Supramolecular networks of silver(I) and iron(II) complexes of the third generation tris(pyrazolyl)methane ligand $Ph_2(O)POCH_2C(pz)_3$ (pz = pyrazolyl ring)†

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The new ligand $Ph_2(O)POCH_2C(pz)_3$ (pz = pyrazolyl ring), prepared from the reaction of $HOCH_2C(pz)_3$ and $Ph_2P(O)Cl$ in the presence of base, reacts with either $AgBF_4$ or $Fe(BF_4)_2\cdot 6H_2O$ in a 2/1 molar ratio to yield $\{[Ph_2(O)POCH_2C(pz)_3]_2Ag\}(BF_4)$ (**1**) and $\{[Ph_2(O)POCH_2C(pz)_3]_2Fe\}(BF_4)_2$ (**4**), respectively. In the structure of **1**, the silver is in an unusual planar geometry with each of the ligands in a κ^2–κ^0 coordination mode. Slow evaporation of a thf solution of **1** yields crystalline $[Ph_2(O)POCH_2C(pz)_3Ag]_2(thf)_2\}(BF_4)_2$ (**2**). In each cationic unit of **2**, the two $Ph_2(O)POCH_2C(pz)_3$ ligands coordinate to the same two silver(I) centers in a κ^2–κ^1 bonding mode, with a silver atom separation of 3.36 Å. The supramolecular structure of both **1** and **2** is dominated by a pair of cooperative hydrogen bonding interactions between the $Ph_2P(O)$ secondary tecton and a hydrogen atom from a methylene group situated on a neighboring building block, which arranges the cations in chains. The reaction of $HC(pz)_3$ and AgO_3SCF_3 (AgOTf) yields $\{[HC(pz)_3]_2Ag_2\}(OTf)_2$ (**3**). The cationic unit in **3** has a structure very similar to that of **2**, but with a much shorter distance between the silver atoms at 2.86 Å. The supramolecular structure of **3** is dominated by an unusual pyrazolyl embrace interaction where the acceptor ring in the C–H $\cdots$ π interaction is the pyrazolyl ring κ^1-bonded to silver in the adjacent dimeric unit rather than the other ring in a κ^2-bonded Cpz_2 unit. This interaction arranges the cations in chains which are further organized into sheets by the triflate anions that link the chains *via* combined Ag $\cdots$ O/CH $\cdots$ O interactions. The iron in **4** is octahedral with each tris(pyrazolyl)methane unit in the κ^3-tripodal coordination mode. The supramolecular structure is sheets formed by hydrogen bonding between the $Ph_2P(O)$ oxygen and a *meta*-position hydrogen on one of the diphenylphosphine rings from an adjacent cation.

Introduction

Crystal engineering is a topic of intense research interest that holds promise for revolutionizing materials design and synthesis.[1] An essential step along the path to predicting solid structures based on specific substituent groups in a chemical species of interest is to more clearly elucidate the factors that govern the noncovalent assembly of molecules or ions into their ultimate solid state architectures. Remarkable strides have been made with both common organic and inorganic systems, as has been the subject of several reviews.[1] Our research focuses on the syntheses and supramolecular aspects of the metal complexes of the ubiquitous scorpionate ligands, first introduced by Trofimenko 40 years ago.[2] We have developed synthetic routes to controllably impart substitution at the scorpionate "backbone," ligands we have termed "third generation," an advancement that is essential for further probing the role of noncovalent forces on supramolecular organization involving these ligands.[3] Of note is the synthesis of the alcohol-appended derivative $HOCH_2C(pz)_3$ that has allowed the preparation of the multitopic $C_6H_{6-n}[CH_2OCH_2C(pz)_3]_n$ ($n = 2$, 3, 4 and 6, pz = pyrazolyl ring) family of semirigid, third generation ligands[3] as well as other types[4] of systems. Metal complexes of these ligands have remarkable topologies that maximize noncovalent interactions of the groups in the ligand backbone. This family of ligands is "structurally adaptive" because they are ideal candidates for studying the self-assembly process and the various factors that might have an influence over such processes.[3i,f,5]

We desire to expand this chemistry in order to develop new types of metal-containing systems. Our approach to the synthesis of such species is, among others, to replace the hydrogen atom from tris(pyrazolyl)ethanol[3l] with either a secondary donor system (SDS) or a secondary tecton (ST), as shown in Scheme 1, that has either coordination properties very different from the tris(pyrazolyl)methane units or has different supramolecular interactions than the HO-group on the backbone of the ligand, respectively.

