly of the three-dimensional supramolecular structure (Figure S4). The two “confused” pyrazolyl arms in **3b** are involved in different hydrogen-bonding interactions (right of Figure 6). First, one “confused” pyrazolyl acts as a hydrogen-bond donor to a triflate oxygen acceptor (N1–H1n···O1, 2.088 Å, 153°). The second “confused” pyrazolyl acts as a hydrogen-bond donor to a nitrogen atom (N1a–H1na···N2', 1.984 Å, 168°) of the triflate-bonded confused pyrazolyl ring on a neighboring complex to form a hydrogen-bonded dimer (Figure 6, right). Such an interaction positions the triflate ion in close van der Waals contact with the pz* ring hydrogen atom and one of the methyl hydrogen atoms on the neighboring complex (C12–H12···O2, 2.793 Å, 140°; C10–H10b···O1, 2.788 Å, 143°), further securing the dimer. The “confused” pyrazolyls in **4b**·acetone·H₂O participate in hydrogen-bonding interactions with analogous rings on a neighboring cation to give a C₂-symmetric dimer (right of Figure 7). The triflate ions are hydrogen-bonded to the methine hydrogen atoms on one cation with Ag1 (C4–H4···O2, 2.215 Å, 162°), while the acetone solvate is weakly hydrogen-bonded to the methine hydrogen atoms on the other cation (C4a–H4a···O4, 2.411 Å, 147°). The solvate H₂O serves as a hydrogen-bond donor to a triflate oxygen atom on one dimer (O5–H5b···O1 2.001 Å, 171°) and the acetone oxygen atom (O5–H5a···O4, 2.133 Å, 152°) of an adjacent dimer to help organize the three-dimensional supramolecular structure (Figure S9).

Solution. The nature of silver(I) complexes in an acetonitrile solution was investigated intensively by spectroscopic methods (one-dimensional and diffusion NMR and IR) and by ESI(+) MS because this solvent is used for the catalytic reactions described later. The collective data indicate that all have dynamic solution structures where the static solid-state structures are not retained. Instead, it is likely that the complexes are dissociated and that multiple species exist in solution as a result of two or more of the following equilibria (eqs 1–4).



The equilibria are demonstrated by multiple different observations. First, crystallizations of analytically pure samples of [AgL](OTf) in either CH₃CN or CH₃OH produce mixtures of crystals. Vapor diffusion of dilute solutions (0.005 M) gives mainly the monoligated silver along with small amounts of the diligated [AgL₂](OTf), whereas more concentrated solutions (0.02–0.04 M) begin to favor the diligated species over the monoligated, as determined by careful analysis of the crystal morphologies and subsequent unit cell measurements. Interestingly, crystallizations of [AgL₂](OTf) did not produce noticeable amounts of [AgL](OTf); the equilibrium constant for eq 3 must be relatively large in all cases. It is conjectured that the lower solubility of [Ag(L)](OTf) versus [AgL₂](OTf) in THF (and the limiting L) allows isolation of the former by precipitation. Upon dissolution of pure [Ag(L)](OTf) in more polar solvents, equilibrium mixtures are obtained.

Second, NMR titrations of the ligands, L, with silver triflate (reverse of eq 2 and forward of eq 3) or of [AgL₂](OTf) with AgOTf (reverse of eq 4) in CD₃CN only gave one set of resonances (with different chemical shifts) regardless of the stoichiometry (see Figures S13 and S14 as examples) or the temperature within the solvent's liquid range, showing that these four species are in rapid equilibrium.

Third, the diffusion-oriented spectroscopy (DOSY) NMR experiments of various metal complexes of the new ligands were acquired at room temperature to provide further insight into their molecularity. Table 4 collects the diffusion constants, the hydrodynamic radii (calculated by using the Stokes–Einstein relation, as detailed in the Supporting Information), and the calculated radii from both X-ray diffraction studies and molecular modeling of the various ionic compounds. The data indicate that the complexes are most likely monomeric in CD₃CN at room temperature because the hydrodynamic radii of all silver(I) complexes are similar to one another (even those with dimeric and polymeric solid-state structures) and to those of the kinetically inert monomeric tricarbonylmanganese(I) complexes of the same ligands described later.

Next, the number and chemical shifts of the resonances in the NMR spectrum of each compound indicate that the complexes have dynamic solution structures that are different from their solid-state structures. Complexation of the ligands to cationic metal centers is characterized by a downfield shift in the “normal” pyrazolyl ring hydrogen H4 resonances, with respect to those in the free ligands. In every silver complex (and for the inert [Mn(CO)₃]⁺ complexes described later), the

Table 3. Selected Bond Distances (Å) and Angles (deg) in 1b·1.5CH₃CN, 2b, 3b, and 4b·acetone·H₂O

1b·1.5CH ₃ CN		2b		3b		4b·acetone·H ₂ O	
Ag1–N11	2.339(2)	Ag1–N11	2.3066(13)	Ag1–N11	2.3839(19)	Ag1a–N11a	2.465 (2)
	2.318(2)						
Ag1–N21	2.315(2)	Ag1–N11a	2.3705(13)	Ag1–N21	2.3067(19)	Ag1a–N21a	2.248 (2)
Ag1–N11a	2.332(2)	Ag1–N21	2.3002(12)	Ag1–N11a	2.3218(19)		
Ag1–N21a		Ag1–N21a	2.2749(12)	Ag1–N21a	2.3387(19)		
Bond Angles (deg)		Bond Angles (deg)		Bond Angles (deg)		Bond Angles (deg)	
N11–Ag1–N21	79.42(7)	N11–Ag1–N11a	130.14(4)	N11–Ag1–N21	83.42(6)	N11a–Ag1a–N11a'	125.30(8)
N11–Ag1–N11a	143.21(7)	N11–Ag1–N21	85.02(4)	N11–Ag1–N11a	143.43(7)	N11a–Ag1a–N21a	85.14(6)
N11–Ag1–N21a	111.72(8)	N21–Ag1–N11a	109.33(4)	N21–Ag1–N21a	125.16(6)	N11a–Ag1a–N21a'	113.16(6)
N21–Ag1–N11a	119.94(7)	N11–Ag1–N21a	127.92(4)	N11a–Ag1–N21	126.25(6)	N11a'–Ag1a–N21a'	85.14(6)
N21–Ag1–N21a	130.92(7)	N21–Ag1–N21a	125.98(5)	N21–Ag1–N11a	100.52(6)	N11a'–Ag1a–N21a	113.16(6)
N11a–Ag1–N21a	80.30(7)	N11a–Ag1–N21a	82.44(4)	N11a–Ag1–N21a	80.31(7)	N21a–Ag1a–N21a'	140.77(10)

Table 4. Summary of the Data from ¹H NMR DOSY Experiments and Radii from the Longest Interatomic Distances in the Reference Structures or Models

compound	$D (\times 10^{-10} \text{ m}^2/\text{s})$	$r_{\text{DOSY}} (\text{Å})$	$r_{\text{X-ray}} (\text{Å})$	$r_{\text{model}} (\text{Å})$	$r_{\text{model}} (\text{bonding})$
NBu ₄ (OTf)	9.3(1)	5.7(2)	6.0 ^a	5.9	
1a	7.0(9)	7.7(9)	6.5	6.8	κ ³ monomer
				7.5	κ ³ , + CH ₃ CN
				8.7	κ ² , + CH ₃ CN
				11.3	κ ² , κ ⁴ N dimer
1b	7.3(1)	7.2(1)	8.5	10.0	tetrahedral
2a	7.6(9)	7.8(8)		7.0	κ ³ monomer
				8.5	κ ² , + CH ₃ CN
				8.9	Ag(^{Ts} L) ₂ , tetrahedral
				11.3	κ ² , κ ⁴ N dimer
3a	9.0(9)	6.1(9)	10.7	11.7	κ ¹ , κ ⁴ N dimer
				6.0	κ ³ monomer
				6.3	κ ³ , + CH ₃ CN
				7.4	Ag(^H L*) ₂ , tetrahedral
4a	7.9(4)	6.9(5)	7.82	8.0	κ ² , κ ⁴ N dimer
				5.33	κ ³ monomer
				7.45	κ ³ , + CH ₃ CN
				7.10	Ag(^H L) ₂ , tetrahedral
5	7.4(1)	7.1(2)		8.2	κ ² , κ ⁴ N dimer
8	8.3(1)	6.4(2)	5.8	6.4	κ ³ monomer
				6.1	κ ³ monomer

^aReference 61.