Reported here is the synthesis and coordination chemistry of $Ph_2(O)POCH_2C(pz)_3$, a ligand with an imbedded bulky, secondary tecton that is also capable of being an acceptor in hydrogen bonding interactions. In this chemistry with silver(I), we observe the formation of unusual dimers with Ag $\cdots$ Ag interactions when the new compounds are crystallized in the presence of oxygen donors. We have previously communicated some of these results.[6,7]

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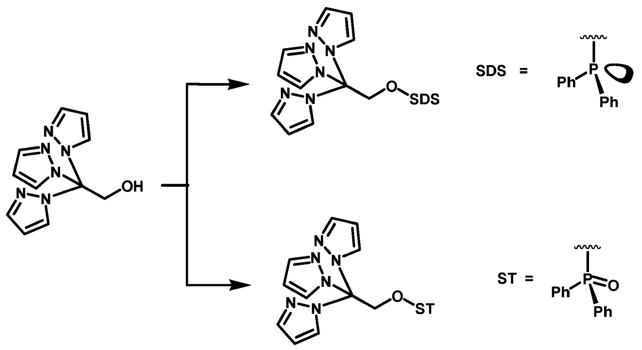


Scheme 1 Synthetic strategy toward functionalized tris(pyrazolyl)-methane ligands: replacement of the hydrogen atom with a secondary donor set (SDS) or with a secondary tecton (ST).

Experimental

General considerations

All operations were carried out under a nitrogen atmosphere using either standard Schlenk techniques or a dry box. All solvents were dried, degassed and distilled prior to use. $AgBF_4$, AgO_3SCF_3 (AgOTf) and $Fe(BF_4)_2{\cdot}6H_2O$ were purchased from Aldrich. Elemental analyses were performed by Robertson Microlit Laboratories (Madison, NJ). Tris(1-pyrazolyl)methane, $HC(pz)_3$, and tris-2,2,2-(1-pyrazoyl)ethanol, $HOCH_2C(pz)_3$, were prepared following literature methods.[31]

Preparation of $Ph_2(O)POCH_2C(pz)_3$. To a stirred solution of tris(pyrazolyl)ethanol, $HOCH_2C(pz)_3$, (2.44 g, 0.010 mol) in dry toluene (75 mL) was added an excess of triethylamine (5 mL) and a solution of chlorodiphenylphosphine oxide (2.36 g, 0.010 mol) in dry toluene (50 mL). The mixture was stirred for two hours, the precipitate filtered, the organic layer washed with water (3 × 100 mL) and then removed to afford the ligand as a white powder (3.86 g, 87%): MP 114–116°C; ^1H NMR (400 MHz, acetone-d_6): 7.70–7.46 (m, 16 H, 3,5-H *pz* and *Ph*), 6.41 (dd, 3 H, J = 1.5, J = 2.1 Hz, 4-H *pz*), 5.49 (d, 2H, J_{PH} = 4.5 Hz, $OCH_2C(pz)_3$); ^{31}P NMR (acetone-d_6): 32.59; ESI$^+$/MS: $[C_{23}H_{21}N_6O_2P + H^+]$ Calcd. 445.1542; Found 445.1534.

Preparation of $\{[Ph_2(O)POCH_2C(pz)_3]_2Ag\}(BF_4)$ (1). $AgBF_4$ (0.097 g, 0.50 mmol) was dissolved in thf (15 mL). With vigorous stirring, a solution of $Ph_2(O)POCH_2C(pz)_3$ (0.444 g, 10 mmol) in thf (20 mL) was added dropwise *via* a syringe during a 10 min. period. The solution became cloudy and the mixture was stirred for an additional 3 h. To promote complete precipitation, hexanes were added (150 mL) and the flask was kept at −20° for two hours. The cold thf/hexanes solution was removed by cannula filtration, the white precipitate washed with cold hexanes (2 × 10 mL) and then vacuum dried to afford 0.487 g (93%) of 1 as a white solid. ^1H NMR (300 MHz, acetone-d_6): 7.94, 7.86 (d, d, J = 2.7, J = 1.6 Hz, 6H, 6H, 3,5-H *pz*), 7.71–7.45 (m, 20 H, *Ph*), 6.60 (dd, 6 H, J = 1.6, J = 2.7 Hz, 4-H *pz*), 5.70 (d, 4H, J_{PH} = 5.2 Hz, $OCH_2C(pz)_3$); ^{31}P NMR (acetone-d_6): 36.27; Calcd. for $C_{46}H_{42}AgBF_4N_{12}O_4P_2$: C, 50.99; H, 3.91; N, 15.51; Found C, 50.62; H, 3.95; N, 15.25.

Crystallization procedure for $\{[Ph_2(O)POCH_2C(pz)_3Ag]_2(THF)_2\}$ $(BF_4)_2$ (2). A 100 mg portion of **1** was dissolved in thf (*ca.* 50 mL) and the beaker covered with aluminum foil. Colorless crystals formed after two days, which were filtered to yield 0.060 g of crystalline material. ^1H NMR (300 MHz, acetone-d_6): 7.96, 7.85 (d, d, J = 2.7, J = 1.6 Hz, 6H, 6H, 3,5-H *pz*), 7.72–7.49 (m, 20 H, *Ph*), 6.58 (dd, 6 H, J = 1.6, J = 2.7 Hz, 4-H *pz*), 5.73 (d, 4H, J_{PH} = 5.2 Hz, $OCH_2C(pz)_3$), 3.64–3.60 (m, 8H, CH_2O, THF), 1.80–1.76 (m, 8H, CH_2, THF); ^{31}P NMR (acetone-d_6): 35.07; Calcd. for $C_{54}H_{58}Ag_2B_2F_8N_{12}O_6P_2$: C, 45.60; H, 4.11; N, 11.82; Found C, 45.95; H, 3.95; N, 12.25.

Preparation of $\{[HC(pz)_3]_2Ag_2\}(OTf)_2$ (3). A thf (20 mL) solution of $HC(pz)_3$, (0.214 g, 1.0 mmol) was added dropwise to a solution of AgOTf (0.256 g, 1.0 mmol) in dry thf (20 mL) under an inert atmosphere. A white precipitate appeared as the mixture was stirred for 2 h. The thf was removed by cannula filtration, the white precipitate was washed with thf (2 × 10 mL) and then vacuum dried to afford 0.392 g (83%) of solid identified as $\{[HC(pz)_3]_2Ag_2\}(OTf)_2$. ^1H NMR (acetone-d_6): δ 9.30 (s, 2H, $HC(pz)_3$), 8.24, 7.85 (s, s, 6H, 6H, 3,5-H *pz*), 6.54 (s, 6H, 4-H *pz*); Calcd. For $C_{22}H_{20}Ag_2F_6N_{12}O_6S_2$: C, 28.04; H, 2.14; N, 17.84; Found C, 28.12; H, 2.53, N, 17.44.