“normal” pincer pyrazolyls have downfield-shifted H4 resonances and, hence, are silver-bound. For the “confused” pyrazolyl ring in each complex, the chemical shift of the resonance for the H5-ring hydrogen (next to the ring nitrogen’s tosyl or N–H group) indicates whether or not this heterocycle is metal-bound. In the spectra of each 3a, 3b, 4a, and 4b (with ^HL or ^HL*), the H5 resonance is shifted downfield, indicating that the “confused” ring is bound, whereas in the remaining cases (with ^{Ts}L or ^{Ts}L*), the chemical shift of this resonance matches that for the free ligand, so the confused ring is likely not bound. Thus, the ligands in 1a, 3b, and 4b have different denticities in solution versus the solid state. It is reasonable that complexes 3b and 4b may be six-coordinate in solution given the sandwich structures of [Ag(κ³-Tp^x)₂]²⁺ and the low energy barrier calculated for κ²/κ³-[Ag(Tp^x)]⁺ interconversions.⁴⁹ Considering the DOSY experiments, [Ag-(CH₃CN)_n(κ²-^{Ts}L^x)]⁺ (*n* = 1–2) would be possible for 1a and 2a (and by analogy for 3a). These formulations do not include a silver-bound triflate because the spectroscopic data for each complex indicates a free (unbound) triflate anion in solution. That is, the ¹⁹F NMR spectrum of each in CD₃CN shows only one resonance at –79.3 ppm that matches that for NBu₄OTf. It is also noteworthy that the solution IR spectra of each has one set of strong bands in the 1280–1025 cm^{–1} range for symmetric and asymmetric SO₃ and CF₃ stretching modes that are characteristic of an unbound triflate anion.⁵⁰ Thus, the solution structures of 1a–4a with unbound triflates are different from the solid structures that showed silver-bound triflates. Although the triflate ion is not bound to silver in an acetonitrile solution, there is evidence for ion pairing in most cases, except 4a and 4b, from anomalous upfield shifts in certain hydrogen resonances, as seen with other metal

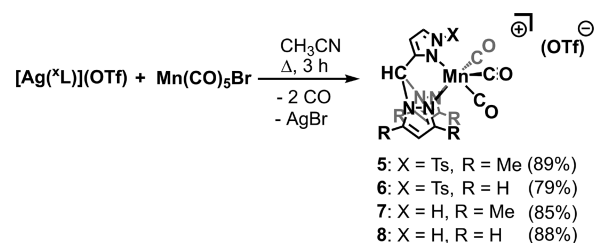
complexes.⁵¹ That is, for complexes **1a**, **1b**, **3a**, and **3b** with pz* groups, the resonance for the acidic methine, that for H₄ of the “confused” pyrazolyl ring, and that for one set of methyl pz* hydrogen atoms (closest to the methine) are unexpectedly shifted *upfield* from those in the spectrum of the free ligand. Given the different groups on the confused pyrazolyls and the propensity for triflate to be located near the methine positions of silver poly(pyrazolyl)methane complexes in the solid state,⁴⁷ it is likely that these hydrogen atoms are shielded by proximity to a nearby triflate ion. It is noted that the ¹H NMR spectrum of a concentrated mixture of NBu₄OTf and each charge-neutral ligand is a simple sum of the individual spectra of the pure components. Because the presence of the triflate does not affect the chemical shift of the charge-neutral ligands, ion pairing is essential for observation of the unusual upfield shifts (charge-assisted weak hydrogen bonding). In **2a** and **2b**, only the resonance for H₄ of the confused ring is significantly shifted upfield. It is unclear why upfield shifts were not observed in the spectrum of either **4a** or **4b**, which were of concentration similar to those of the other complexes. The simplicity of the ¹H NMR spectrum of **2a** also indicates that the static solid-state structure is not retained in solution. If it was retained, then two sets of resonances would be expected because the tosyl pyrazolyl arm points toward one of the “normal” pyrazolyls (see the right side of Figure 3) and would differentiate these heterocycles. Fast free rotation about the C_{methine}–C bond of the “confused” pyrazolyl could explain equivalence at room temperature. Again, it was not possible to slow the dynamic behavior in the liquid range of CH₃CN. Given the results of the NMR titrations and the DOSY experiment described above, it is most likely that rather than retaining a dimeric solid-state structure, complex **2a** likely dissociates to a monomeric structure (eq 1), which then participates multiple fast dynamic equilibria according to eqs 2–4. Similarly, the spectrum of **4a** is simpler than expected based on the polymeric solid-state structure. There was only one set of sharp resonances for the “normal” pyrazolyls when two sets would be expected if the solid-state structure of **4a** remained intact and static in solution (those pyrazolyls in Figure 6 with N11 would be different from those with N21 by proximity to the confused pyrazolyl or to the pseudo-C₂ axis that passes through Ag3). In this case, direct dissociation (by breaking the Ag–N bonds on two-coordinate Ag) to give **4b** and AgOTf directly (eq 4) or dissociation to monomeric [Ag(CH₃CN)_n(κ³-HL)]⁺ are reasonable possibilities.

Finally, ESI(+) MS spectral data of discrete complexes and coordination polymers of *inert* metal ions are generally accepted to be representative of solution structures.⁵² Electrospray ionization is soft enough that labile complexes, including supramolecular species held together by noncovalent interactions, can also be measured by this technique.⁵³ The results described here, the extensive studies by the Reger group on the structures, and ESI(+) MS spectra of silver(I) poly(pyrazolyl)-methane complexes demonstrate the existence of multiple solution species.^{22,54,55} For instance, the ESI(+) MS spectrum of a solution of analytically pure **1a**, which had a monomeric Ag(^{Ts}L*)(OTf) solid structure, consists of a parent 100% relative abundance peak at *m/z* 329 for a ligand fragment (^{Ts}L* – pz*), a lower intensity peak (with 87% relative abundance) at *m/z* 957 for [Ag(^{Ts}L*)₂]⁺, and a still lower intensity peak (41% relative abundance) at *m/z* 531 for the expected parent ion, [Ag(^{Ts}L*)]⁺. Clearly, the [Ag(^{Ts}L*)₂]⁺ species could arise from a redistribution reaction (eq 4) or from the self-assembly of

fragments that are already present in solution (eq 3) or, less likely, that are generated during ionizing conditions. Unfortunately, the peaks for [Ag(CH₃CN)_n]⁺ (*n* = 3, 4) species were not observed in the *m/z* >200 spectral window. The mass spectrum of **1b** differs from that of **1a** only by the intensities of the peaks. Given the NMR titration data and the fact that mixtures of crystals are obtained from the crystallization of analytically pure **1a** in CH₃CN [the solvent also used in ESI(+) MS experiments], the ESI(+) MS data are indeed more likely representative of solution structures partitioned via eqs 2–4 rather than being representative of species generated during or after ionization. The mass spectral data for the remaining silver complexes agree with many (but not all) trends outlined previously by the Reger group on related systems. Thus, the spectra of **2a** and **3a**, which exhibit dimeric solid-state structures, feature weak-intensity (<30% relative abundance) peaks corresponding to [Ag₂L₂(OTf)]⁺ and, for **3a**, to [Ag₂(^HL*)₂OTf – pz*]⁺ and [Ag₂(^HL*)]⁺ (L* = deprotonated ligand). The highest-intensity peaks in each spectrum were for [AgL₂]⁺ (100% relative abundance) and [AgL]⁺ (>70% relative abundance). The lack of half-integer *m/z* peaks establishes the monomeric nature of the [AgL]⁺ species. The mass spectrum of **4a**, which has a polymeric solid-state structure, displayed very weak intensity (<5% relative abundance) peaks for [Ag₃(^HL)₃(OTf)₂]⁺, [Ag₃(^HL)₂(OTf)₂]⁺, [Ag₃(^HL)₂(OTf)(Cl)]⁺, [Ag₃(^HL)(L)(OTf)]⁺, and [Ag₃(L)₂]⁺, where L is a deprotonated ligand and Cl[–] comes from the trace ions normally present in the mass spectrometer. There is also a series of higher-intensity (between 5 and 40% relative abundance) peaks for dimeric monocationic species such as [Ag₂(^HL)₂(OTf)]⁺ as well as disilver fragments [Ag₂L(X)]⁺ (X = Cl, OTf). These peaks are rather unexpected because Reger had indicated that, in the cases of silver(I) poly(pyrazolyl)-methanes with polymeric solid-state structures, peaks for dimeric units were notably absent.^{54a,c} It may be possible that crystallization under different conditions may lead to a yet-to-be-discovered dimeric form of **4a**. As with the other three [AgL]⁺ complexes, the most abundant peaks in the mass spectrum of **4a** were for [Ag(^HL)]⁺ (95% relative abundance) and [Ag(^HL)]⁺ (100% relative abundance). The origin of the relatively high abundance of monomeric monocations and decreasing abundance of higher-order monocations is most likely the result of the overall equilibrium constant of eqs 1–4. It is also noteworthy that the mass spectrum of **2b**, **3b**, or **4b** is devoid of peaks for disilver or other higher-order fragments. So, the equilibrium constant for eq 3 must again be relatively large.

Reactivity. The synthetic utility of the silver complexes as ligand delivery agents was demonstrated first via the preparation of tricarbonylmanganese(I) complexes (Scheme 4). The reactions between any of **1a**, **2a**, **3a**, or **4a** and

Scheme 4. Preparation of Tricarbonylmanganese(I) Complexes



Mn(CO)₅Br in refluxing CH₃CN for 3 h gave high yields of **5**, **6**, **7**, or **8** as appropriate. Given the high yields and availability of silver complexes, no attempt was made to further improve the syntheses of **5–8** by performing the reaction in one pot (i.e., starting from free ligand, Mn(CO)₅Br, and AgOTf), although this may be a useful route. Complexes **5–8** are slightly light-sensitive yellow solids that are soluble in many organic solvents except hydrocarbons and Et₂O. Solutions of the complexes are noticeably more light-sensitive than the solids. So, solution characterization data were obtained only for freshly prepared solutions and with precautions to exclude light *vide infra*. The IR spectra of **5–8** (Table 5) give characteristic bands

Table 5. IR Spectral Data (CH₂Cl₂, KBr) for [(^κL)Mn(CO)₃](O₃SCF₃) Complexes

complex	ν_{CO} (cm ⁻¹)	ref
{[HC(pz [*]) ₃]Mn(CO) ₃ }(OTf)	2044, 1949; wt avg = 1981	25
{[HC(pz) ₃]Mn(CO) ₃ }(OTf)	2051, 1956; wt avg = 1988	25
5	2046, 1957, 1942; avg = 1982	this work
6	2052, 1965, 1952; avg = 1990	this work
7	2046, 1955, 1943; avg = 1981	this work
8	2050, 1955; wt avg = 1987	this work

for the *fac*-Mn(CO)₃ moiety. That is, one sharp, higher-energy band and one broad, lower-energy band are found in the spectra of the solids. In CH₂Cl₂ solutions, the broad band is split to give three resolved bands in the cases of **5–7**; the local symmetry about manganese in **8** is probably high enough (*C*_{3*v*}) that the nominal *E* stretching mode is not split. The larger band broadening in the solids compared to solution likely does not allow resolution of any splitting in the broader band in this state. Also, as usual, the (weighted) average energies of the CO stretching frequencies in the solid are 10–20 cm⁻¹ lower than those in solution. In either medium, complexes **5** and **7**, with 3,5-dimethylpyrazolyl donors, exhibit lower average CO stretching frequencies than **6** and **8** with unsubstituted pyrazolyls because the ligands in the former are stronger donors than those in the latter and increase the back-bonding capabilities of the manganese(I) center to the carbonyl. These findings are in agreement with those previously reported for [(HC(pz^{R3,R5})₃)Mn(CO)₃](O₃SCF₃) (R = H, Me) (in CH₂Cl₂).²⁵ In the current complexes, the replacement of a tosyl group with a hydrogen has a marginal impact on the average CO stretching frequencies in a CH₂Cl₂ solution.

The *fac* coordination mode was verified by X-ray diffraction for **6** and **8** (Figure 8 and Table 6). In each, the ligands exhibit $\kappa^3\text{N}$ coordination to the metal center. In **6**, there are two independent cations in the asymmetric unit. In each, the Mn–

N bond involving the tosyl pyrazolyl (avg 2.140 Å) is significantly longer than the other two Mn–N bonds (averaging 2.057 Å). The overall average Mn–N distance of 2.085 Å is longer than 2.07 Å found in [HC(3-*i*Prpz)₃]Mn(CO)₃](O₃SCF₃)²⁵ and 2.040 Å in [(PhCpz₂py)Mn(CO)₃](O₃SCF₃).³⁶ The disparity in the Mn–N distances also leads to a dichotomy in the Mn–C distances, where the Mn–C bond trans to the tosyl pyrazolyl (avg 1.805 Å) is shorter than the other two Mn–C bonds (avg 1.821 Å). There is no significant discrepancy in the C–O bond distances, which average at 1.141(3) Å. In **8**, the average Mn–N bond distance of 2.052 Å is shorter than that found for **6**, and the distances are more uniform, as might be expected after considering the relative steric demands of the “confused” pyrazolyls in each complex. The triflate anions in **6** and **8** are affixed to the cations via short CH...O (cyan dotted lines; Figure 8) and CH...F (green dotted lines; Figure 8) interactions and, in the case of **8**, NH...O weak hydrogen bonding (not shown) and serve to organize the three-dimensional supramolecular structure, as is more fully described in the Supporting Information.

In a CD₃CN solution, the NMR spectra for each **7** and **8** were in accordance with expectations of complexes with $\kappa^3\text{N}$ ligands coordinated to the *fac*-Mn(CO)₃ fragment. At room temperature, the resonances for ligand hydrogen atoms are broadened slightly by the quadrupolar ⁵⁵Mn nucleus (*I* = 5/2, 100%) but sharpen upon heating. All resonances are shifted downfield from those found in the free ligand. The spectrum of each **5** and **6** in CD₂Cl₂ or acetone-*d*₆ is in accordance with expectations, but those in CD₃CN are more complicated than expected because two sets of resonances in a 5:1 ratio are observed. The major resonances agree with the expectations for a $\kappa^3\text{N}$ -ligated species, where all resonances for ligand hydrogen nuclei are shifted downfield compared to those of the free ligand. The minor resonances all have downfield-shifted resonances except for those of the confused pyrazolyl, which are shifted upfield from those in the free ligand. It is likely that the minor species has a dissociated tosylpyrazolyl group and a solvent bound to the metal instead. Because of the different relaxation times of the ¹³C nuclei versus ¹H, the ¹³C NMR spectra of **7** and **8** are not broadened. The resonances for the carbonyl carbon atoms are observed at room temperature near 221 and 215 ppm, consistent with the chemical shifts reported for the tricarbonylmanganese(I) complexes of tris(pyrazolyl)-methane derivatives.²⁵ The electronic absorption spectrum of each of **5–8** consists of a medium-intensity ($\epsilon \sim 2500 \text{ M}^{-1} \text{ cm}^{-1}$), low-energy metal-to-ligand charge-transfer (MLCT) band (*d*_{Mn}– π^*_{CO}) with λ_{max} near 360 nm that trails into the violet, which is responsible for the yellow color of the complexes. The intraligand transitions are found at higher

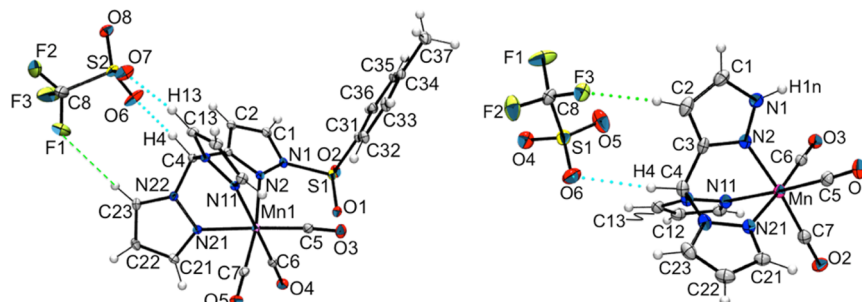


Figure 8. (Left) Structure of one of two symmetry independent units in the crystal of **6**. (Right) Structure of **8** with partial atom labeling.

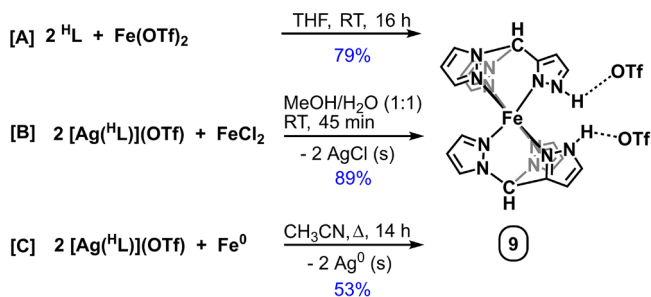
Table 6. Selected Bond Distances (Å) and Angles (deg) in 6 and 8

6		8			
Bond Distances (Å)					
Mn1–N2	2.1354(18)	Mn1a–N2a	2.149(2)	Mn1–N2	2.041(2)
Mn1–N11	2.0501(18)	Mn1a–N11a	2.0494(19)	Mn1–N11	2.058(2)
Mn1–N21	2.0652(18)	Mn1a–N21a	2.0613(19)	Mn1–N21	2.059(2)
Mn1–C5	1.822(2)	Mn1a–C5a	1.805(3)	Mn1–C5	1.807(3)
Mn1–C6	1.824(2)	Mn1a–C6a	1.826(2)	Mn1–C6	1.815(3)
Mn1–C7	1.803(2)	Mn1a–C7a	1.812(2)	Mn1–C7	1.812(3)
Bond Angles (deg)					
N2–Mn1–N11	82.18(7)	N2a–Mn1a–N11a	81.89(7)	N2–Mn1–N11	84.08(10)
N2–Mn1–N21	83.47(7)	N2a–Mn1a–N21a	83.78(7)	N2–Mn1–N21	82.55(10)
N11–Mn1–N21	86.84(7)	N11a–Mn1a–N21a	86.07(7)	N11–Mn1–N21	84.86(9)
C5–Mn1–C6	89.98(10)	C5a–Mn1a–C6a	89.64(12)	C5–Mn1–C6	87.91(12)
C5–Mn1–C7	87.31(10)	C5a–Mn1a–C7a	85.08(11)	C5–Mn1–C7	91.49(13)
C6–Mn1–C7	90.17(10)	C6a–Mn1a–C7a	90.01(11)	C6–Mn1–C7	89.54(12)
C5–Mn1–N2	99.57(8)	C5a–Mn1a–N2a	172.24(10)	C5–Mn1–N2	92.52(11)
C5–Mn1–N11	91.86(8)	C5a–Mn1a–N11a	92.45(10)	C5–Mn1–N11	176.59(11)
C5–Mn1–N21	176.51(9)	C5a–Mn1a–N21a	90.55(10)	C5–Mn1–N21	94.71(11)
C6–Mn1–N2	95.95(8)	C6a–Mn1a–N2a	95.80(9)	C6–Mn1–N2	94.33(11)
C6–Mn1–N11	177.57(9)	C6a–Mn1a–N11a	176.88(9)	C6–Mn1–N11	92.35(11)
C6–Mn1–N21	91.42(9)	C6a–Mn1a–N21a	91.59(9)	C6–Mn1–N21	176.01(10)
C7–Mn1–N2	170.76(8)	C7a–Mn1a–N2a	100.41(9)	C7–Mn1–N2	174.52(11)
C7–Mn1–N11	90.17(10)	C7a–Mn1a–N11a	92.48(9)	C7–Mn1–N11	91.91(12)
C7–Mn1–N21	89.48(9)	C7a–Mn1a–N21a	175.34(10)	C7–Mn1–N21	93.40(11)

energy. The light sensitivity of the complexes is likely due to the known photoactivated CO-releasing properties of $[(\text{HCpz}_3)\text{Mn}(\text{CO})_3]^+$ and related complexes (thereby removing the chromophore).⁵⁷ This property is outside the scope of the current work, so it was not investigated further here.