Preparation of $\{[Ph_2(O)POCH_2C(pz)_3]_2Fe\}(BF_4)_2$ (4). $Fe(BF_4)_2{\cdot}6H_2O$ (0.168 g, 0.50 mmol) was dissolved in thf (20 mL). A solution of $Ph_2(O)POCH_2C(pz)_3$ (0.444 g, 1.0 mmol) in thf (20 mL) was added dropwise. A purple precipitate formed and the solution was stirred for an additional 10 minutes. The solvent was removed by cannula filtration, the precipitate washed with thf (2 × 10 mL) and then vacuum dried to afford 0.532 g (87%) of **4** as a purple solid. ^1H NMR (300 MHz, acetone-d_6): 7.94, 7.86 (d, d, J = 2.7, J = 1.6 Hz, 6H, 6H, 3,5-H *pz*), 7.71–7.45 (m, 20 H, *Ph*), 6.60 (dd, 6 H, J = 1.6, J = 2.7 Hz, 4-H *pz*), 5.70 (d, 4H, J_{PH} = 5.2 Hz, $OCH_2C(pz)_3$); ^{31}P NMR (acetone-d_6): 36.27; Calcd. for $C_{46}H_{42}B_2F_8FeN_{12}O_4P_2$: C, 49.40; H, 3.79; N, 15.03; Found C, 48.99 H, 3.99; N, 15.25.

Crystallography

X-Ray intensity data for **1**–**4**$\cdot 2C_3H_6O$ were measured at 150 K on a Bruker SMART APEX CCD-based diffractometer (Mo Kα radiation, λ = 0.71073 Å).[8] The raw data frames were processed with SAINT+.[8] The reported unit cell parameters were determined by least-squares refinement of >5000 reflections from the respective data sets. Analyses showed negligible crystal decay during collections and the data were not corrected for absorption. Direct methods structure solutions, difference Fourier calculations and full-matrix least-squares refinements against F^2 were performed with SHELXTL.[9] All non-hydrogen atoms were refined with anisotropic displacement parameters and all hydrogen atoms were placed in geometrically idealized positions and included as riding atoms. Notes regarding the structure solution and refinement for each structure are collected below and the numerical results are given in Table 1.

Compound **1** crystallizes in the triclinic system. The space group $P\bar{1}$ was assumed and confirmed by the successful solution and refinement of the data. The $\{[Ph_2PO_2CH_2C(pz)_3]_2Ag\}^+$ cation resides on a crystallographic inversion center. The BF_4^- anion is disordered about an inversion center. Compound **2** crystallizes in the triclinic system. The space group $P\bar{1}$ was assumed and confirmed by the successful solution and refinement of the data. The asymmetric unit consists of half of the $[(Ph_2PO_2CH_2C(pz)_3Ag]_2$

Table 1 Selected crystal data and structure refinement results

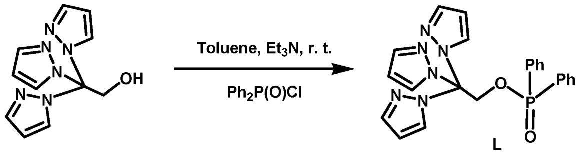
	1	**2**	**3**	**4**·2C_3H_6O
Formula	$C_{46}H_{42}AgBF_4N_{12}O_4P_2$	$C_{54}H_{58}Ag_2B_2F_8N_{12}O_6P_2$	$C_{22}H_{20}Ag_2F_6N_{12}O_6S_2$	$C_{52}H_{54}B_2F_8FeN_{12}O_6P_2$
Fw/g mol^{-1}	1083.54	1422.42	942.36	1234.48
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
T/K	150	150	150	150
a/Å	9.0846(7)	10.9754(8)	8.6922(6)	12.3175(7)
b/Å	10.9600(9)	11.4045(8)	9.4966(7)	18.4056(10)
c/Å	13.9140(12)	12.9314(9)	10.3316(8)	12.3750(7)
α/°	67.246(2)	109.108(1)	71.587(1)	90
β/°	73.530(2)	98.409(1)	68.453(1)	96.839(1)
γ/°	71.977(2)	102.747(1)	81.847(1)	90
V/Å^3	1193.48(17)	1449.22(18)	752.30(10)	2785.6(3)
Z	1	1	1	2
R_1 $I > 2\sigma(I)$	0.0461	0.0404	0.0247	0.0422
wR_2 $I > 2\sigma(I)$	0.0767	0.0993	0.0600	0.1026