The use of silver complexes as stoichiometric ligand delivery agents was also demonstrated in the preparation of the iron(II) complex **9** by two routes (Scheme 5). First, the metathesis

Scheme 5. Preparative Routes to **9**



reaction between a MeOH solution of **4a** (2 equiv) and an aqueous solution of FeCl_2 (1 equiv) gave a high yield of pure **9** after the simple removal of AgCl by filtration and solvent under vacuum. Alternatively, a lower yield of **9** was obtained by the redox reaction between 2 equiv of **4a** and the iron metal in CH_3CN . The lower yield of this latter route was a result of both incomplete reaction and difficulties associated with separating **9** from residual **4a** by fractional crystallization. It is noted that the direct reaction between 2 equiv of ligand and commercial $\text{Fe}(\text{OTf})_2$ to give **9** gave a lower yield than the metathetical route because of issues with the solubility of the reagents, as well as the difficulties in separating the product from an unidentified yellow intermediate. Thus, the alternative routes to **9** proved useful when unexpected difficulties occurred in the direct reaction and could be useful in the future with certain

cases where a metal triflate salt is not readily available or is more expensive than a metal halide or elemental metal (cobalt, for instance).

Vapor diffusion of Et_2O into a MeOH solution of **9** gave crystals suitable for X-ray diffraction. The structure of **9** obtained at 100 K is given in Figure 9. The complex crystallizes

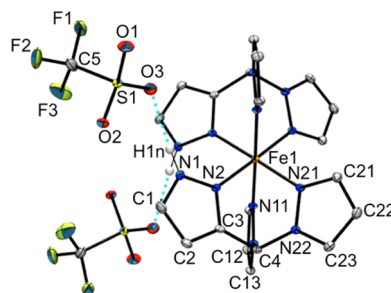


Figure 9. Structure of **9** with most hydrogen atoms removed for clarity.

as a cis isomer in the $P2_1/c$ space group, where iron resides on a C_2 crystallographic axis that bisects the “confused” pyrazolyls through the iron, giving only three inequivalent Fe–N bonds in the FeN_6 kernel. The Fe1–N2 bond of the “confused” pyrazolyl of 1.941(3) Å is shorter than the similar bonds of the other two pyrazolyls (Fe1–N11 = 1.978(3) Å and Fe1–N21 = 1.983(3) Å), and all are consistent with low-spin rather than high-spin iron(II). The triflate counterions are affixed to the dication via charge-assisted weak hydrogen bonding with the confused pyrazolyl ($\text{N1–H1n} \cdots \text{O3}$, 2.025 Å, 176°). Further weak $\text{CH} \cdots \text{O}$ interactions between the triflate oxygen and acidic (methine and pyrazolyl) hydrogen atoms of neighboring dications serve to organize the three-dimensional supramolecular structure, as detailed in Figure S12.

Although complex **9** is pink, a color characteristic of low-spin iron(II), it is slightly paramagnetic at room temperature.

Crystalline or powder samples reversibly change between pink and colorless upon cycling between heating to 150 °C and then cooling to room temperature. This behavior is similar to that of $[\text{Fe}(\text{H}_2\text{L})_2](\text{BF}_4)_2$ (**10**), a compound that showed a gradual (from $S = 0$ to 2) spin transition with $T_{1/2}$ near 360 K (beginning at ca. 275 K and is only 80% complete at 400 K).³¹ The solid-state magnetic behavior of **9** (Figure 10) shows a spin

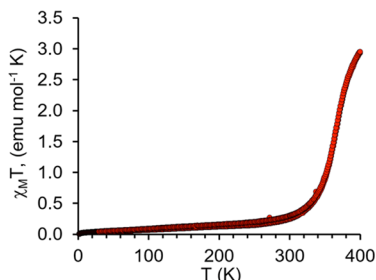


Figure 10. Temperature dependence of $\chi_M T$ for **9** from SQUID magnetometry.

transition $T_{1/2}$ near 365 K, but the spin-crossover (SCO) is more abrupt than that in **10**. The SCO in **9** begins at ca. 330 K and reaches ca. 95% completion at 400 K. Weak charge-assisted hydrogen bonding organizes the solid-state structure in each **9** and **10**. Clearly, the abruptness of the $\chi_M T$ versus T curve in the 300–400 K range indicates that the $\text{NH}\cdots\text{O}$ and $\text{CH}\cdots\text{O}$ interactions in **9** are stronger than the $\text{NH}\cdots\text{F}$ and $\text{CH}\cdots\text{F}$ interactions in **10**, as might be expected. It is also noteworthy that solutions of **9** are also slightly paramagnetic despite being pink. The solution magnetic moment of $2.0 \mu_B$ (Evan's method) for **9** in CD_3OD at 295 K is indicative of a significant fraction of high-spin iron(II) and is similar to the solid-state magnetic moment at 295 K. The electronic absorption spectrum shows characteristic bands for d–d transitions, MLCT bands of low-spin iron, and a very weak feature in the near-IR (ca. 9000 cm^{-1}) for the weak d–d transition for high-spin iron(II).

Nitrene-Transfer Catalysis. The ability for the new silver complexes to catalyze nitrene transfer at 2 mol % loading was probed by the reaction between styrene, *N*-tosylamine, and a commercial hypervalent iodine reagent, $\text{PhI}(\text{OAc})_2$, in CH_3CN . Table 7 summarizes the results of these initial investigations. Surprisingly, the best-performing catalyst of those tested was **1b** followed by **1a** \approx **2a** and then **3a**. The other new silver complexes performed similarly to control experiments that show activated molecular sieves alone have some activity under these conditions (16 h at 80 °C). It is noted that the aziridination reactions did not proceed either at room temperature, in CH_2Cl_2 , or even when using preformed $\text{PhI}=\text{NTs}$ (as in other silver-catalyzed aziridination reactions). For those complexes that successfully catalyzed the aziridination of styrene, the use of strictly anhydrous silver triflate (for in situ reactions) or oven-dried samples of preformed complexes was crucial for ensuring both reproducibility and maximum activity (as reported in other cases). Interestingly, in the reactions where catalysis was successful, a small amount (1–2%) of a statistical diastereomeric mixture of 2,4-diphenyl-*N*-tosylpyrrolidine (**B**; see Table 7) was also identified [by ^1H NMR and ESI(+) MS; see Figures S17 and S18]. This side product, **B**, is a result of [3 + 2] cycloaddition between styrene and 2-phenyl-*N*-tosylaziridine (**A**). While this particular transformation has been reported to be catalyzed by manganese(III)

Table 7. Summary of Results from Nitrene-Transfer Reactions^a

entry	[Ag]	NMR yield of A	% yield of A ^b	% yield of B ^b	TON ^c
1	none	3 (2)	0	0	0
2	AgOTf	3 (2)	0	0	0
3	1a	17 (6)	18 (5)	2.2 (0.1)	10
4	1b	34 (4)	27 (3)	2 (1)	15
5	1b ^d	27 (3)			
6	2a	16 (8)	10 (2)	2.1 (0.5)	11
7	2a ^e	trace			
8	2b	6 (2)	8 (2)	0	4
9	3a	15 (3)	12 (4)	1 (0.2)	7
10	3b	6 (1)			
11	4a	8 (2)	2	0	1
12	4b ^d	6 (1)			

^aConditions: 5 mmol of styrene, 1 mmol of $\text{PhI}(\text{OAc})_2$, 1 mmol of H_2NTs , 0.02 mmol of $[\text{Ag}]$, 0.5 g of 4 Å molecular sieves, 4 mL of CH_3CN , 16 h, 80 °C. ^bIsolated yields based on H_2NTs ; average of three runs (average deviation in parentheses). ^cTON = mmol (**A** + **B**, isolated)/mmol $[\text{Ag}]$. ^dIn situ. ^eRoom temperature, 16 h.

tetraphenylporphyrin,³⁶ to our knowledge, it has never previously been effected by a silver(I) complex. However, [3 + 2] cycloadditions between aziridines and either alkynes,⁵⁸ aldehydes,⁵⁹ or naphthols⁶⁰ are known to be catalyzed (or promoted) by AgSbF_6 or AgOTf . Control reactions on the NMR scale showed that heating a mixture of styrene and aziridine did not lead to any productive transformation (other than the slow formation of polystyrene). The addition of **1a** also did not give pyrrolidine (**B**). Clearly, the presence of the byproduct requires the oxidant and heating at 80 °C. The higher activity of **1b** versus **1a** in aziridination is rather surprising, considering the relative reactivity of the remaining complexes that favor complexes with 1:1 rather than 2:1 ligand/metal ratios. It can be speculated that both $[\text{AgL}]^+$ and $[\text{AgL}_2]^+$ may catalyze the reactions (and both exist in solution via eqs 1–4), but the larger steric requirements of Ts^*L decrease the likelihood for the diligated species to adopt a six-coordinate (and presumably catalytically inactive) silver center in solution. Future experimental and computational efforts will be directed toward determining the mechanism of catalysis and whether altering ligand sterics or electronics can give silver C-scorpionate catalysts that are more competitive with the AgTp^x or other silver catalysts for aziridination reactions.

CONCLUSIONS

Two new N-confused C-scorpionate ligands with 3,5-dimethylpyrazolyl “pincers” and either an *N*-tosyl (Ts^*L) or an *N*-H (H^*L) “stinger” have been prepared in high yield. Together with the previously known, less bulky derivatives, a complete set of four nitrogen-confused scorpionate ligands with a wide range of steric profiles is now available for coordination chemistry studies. It was possible to structurally characterize the complete set of eight silver complexes that had both 1:1 and 2:1 L/Ag ratios. In the solid state, the 2:1 complexes had four-coordinate silver by binding only the pincers; the confused scorpionate stinger was not bound. This is a remarkable finding

in light of the structures of the $[\text{Ag}(\text{Tpm}^*)_2]^+$ complexes that showed only six-coordinate sandwich structures and of theoretical studies that showed a barrierless transition from $\kappa^2\text{-Tpm}$ to $\kappa^3\text{-Tpm}$ complexation. Steric bulk and electronic effects may both favor the formation of four-coordinate complexes of the N-tosylated ligands, while stabilization through hydrogen-bonding interactions in the solid state may play an integral role for $[\text{Ag}(\text{H}^*\text{L})_2]^+$ and $[\text{Ag}(\text{H}^*\text{L})_2]^+$. In 1:1 complexes, the bulkiest derivative, T^*L^* , gave a monomeric species, the least bulky derivative, H^*L , gave a polymeric species and the other two ligands of medium steric profiles gave dimeric complexes in the solid state. The ^1H NMR, DOSY NMR, and ESI(+) MS spectral studies indicate that the solid-state structures are not preserved in solution. Rather, all have dynamic solution behavior and are involved in multiple rapid equilibria. The labile nature of silver(I) complexes is expected and allows for the use of silver(I) complexes as effective ligand delivery agents. This property was demonstrated by the preparation of tricarbonylmanganese(I) complexes and **9**, a complex with SCO properties. Also, for the first time, the use of silver(I) C-scorpionates as nitrene-transfer catalysts has been demonstrated by the aziridination of styrene in CH_3CN using H_2NTs and $\text{PhI}(\text{OAc})_2$ as oxidants. The activity of these species is low especially compared to those reported for AgTp^x complexes probably because of the more complex solution behavior of the former, including the possibility for coordination to ions.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.7b02927.

Tables of crystal data and structure refinement details, supramolecular structures, and details of DOSY and other NMR experiments (PDF)

Accession Codes

CCDC 1585684–1585695 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: james.gardinier@marquette.edu.

ORCID

James R. Gardinier: 0000-0001-7554-924X

Author Contributions

All authors have approved the final version of this manuscript.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

J.R.G. thanks Marquette University for support.

■ REFERENCES

- (1) (a) Trofimenko, S. *Scorpionates: The Coordination Chemistry of Polypyrazolylborate Ligands*; Imperial Press: London, 1999. (b) Pettinari, C. *Scorpionates II: Chelating Borate Ligands*; Imperial Press: London, 2008.
- (2) Spicer, M. D.; Reglinski, J. Soft Scorpionate Ligands Based on Imidazole-2-thione Donors. *Eur. J. Inorg. Chem.* **2009**, 12, 1553–1574.
- (3) (a) Alkorta, I.; Claramunt, R. M.; Díez-Barra, E.; Elguero, J.; de la Hoz, A.; Lopez, C. The Organic Chemistry of Poly(1H-pyrazol-1-yl)methanes. *Coord. Chem. Rev.* **2017**, 339, 153–182. (b) Pettinari, C.; Pettinari, R. Metal Derivatives of Poly(pyrazolyl)alkanes: 1. Tris(pyrazolyl)alkanes and related systems. *Coord. Chem. Rev.* **2005**, 249, 525–543. (c) Bigmore, H. R.; Lawrence, S. C.; Mountford, P.; Tredget, C. S. Coordination, organometallic and related chemistry of tris(pyrazolyl)methane ligands. *Dalton Trans.* **2005**, 635–651. (d) Reger, D. L. Tris(pyrazolyl)methane ligands: the neutral analogs of tris(pyrazolyl)borate ligands. *Comments Inorg. Chem.* **1999**, 21, 1–28.
- (4) (a) Kläui, W.; Berghahn, M.; Rheinwald, G.; Lang, H. Tris(pyrazolyl)methanesulfonates: A Novel Class of Water-Soluble Ligands. *Angew. Chem., Int. Ed.* **2000**, 39, 2464–2466. (b) Kläui, W.; Schramm, D.; Peters, W.; Rheinwald, G.; Lang, H. Tris(pyrazolyl)methanesulfonate (Tpms) – A Versatile Alternative to Tris(pyrazolyl)borate in Rhodium(I) Chemistry. *Eur. J. Inorg. Chem.* **2001**, 2001, 1415–1424. (c) Kläui, W.; Berghahn, M.; Frank, W.; Reiß, G. J.; Schönherr, T.; Rheinwald, G.; Lang, H. Tris(pyrazolyl)methanesulfonates: More Than Just Analogues of Tris(pyrazolyl)borate Ligands; N,N,N-, N,N,O-, and Other Coordination Modes. *Eur. J. Inorg. Chem.* **2003**, 2003, 2059–2070. (d) Papish, E. T.; Taylor, M. T.; Jernigan, F. E., 3rd; Rodig, M. J.; Shawhan, R. R.; Yap, G. P. A.; Jove, F. A. Synthesis of zinc, copper, nickel, cobalt, and iron complexes using tris(pyrazolyl)methane sulfonate ligands: a structural model for N,N,O binding in metalloenzymes. *Inorg. Chem.* **2006**, 45, 2242–2250.
- (5) Pettinari, C.; Cingolani, A.; Lobbia, G. G.; Marchetti, F.; Martini, D.; Pellei, M.; Pettinari, R.; Santini, C. Copper and Silver Derivatives of Scorpionates and Related Ligands. *Polyhedron* **2004**, 23, 451–469.
- (6) Other reviews: (a) Caballero, Ana; Mar Díaz-Requejo, M.; Frutos, M. R.; Urbano, Juan; Pérez, P. J. Modern Applications of Trispyrazolylborate Ligands in Coinage Metal Catalysis. In *Ligand Design in Metal Chemistry: Reactivity and Catalysis*; Stradiotto, M., Lundgren, R. J., Eds.; John Wiley & Sons, Ltd.: Chichester, U.K., 2016; pp 308–329; 10.1002/9781118839621.ch11. (b) Pettinari, C.; Pettinari, R.; Marchetti, F. Golden Jubilee for Scorpionates: Recent Advances in Organometallic Chemistry and Their Role in Catalysis. *Adv. Organomet. Chem.* **2016**, 65, 175–260. (c) Caballero, A.; Perez, P. Catalyst design in the alkane C-H bond functionalization of alkanes by carbene insertion with Tp^xM complexes (Tp^x = hydrotrispyrazolylborate ligand; M = Cu, Ag). *J. Organomet. Chem.* **2015**, 793, 108–113. (d) Diaz-Requejo, M. M.; Perez, P. J. Coinage Metal Catalyzed C-H Bond Functionalization of Hydrocarbons. *Chem. Rev.* **2008**, 108, 3379–3394. (e) Diaz-Requejo, M. M.; Perez, P. J. Copper, silver and gold-based catalysts for carbene addition or insertion reactions. *J. Organomet. Chem.* **2005**, 690, 5441–5450.
- (7) Dias, H. V. R.; Browning, R. G.; Polach, S. A.; Diyabalanage, H. V. K.; Lovely, C. J. Activation of Alkyl Halides via a Silver-Catalyzed Carbene Insertion Process. *J. Am. Chem. Soc.* **2003**, 125, 9270–9271.
- (8) Lovely, C. J.; Browning, R. G.; Badarinarayana, V.; Dias, H. V. R. A Silver-Catalyzed Büchner Reaction. *Tetrahedron Lett.* **2005**, 46, 2453–2455.
- (9) Dias, H. V. R.; Browning, R. G.; Richey, S. A.; Lovely, C. J. Silver(I) Scorpionate Mediated Insertion of Carbenes into Aliphatic C-H Bonds. *Organometallics* **2004**, 23, 1200–1202.
- (10) (a) Alvarez, M.; Gava, R.; Rodriguez, M. R.; Rull, S. G.; Perez, P. J. Water as the Reaction Medium for Intermolecular C–H Alkane Functionalization in Micellar Catalysis. *ACS Catal.* **2017**, 7, 3707–3711. (b) Caballero, A.; Despagnet-Ayoub, E.; Mar Díaz-Requejo, M.; Diaz-Rodriguez, A.; Gonzalez-Nunez, M. E.; Mello, R.; Munoz, B. K.; Ojo, W.-S.; Asensio, G.; Etienne, M.; Perez, P. J. Silver-Catalyzed C-C Bond Formation Between Methane and Ethyl Diazoacetate in Supercritical CO_2 . *Science* **2011**, 332, 835–838. (c) Despagnet-Ayoub, E.; Jacob, K.; Vendier, L.; Etienne, M.; Alvarez, E.; Caballero, A.; Diaz-Requejo, M. M.; Perez, P. J. A New Perfluorinated F21-Tp

Scorpionate Ligand: Enhanced Alkane Functionalization by Carbene Insertion with (F21-Tp)M Catalysts (M = Cu, Ag). *Organometallics* **2008**, 27, 4779–4787. (d) Gomez-Emeterio, B. P.; Urbano, J.; Diaz-Requejo, M. M.; Perez, P. J. Easy Alkane Catalytic Functionalization. *Organometallics* **2008**, 27, 4126–4130. (e) Braga, A. A. C.; Maseras, F.; Urbano, J.; Caballero, A.; Diaz-Requejo, M. M.; Perez, P. J. Mechanism of Alkane C-H Bond Activation by Copper and Silver Homoscorpionate Complexes. *Organometallics* **2006**, 25, 5292–5300. (f) Urbano, J.; Belderrain, T. R.; Nicasio, M. C.; Trofimenko, S.; Diaz-Requejo, M. M.; Perez, P. J. Functionalization of Primary Carbon-Hydrogen Bonds of Alkanes by Carbene Insertion with a Silver-Based Catalyst. *Organometallics* **2005**, 24, 1528–1532.