complex situated on an inversion center, a BF_4^- anion and a THF molecule. Compound **3** crystallizes in the triclinic system. The space group $P\bar{1}$ was confirmed by the successful solution and refinement of the data. The asymmetric unit consists of half of a centrosymmetric $[\mu\text{-}(HC(pz)_3)_2Ag_2]^{2+}$ cation and one triflate anion. Compound **4**·2C_3H_6O crystallizes in the space group $P2_1/n$ as determined uniquely by the pattern of systematic absences in the intensity data. The asymmetric unit consists of half of the $\{[Ph_2PO_2CH_2C(pz)_3]_2Fe\}^{2+}$ cation located on an inversion center, one BF_4^- counterion and one acetone molecule of crystallization.

Results

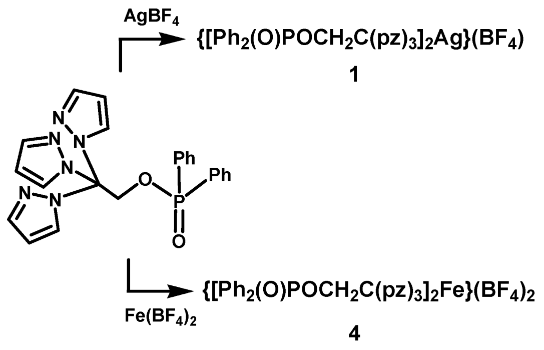
Syntheses

As shown in eqn (1), the $Ph_2(O)POCH_2C(pz)_3$ ligand is prepared from previously reported $HOCH_2C(pz)_3$ by reaction with $Ph_2P(O)Cl$ in the presence of base.



(1)

The reaction of this new ligand with either $AgBF_4$ or $Fe(BF_4)_2 \cdot 6H_2O$ in a 2/1 molar ratio yields $\{[Ph_2(O)POCH_2C(pz)_3]_2Ag\}(BF_4)$ (**1**) and $\{[Ph_2(O)POCH_2C(pz)_3]_2Fe\}(BF_4)_2$ (**4**), respectively, eqn (2). A similar reaction of $HC(pz)_3$ and AgOTf in either a 1/1 or 2/1 molar ratio yields $\{[HC(pz)_3]_2Ag_2\}(OTf)_2$ (**3**). The compound $[Ph_2(O)POCH_2C(pz)_3Ag]_2(thf)_2\}(BF_4)_2$ (**2**) forms when thf solutions of **1** are allowed to partially evaporate.



(2)

Solid state structures

$\{[Ph_2(O)POCH_2C(pz)_3]_2Ag\}(BF_4)$ (1). Compound **1** was crystallized by vapor phase diffusion of diethyl ether into a nitromethane solution. Bond lengths and angles are listed in Table 2. Two $Ph_2PO_2CH_2C(pz)_3$ ligands coordinate to the silver(I) center in the κ^2–κ^0 coordination mode, see Fig. 1. The silver atom is in an unusual planar geometry (sum of the four N–Ag–N angles is 360°), defined by the four coordinated pyrazolyl rings which lie in the corners of a rectangle rather that a perfect square, with the edges of the rectangle being 3.05 Å and 3.59 Å, respectively. This slight deviation is due to the restraints imposed by the bite angle (80.63(10)°) of the two chelating pyrazolyl rings. The non-coordinating pyrazolyl rings are oriented with their nitrogen atoms away from the silver atom, but with their π-clouds toward the silver(I) center. However, the rings are *ca.* 3.5 Å away from the Ag(I) atoms, a distance too long to indicate any cation–π interaction between the two moieties.