(11) Iglesias, M. J.; Nicasio, M. C.; Caballero, A.; Perez, P. J. Silver-catalyzed silicon-hydrogen bond functionalization by carbene insertion. *Dalton Trans.* **2013**, 42, 1191–1195.

(12) Urbano, J.; Braga, A. A. C.; Maseras, F.; Alvarez, E.; Diaz-Requejo, M. M.; Perez, P. J. The mechanism of the catalytic functionalization of haloalkanes by carbene insertion: an experimental and theoretical study. *Organometallics* **2009**, 28, 5968–5981.

(13) Rivilla, I.; Sameera, W. M. C.; Alvarez, E.; Diaz-Requejo, M. M.; Maseras, F.; Perez, P. J. Catalytic cross-coupling of diazo compounds with coinage metal-based catalysts: an experimental and theoretical study. *Dalton Trans.* **2013**, 42, 4132–4138.

(14) Maestre, L.; Sameera, W. M. C.; Díaz-Requejo, M. M.; Maseras, F.; Pérez, P. J. A general mechanism for the copper- and silver-catalyzed olefin aziridination reactions: Concomitant involvement of the singlet and triplet pathways. *J. Am. Chem. Soc.* **2013**, 135, 1338–1348.

(15) Llavera, J.; Beltrán, A.; Diaz-Requejo, M. M.; Matheu, M. I.; Castillon, S.; Perez, P. J. Efficient Silver-Catalyzed Regio- and Stereospecific Aziridination of Dienes. *Angew. Chem., Int. Ed.* **2010**, 49, 7092–7095.

(16) Beltrán, A.; Lescot, C.; Díaz-Requejo, M. M.; Pérez, P. J.; Dauban, P. Catalytic C-H amination of alkanes with sulfonimidamides: Silver(I)-scorpionates vs. dirhodium(II) carboxylates. *Tetrahedron* **2013**, 69, 4488–4492.

(17) Maestre, L.; Dorel, R.; Pablo, Ó.; Escofet, I.; Sameera, W. M. C.; Álvarez, E.; Maseras, F.; Díaz-Requejo, M. M.; Echavarren, A. M.; Pérez, P. J. Functional group tolerant, Silver-catalyzed N-N bond formation by Nitrene Transfer to amines. *J. Am. Chem. Soc.* **2017**, 139, 2216–2223.

(18) Lam, T. L.; Tso, K. C. – H.; Cao, B.; Yang, C.; Chen, D.; Chang, X. – Y.; Huang, J. – S.; Che, C. – M. Tripodal S-Ligand Complexes of Copper(I) as Catalysts for Alkene Aziridination, Sulfide Sulfimidation and C-H Amidation. *Inorg. Chem.* **2017**, 56, 4253–4257.

(19) Arenas, I.; Fuentes, M. A.; Álvarez, E.; Díaz, Y.; Caballero, A.; Castillón, S.; Pérez, P. J. Syntheses of a Novel Fluorinated Trisphosphinoborate Ligand and Its Copper and Silver Complexes. Catalytic Activity toward Nitrene Transfer Reactions. *Inorg. Chem.* **2014**, 53, 3991–3999.

(20) (a) Smolenski, P.; Pettinari, C.; Marchetti, F.; Guedes da Silva, M. F. C.; Lupidi, G.; Badillo Patzmay, G. V.; Petrelli, D.; Vitali, L. A.; Pombeiro, A. J. L. Syntheses, structures, and antimicrobial activity of new remarkably light-stable and water-soluble tris(pyrazolyl) methanesulfonate silver(I) derivatives of N-methyl-1, 3, 5-triaza-7-phosphaadamantane salt - [mPTA] BF₄. *Inorg. Chem.* **2015**, 54, 434–440. (b) Pettinari, C.; Marchetti, F.; Lupidi, G.; Quassinti, L.; Bramucci, M.; Petrelli, D.; Vitali, L. A.; Guedes da Silva, M. F. C.; Martins, L. M. D. R. S.; Smolenski, P.; Pombeiro, A. J. L. Synthesis, Antimicrobial and Antiproliferative Activity of Novel Silver(I) Tris(pyrazolyl)methanesulfonate and 1, 3, 5-Triaza-7-phosphadaman-tane Complexes. *Inorg. Chem.* **2011**, 50, 11173–11183.

(21) Cingolani, A.; Effendy; Martini, D.; Pellei, M.; Pettinari, C.; Skelton, B. W.; White, A. H. Silver Derivatives of Tris(pyrazol-yl)methanes. A silver(I) nitrate complex containing tris(pyrazol-yl)methane coordinated in a bridging mode. *Inorg. Chim. Acta* **2002**, 328, 87–95.

(22) (a) Reger, D. L.; Collins, J. E.; Rheingold, A. L.; Liable-Sands, L. M.; Yap, G. P. A. Syntheses and Characterization of cationic (Tris(pyrazolyl)methane)Silver(I) Complexes. Solid State Structures

of {[HC(3,5-Me₂pz)₃]₂Ag}(O₃SCF₃), {[HC(3Bu^tpz)₃]₂Ag}-(O₃SCF₃), and {[HC(3Bu^tpz)₃]₂Ag(CNBut¹)}(O₃SCF₃). *Organometallics* **1997**, 16, 349–353. (b) Reger, D. L.; Semeniuc, R. F.; Smith, M. D. Influence of the Crystallization Solvent on Molecular and Supramolecular Structures of Silver(I) Tris(3-Phenylpyrazolyl)-methane Complexes. *Eur. J. Inorg. Chem.* **2003**, 2003, 3480–3494. (c) Semeniuc, R. F.; Reger, D. L. Metal Complexes of Multitopic, Third Generation Poly(pyrazolyl)-methane Ligands: Multiple Coordination Arrangements. *Eur. J. Inorg. Chem.* **2016**, 2016, 2253–2271.

(23) Hückel, W.; Chneider, H. B. N-Tripyrazolyl-methan. *Ber. Dtsch. Chem. Ges. B* **1937**, 70, 2024–2026.

(24) Julia, S.; del Mazo, J.; Avila, L.; Elguero, J. Improved Synthesis Of Polyazolylmethanes Under Solid-Liquid Phase-Transfer Catalysis. *Org. Prep. Proced. Int.* **1984**, 16, 299–307.

(25) Reger, D. L.; Grattan, T. C.; Brown, K. J.; Little, C. A.; Lamba, J. J. S.; Rheingold, A. L.; Sommer, R. D. Syntheses of tris(pyrazolyl)-methane ligands and {[tris(pyrazolyl)methane]Mn(CO)₃}SO₃CF₃ complexes: Comparison of Ligand Donor Properties. *J. Organomet. Chem.* **2000**, 607, 120–128.

(26) Li, Z.; Capretto, D. A.; He, C. Silver-Mediated Oxidation Reactions: Recent Advances and New Prospects. *Prog. Inorg. Chem.* **2009**, 56, 1–48. (b) Li, Z.; Capretto, D. A.; Rahaman, R.; He, C. Silver-Catalyzed Intermolecular Amination of C-H Groups. *Angew. Chem., Int. Ed.* **2007**, 46, 5184–5186. (c) Li, Z.; He, C. Recent Advances in Silver-Catalyzed Nitrene, Carbene, and Silylene-Transfer Reactions. *Eur. J. Org. Chem.* **2006**, 2006, 4313–4322. (d) Cui, Y.; He, C. A Silver-Catalyzed Intramolecular Amidation of Saturated C-H Bonds. *Angew. Chem., Int. Ed.* **2004**, 43, 4210–4212. (e) Cui, Y.; He, C. Efficient Aziridination of Olefins Catalyzed by a Unique Disilver(I) Compound. *J. Am. Chem. Soc.* **2003**, 125, 16202–16203.

(27) (a) Yang, M.; Su, B.; Wang, Y.; Chen, K.; Jiang, X.; Zhang, Y. – F.; Zhang, X. – S.; Chen, G.; Cheng, Y.; Cao, Z.; Guo, Q. – Y.; Wang, L.; Shi, Z. – J. Silver-Catalyzed Direct Amination of Unactivated C-H Bonds of Functionalized Molecules. *Nat. Commun.* **2014**, 5, 4707. (b) Zhang, X. Mechanistic Study on Silver-catalyzed Direct Amination of Unactivated C-H Bond. *J. Organomet. Chem.* **2017**, 832, 1–8.

(28) (a) Corbin, J. R.; Schomaker, J. M. Tunable differentiation of tertiary C-H bonds in intramolecular transition metal-catalyzed nitrene transfer reactions. *Chem. Commun.* **2017**, 53, 4346–4349. (b) Alderson, J. M.; Corbin, J. R.; Schomaker, J. M. Tunable, Chemo- and Site Selective Nitrene Transfer Reactions through the Rational Design of Silver(I) Catalysts. *Acc. Chem. Res.* **2017**, 50, 2147–2158. (c) Weatherly, C. D.; Alderson, J. M.; Berry, J. F.; Hein, J.; Schomaker, J. M. Catalyst-Controlled Nitrene Transfer by Tuning Metal:Ligand Ratios: Insight into the Mechanisms of Chemoselectivity. *Organometallics* **2017**, 36, 1649–1661. (d) Huang, M.; Corbin, J. R.; Dolan, N. S.; Fry, C. G.; Vinokur, A. A.; Guzei, I. A.; Schomaker, J. M. Synthesis, Characterization, and Variable Temperature NMR Studies of Silver(I) Complexes for Selective Nitrene Transfer. *Inorg. Chem.* **2017**, 56, 6725–6733. (e) Dolan, N. S.; Scamp, R. J.; Yang, T.; Berry, J. F.; Schomaker, J. M. Catalyst-Controlled and Tunable, Chemoselective Silver-Catalyzed Intermolecular Nitrene Transfer: Experimental and Computational Studies. *J. Am. Chem. Soc.* **2016**, 138, 14658–14667. (f) Scamp, R. J.; Jirak, J. G.; Dolan, N. S.; Guzei, I. A.; Schomaker, J. M. A General Catalyst for Site-Selective C(sp³)-H Bond Amination of Activated Secondary over Tertiary Alkyl C(sp³)-H Bonds. *Org. Lett.* **2016**, 18, 3014–3017. (g) Rigoli, J. W.; Weatherly, C. D.; Alderson, J. M.; Vo, B. T.; Schomaker, J. M. Tunable, Chemoselective Amination via Silver Catalysis. *J. Am. Chem. Soc.* **2013**, 135, 17238–17241.

(29) (a) Martins, L. M. D. R. S. C-Homoscorpionate Oxidation Catalysts- Electrochemical and Catalytic Activity. *Catalysts* **2017**, 7, 12. (b) Wathier, M.; Love, J. A. Hydroelementation of unsaturated C-C bonds Catalyzed by Metal Scorpionate Complexes. *Eur. J. Inorg. Chem.* **2016**, 2016, 2391–2402.

(30) Liang, S.; Jensen, M. P. Half Sandwich scorpionates as nitrene transfer catalysts. *Organometallics* **2012**, 31, 8055–8088.

(31) Gardinier, J. R.; Treleven, A. R.; Meise, K. J.; Lindeman, S. V. Accessing Spin-Crossover Behaviour in Iron(II) complexes of N-Confused Scorpionate Ligands. *Dalton Trans.* **2016**, 45, 12639–12643.

- (32) Carrión, M. C.; Jalon, F. A.; Manzano, B. R.; Rodríguez, A. M.; Sepúlveda, F.; Maestro, M. (Arene)ruthenium(II) Complexes Containing Substituted Bis(pyrazolyl)methane Ligands – Catalytic Behaviour in Transfer Hydrogenation of Ketones. *Eur. J. Inorg. Chem.* **2007**, 2007, 3961–3973.
- (33) (a) Evans, D. F. The determination of the paramagnetic susceptibility of substances in solution by nuclear magnetic resonance. *J. Chem. Soc.* **1959**, 2003–2005. (b) Evans, D. F.; Fazakerley, G. V.; Phillips, R. F. Organometallic compounds of bivalent europium, ytterbium, and samarium. *J. Chem. Soc. A* **1971**, 1931–1934. (c) Piguet, C. Paramagnetic Susceptibility by NMR: The “Solvent Correction” Removed for Large Paramagnetic Molecules. *J. Chem. Educ.* **1997**, 74, 815–816.
- (34) Morrison, G.; zur Loye, H.-C. Simple correction for the sample shape and radial offset effects on SQUID magnetometers: Magnetic measurements on Ln_2O_3 ($\text{Ln}=\text{Gd}$, Dy , Er) standards. *J. Solid State Chem.* **2015**, 221, 334–337.
- (35) Bain, G. A.; Berry, J. F. Diamagnetic Corrections and Pascal’s Constants. *J. Chem. Educ.* **2008**, 85, 532–536.
- (36) Ozawa, T.; Kurahashi, T.; Matsubara, S. [3 + 2] Cycloaddition of Aziridines and Alkenes Catalyzed by a Cationic Manganese Porphyrin. *Synlett* **2013**, 24, 2763–2767.
- (37) Agilent Technologies. *CrysAlisPro*, version 1.171.34.46 (release 25-11-2010 CrysAlis171.NET; compiled Nov 25, 2010, 17:55:46).
- (38) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* **2009**, 42, 339–341.
- (39) Sheldrick, G. M. *SHELXTL*, version 6.12; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 2001.
- (40) (a) The, K. I.; Peterson, L. K. Synthesis And Characterization Of Dipyrazolylalkanes, And Some Of Their Complexes With Cobalt(II) Chloride. *Can. J. Chem.* **1973**, 51, 422–426. (b) The, K. I.; Peterson, L. K.; Kiehlmann, E. Preparation Of 1,1'-Carbonyl- And 1,1'-Sulfinyldipyrazoles And Their Reactions With Carbonyl Compounds. *Can. J. Chem.* **1973**, 51, 2448–2451. (c) Peterson, L. K.; Kiehlmann, E.; Sanger, A. R.; The, K. I. Mechanism of The Transition Metal-Catalyzed Reaction Of 1,1'-Carbonyldipyrazoles With Aldehydes And Ketones. *Can. J. Chem.* **1974**, 52, 2367–2374.
- (41) Gowda, B. T.; Jyothi, K.; D'Souza, J. D. Infrared and NMR Spectra of Arylsulphonamides, 4-X-C₆H₄SO₂NH₂ and i-X, j-YC₆H₃SO₂NH₂ (X = H; CH₃; C₂H₅; F; Cl; Br; I or NO₂ and i-X, j-Y = 2,3-(CH₃)₂; 2,4-(CH₃)₂; 2,5-(CH₃)₂; 2-CH₃, 4-Cl; 2-CH₃, 5-Cl; 3-CH₃, 4-Cl; 2,4-Cl₂ or 3,4-Cl₂). *Z. Naturforsch., A: Phys. Sci.* **2002**, 57, 967–973.
- (42) Liddle, B. J.; Hall, D.; Lindeman, S. V.; Smith, M. D.; Gardinier, J. R. Manipulating Self-assembly in Silver(I) Complexes of 1,3-Di(N-pyrazolyl)organyls. *Inorg. Chem.* **2009**, 48, 8404–8414.
- (43) Reger, D. L.; Semeniuc, R. F.; Little, C. A.; Smith, M. D. Crystal Retro-Engineering: Structural Impact on Silver(I) Complexes with Changing Complexity of Tris(pyrazolyl)methane Ligands. *Inorg. Chem.* **2006**, 45, 7758–7769.
- (44) Pilar Carranza, M.; Manzano, B. R.; Jalón, F.; Rodríguez, A. M.; Santos, L.; Moreno, M. Experimental and Theoretical Evidence of Unsupported Ag-Ag Interactions in Complexes with Triazine-based ligands. Subtle Effects of the Symmetry of the triazine Substituents. *New J. Chem.* **2013**, 37, 3183–3194.
- (45) Wen, M.; Munakata, M.; Suenaga, Y.; Kuroda-Sowa, T.; Maekawa, M.; Kodai, I. Dinuclear silver(I) complexes of N, N-dibenzyl-4,13-diaza-18-crown-6-ether and dibenzo-24-crown-8-ether. *Polyhedron* **2004**, 23, 2117–2123.
- (46) Reineke, M. H.; Sampson, M. D.; Rheingold, A. L.; Kubiak, C. P. Synthesis and Structural Studies of Nickel(0) Tetracarbene Complexes with the Introduction of a New Four-Coordinate Geometric Index, τ_8 . *Inorg. Chem.* **2015**, 54, 3211–3217.
- (47) Gardinier, J. R.; Hewage, J. S.; Lindeman, S. V. Isomer Dependence in the Assembly and Lability of Silver(I) Trifluoromethanesulfonate Complexes of the Heteroditopic Ligands 2-, 3-, and 4-[di(1H-pyrazolyl)methyl]phenyl(di-p-tolyl)phosphine. *Inorg. Chem.* **2014**, 53, 12108–12121.
- (48) Davis, T. L.; Watts, J. L.; Brown, K. J.; Hewage, J. S.; Treleven, A. R.; Lindeman, S. V.; Gardinier, J. R. Structural Classification of Metal Complexes with Three-Coordinate Centres. *Dalton Trans.* **2015**, 44, 15408–15412.
- (49) (a) Casarin, M.; Forrer, D.; Garau, F.; Pandolfo, L.; Pettinari, C.; Vittadini, A. Tris(pyrazol-1-yl)borate and Tris(pyrazol-1-yl)-methane: A DFT study of their different Binding Capability toward Ag(I) and Cu(I) cations. *Inorg. Chim. Acta* **2009**, 362, 4358–4364. (b) Casarin, M.; Forrer, D.; Garau, F.; Pandolfo, L.; Pettinari, C.; Vittadini, A. Density Functional Theory Study of the Binding Capability of Tris(Pyrazol-1-yl)methane Toward Cu(I) and Ag(I) Cations. *J. Phys. Chem. A* **2008**, 112, 6723–6731.
- (50) (a) Grochala, W.; Cyranski, M. K.; Derzsi, M.; Michalowski, T.; Malinowski, P. J.; Mazej, Z.; Kurzydowski, D.; Kozminski, W.; Budzianowski, A.; Leszczynski. Crystal and electronic structure, lattice dynamics and thermal properties of Ag(I)(SO₃)R (R = F, CF₃) Lewis acids in the solid state. *Dalton Trans.* **2012**, 41, 2034–2047. (b) Johnston, D. H.; Shriver, D. F. Vibrational Study of the Trifluoromethanesulfonate Anion: Unambiguous Assignment of the Asymmetric Stretching modes. *Inorg. Chem.* **1993**, 32, 1045–1047. (c) Lawrence, G. A. Coordinated Trifluoromethanesulfonate and Fluorosulfate. *Chem. Rev.* **1986**, 86, 17–33.
- (51) (a) Camp, A. M.; Kita, M. R.; Grajeda, J.; White, P. S.; Dickie, D. A.; Miller, A. J. M. Mapping the Binding Modes of Hemilabile Pincer–Crown Ether Ligands in Solution Using Diamagnetic Anisotropic Effects on NMR Chemical Shift. *Inorg. Chem.* **2017**, 56, 11141–11150. (b) Aldrich, K. E.; Billow, B. S.; Holmes, D.; Bemowski, R. D.; Odom, A. L. Weakly Coordinating yet Ion Paired: Anion Effects on an Internal Rearrangement. *Organometallics* **2017**, 36, 1227–1237. (c) Ward, W. M.; Farnum, B. H.; Siegler, M.; Meyer, G. J. Chloride Ion-Pairing with Ru(II) Polypyridyl Compounds in Dichloromethane. *J. Phys. Chem. A* **2013**, 117, 8883–8894. (d) Ammer, J.; Nolte, C.; Karaghiosoff, K.; Thallmair, S.; Mayer, P.; de Vivie-Riedle, R.; Mayr, H. Ion-pairing of phosphonium salts in solution: C-H...halogen and C-H... π hydrogen bonds. *Chem. - Eur. J.* **2013**, 19, 14612–14630. (e) Kleinpeter, E.; Koch, A.; Sahoo, H. S.; Chand, D. K. *Tetrahedron* **2008**, 64, 5044–5050. (f) Sahoo, H. S.; Chand, D. K.; Mahalakshmi, S.; Hedayetullah Mir, M.; Raghunathan, R. Manifestation of diamagnetic chemical shifts of proton NMR signals by an anisotropic shielding effect of nitrate anions. *Tetrahedron Lett.* **2007**, 48, 761–765. (g) Macchioni, A. Ion-Pairing in Transition Metal Chemistry. *Chem. Rev.* **2005**, 105, 2039–2073. (h) La Mar, G. N. Isotropic Shifts of Some Ionic Complexes of Cobalt(II) and Nickel(II): Evidence for Ion Pairing. *J. Chem. Phys.* **1964**, 41, 2992.
- (52) (a) Miras, H. N.; Wilson, E. F.; Cronin, L. Unravelling the complexities of inorganic and supramolecular self-assembly in solution with electrospray and cryospray mass spectrometry. *Chem. Commun.* **2009**, 1297–1311. (b) Baytekin, B.; Baytekin, H. T.; Schalley, C. A. Mass spectrometric studies of non-covalent compounds: why supramolecular chemistry in the gas phase? *Org. Biomol. Chem.* **2006**, 4, 2825.
- (53) (a) Banerjee, S.; Mazumdar, S. Electrospray Ionization Mass Spectrometry: A Technique to Access the Information Beyond the Molecular Weight of the Analyte. *Int. J. Anal. Chem.* **2012**, 2012, 1. (b) Schalley, C. A. Molecular Recognition and Supramolecular Chemistry in the Gas Phase. *Mass Spectrom. Rev.* **2001**, 20, 253–309. (c) Loo, J. A. Electrospray Ionization Mass Spectrometry: A Technology for Studying Noncovalent Macromolecular Complexes. *Int. J. Mass Spectrom.* **2000**, 200, 175–186. (d) Smith, R. D.; Light-Wahl, K. J. The Observation of Non-covalent Interactions in solution by Electrospray Ionization Mass Spectrometry: Promises, Pitfalls and Prognosis. *Biol. Mass Spectrom.* **1993**, 22, 493–501. (e) Su, C. – Y.; Cai, Y.-P.; Chen, C. – L.; Smith, M. D.; Kaim, W.; zur Loye, H. C. *J. Am. Chem. Soc.* **2003**, 125, 8595–8613.
- (54) (a) Reger, D. L.; Watson, R. P.; Gardinier, J. R.; Smith, M. D. Impact of Variations in Design of Flexible Bitopic Bis(pyrazolyl)-methane Ligands and Counterions on the Structures of Silver(I) Complexes: Dominance of Cyclic Dimeric Architecture. *Inorg. Chem.* **2004**, 43, 6609–6619. (b) Reger, D. L.; Gardinier, J. R.; Semeniuc, R.