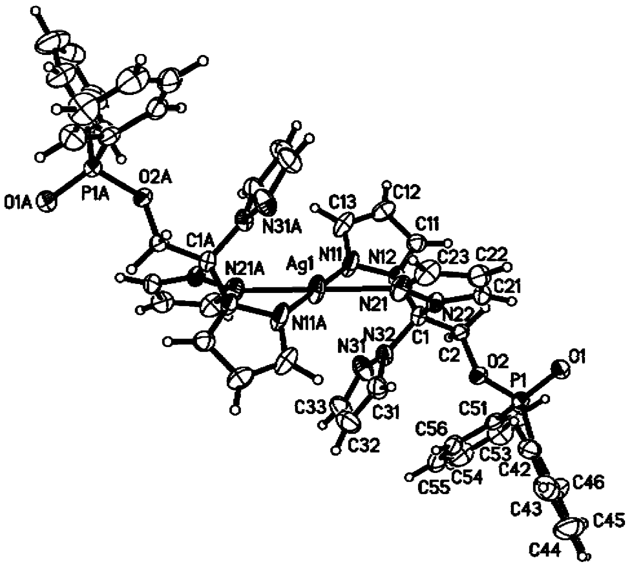


Fig. 1 ORTEP diagram of $\{[Ph_2(O)POCH_2C(pz)_3]_2Ag\}(BF_4)$ (**1**) with atom labeling scheme. Displacement ellipsoids drawn at the 50% probability level.

Table 2 Selected bond distances (Å) and angles (°) for $\{[Ph_2(O)POCH_2C(pz)_3]_2Ag\}(BF_4)$ (**1**), $\{[Ph_2(O)POCH_2C(pz)_3Ag]_2(THF)_2\}(BF_4)_2$ (**2**), $\{[HC(pz)_3]_2Ag_2\}(OTf)_2$ (**3**) and $\{[Ph_2(O)POCH_2C(pz)_3]_2Fe\}(BF_4)_2{\cdot}2[(CH_3)_2CO]$ (**4**·2[(CH$_3$)$_2$CO])[a]

	1	**2**	**3**	**4**·2[(CH$_3$)$_2$CO]
Ag(1)–N(11)	2.362(3)	2.464(2)	2.407(2)	
Ag(1)–N(21)	2.352(3)	2.257(2)	2.413(2)	
Ag(1)–N(31)		2.182(2)	2.237(2)	
Ag(1)–O(1)			2.821(2)	
Ag(1)–O(2)			2.971(2)	
Ag(1)–O(3)		2.795(3)		
Ag(1)–Ag(1)*		3.3690(5)	2.8664(4)	
Fe(1)–N(11)				1.948(2)
Fe(1)–N(21)				1.946(2)
Fe(1)–N(31)				1.931(2)
N(11)–Ag(1)–N(21)	80.63(10)	75.79(8)	79.22(7)	
N(11)–Ag(1)–N(21)*	99.37(10)			
N(11)–Ag(1)–N(11)*	180			
N(21)–Ag(1)–N(21)*	180			
N(21)–Ag(1)–N(31)*		149.94(9)	138.91(7)	
N(31)*–Ag(1)–N(21)*				
N(11)–Ag(1)–N(31)*		134.01(8)	140.42(7)	
N(31)–Fe(1)–N(21)				87.74(6)
N(21)–Fe(1)–N(31)*				92.26(6)
N(11)–Fe(1)–N(31)*				93.00(6)
N(11)–Fe(1)–N(31)				87.00(6)
N(11)–Fe(1)–N(21)				87.65(6)
N(11)–Fe(1)–N(21)*				92.35(6)

[a] Asterisk denotes a symmetry-equivalent atom.

A pair of cooperative hydrogen bonding interactions connects these cationic building blocks into chains that run within the *bc* plane of the unit cell (Fig. 2). Each oxygen atom from a $Ph_2P(O)$ secondary tecton interacts with a hydrogen atom from a methylene group situated on a neighboring building block, The H···O distance is 2.18 Å (C···O distance = 3.16 Å), and a C–H–O angle of 169.4°. Unfortunately, the disorder of the BF_4^- anion prevents us from addressing its contribution to the crystal packing.