F.; Smith, M. D. Silver complexes of 1,1',3,3'-tetrakis(pyrazol-1-yl)propane: the "quadruple pyrazolyl embrace" as a supramolecular synthon. *J. Chem. Soc., Dalton Trans.* **2003**, 1712–1718. (c) Reger, D. L.; Gardinier, J. R.; Christian Grattan, T.; Smith, M. R.; Smith, M. D. Synthesis of the silver(I) complex of $\text{CH}_2[\text{CH}(\text{pz}^{4\text{Et}})_2]_2$ containing the unprecedented $[\text{Ag}(\text{NO}_3)_4]^{5-}$ anion: A general method for the preparation of 4-(alkyl)pyrazoles. *New J. Chem.* **2003**, 27, 1670–1677. (d) Reger, D. L.; Foley, E. A.; Semeniuc, R. F.; Smith, M. D. Structural Comparisons of Silver(I) Complexes of Third- Generation Ligands Built from Tridentate (o- $\text{C}_6\text{H}_4[\text{CH}_2\text{OCH}_2\text{C}(\text{pz})_3]_2$) versus Bidentate Poly(1- pyrazolyl) methane Units (o- $\text{C}_6\text{H}_4[\text{CH}_2\text{OCH}_2\text{CH}(\text{pz})_2]_2$) (pz = Pyrazolyl Ring). *Inorg. Chem.* **2007**, 46, 11345–11355. (e) Reger, D. L.; Semeniuc, R. F.; Rassolov, V.; Smith, M. D. Supramolecular Structural Variations with Changes in Anion and Solvent in Silver(I) Complexes of a Semirigid, Bitopic Tris(pyrazolyl) methane Ligand. *Inorg. Chem.* **2004**, 43, 537–554.

(55) (a) Reger, D. L.; Gardinier, J. R.; Smith, M. D. Tuning the Coordination Geometry of Silver in Bis(pyrazolyl)alkane Complexes. *Inorg. Chem.* **2004**, 43, 3825–3832. (b) Reger, D. L.; Foley, E. A.; Smith, M. D. Mononuclear Metallacyclic Silver(I) Complexes of Third Generation Bis(1-pyrazolyl)methane Ligands. *Inorg. Chem.* **2009**, 48, 936–945. (c) Reger, D. L.; Watson, R. P.; Smith, M. D. Silver(I) complexes of fixed, polytopic bis(pyrazolyl)methane ligands: influence of ligand geometry on the formation of discrete metallacycles and coordination polymers. *Inorg. Chem.* **2006**, 45, 10077–10087.

(56) Reger, D. L.; Gardinier, J. R.; Grattan, T. J.; Smith, M. D. Tricarbonylmanganese(I) derivatives of $[\text{Di}(\text{pyrazolyl})(2\text{-pyridyl-methyl})\text{aryl Scorpionates}]$. *J. Organomet. Chem.* **2005**, 690, 1901–1912.

(57) (a) Niesel, J.; Pinto, A.; Peindy N'Dongo, H. W.; Merz, K.; Ott, I.; Gust, R.; Schatzschneider, U. Photoinduced CO release, cellular uptake and cytotoxicity of a tris(pyrazolyl)methane (tpm) manganese tricarbonyl complex. *Chem. Commun.* **2008**, 0, 1798–1800. (b) Pfeiffer, H.; Rojas, A.; Niesel, J.; Schatzschneider, U. Sonogashira and "Click" reactions for the N-terminal and side-chain functionalization of peptides with $[\text{Mn}(\text{CO})_3(\text{tpm})]^+$ -based CO releasing molecules (tpm = tris(pyrazolyl)methane). *Dalton Trans.* **2009**, 4292–4298. (c) Pai, S.; Hafflang, M.; Atongo, G.; Nagel, C.; Niesel, J.; Botov, S.; Schmalz, H.-G.; Yard, B.; Schatzschneider, U. New modular manganese(I) tricarbonyl complexes as PhotoCORMs: in vitro detection of photoinduced carbon monoxide release using COP-1 as a fluorogenic switch-on probe. *Dalton Trans.* **2014**, 43, 8664–8678.

(58) Feng, J. – J.; Zhang, J. Synthesis of Unsaturated N-Heterocycles by Cycloadditions of Aziridines and Alkynes. *ACS Catal.* **2016**, 6, 6651–6661. (b) Wender, P. A.; Strand, D. Cyclocarboamination of Alkynes with Aziridines: Synthesis of 2,3-Dihydropyrroles by a Catalyzed Formal $[3 + 2]$ Cycloaddition. *J. Am. Chem. Soc.* **2009**, 131, 7528–7529.

(59) Maeda, R.; Ishibashi, R.; Kamaishi, R.; Hirota, K.; Furuno, H.; Hanamoto, T. AgSbF₆-Promoted Cycloaddition Reaction of 2-Trifluoromethyl-N-Tosylaziridine with Aldehydes. *Org. Lett.* **2011**, 13, 6240–6243.

(60) Kaicharla, T.; Jacob, A.; Gonnade, R. G.; Biju, A. T. AgOTf-Catalyzed dehydrative $[3 + 2]$ Annulation of Aziridines with 2-Naphthols. *Chem. Commun.* **2017**, 53, 8219–8222.

(61) (a) Blake, A. J.; Radek, C.; Schröder, M. Tetra(n-butyl)-ammonium Trifluoromethanesulfonate. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1993**, 49, 1652–1654. (b) Leclercq, L.; Suisse, I.; Nowogrocki, G.; Agbossou-Niedercorn, F. On the solid state inclusion of tetrabutylammonium cation in the imidazolium/trifluoromethanesulfonate H-bonds network observed in ionic co-crystals. *J. Mol. Struct.* **2008**, 892, 433–437.