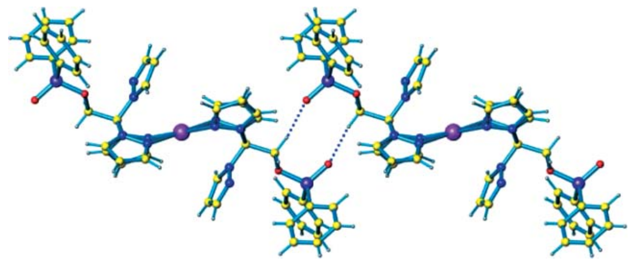


Fig. 2 Two $\{[Ph_2(O)POCH_2C(pz)_3]_2Ag\}^+$ building blocks linked in a chain by the hydrogen bonding pattern involving the $Ph_2P(O)$ tecton, color code: magenta—silver, yellow—carbon; gray—hydrogen, blue—nitrogen, red—oxygen, purple—phosphorus.

$\{[Ph_2(O)POCH_2C(pz)_3Ag]_2(THF)_2\}(BF_4)_2$ (2). Crystallization of compound **1** by slow evaporation of its thf solution causes the ligand:metal ratio to change from 2:1 to 1:1 and dramatically alters the coordination mode of the ligand (see Table 2 for bond lengths and angles). Two $Ph_2(O)POCH_2C(pz)_3$ ligands coordinate to the same two silver(I) centers in a κ^2–κ^1 bonding mode. In addition, a thf molecule makes a secondary bond to each silver atom; these Ag–O bonds are long at 2.79 Å. The silver atom separation is 3.36 Å, less that the sum of silver–silver van der Waals radii (3.44 Å),[10] indicative of a weak Ag–Ag interaction. Each silver is equatorially surrounded by the three nitrogen atoms, two from one ligand and one from the second. The sum of the three N–Ag–N angles around the silver is 359.7°. The geometry is pseudotrigonal planar, but with a significant distortion caused by the restricted angle (75.79°) of the κ^2-bonded ligands. If the thf molecules and the second silver atom are also considered, the geometry around each silver becomes pseudotrigonal bipyramidal. In this compound, the tris(pyrazolyl)methane ligand has an unprecedented coordination mode in which two pyrazolyl rings bridge two silver atoms using σ-type orbitals on the nitrogen donor atoms and the third pyrazolyl ring coordinates to one of the silver atoms with a π-type orbital on the nitrogen atom, Fig. 3.[7]

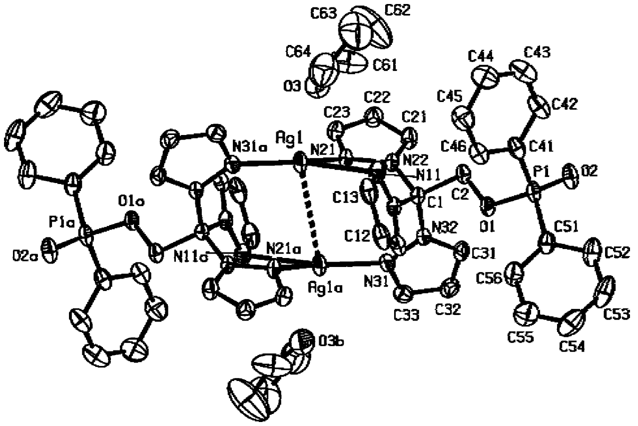


Fig. 3 ORTEP diagram of $\{[Ph_2(O)POCH_2C(pz)_3Ag]_2(THF)_2\}(BF_4)_2$ (**2**). Displacement ellipsoids drawn at the 50% probability level.

The supramolecular structure of **2** is based on the same cooperative hydrogen bonding pattern as shown in Fig. 2 for

1, involving the $Ph_2P(O)$ secondary tecton and the methylene group. Each oxygen atom interacts with a hydrogen atom from a neighboring methylene group, with a H···O distance of 2.22 Å (C···O distance = 3.20 Å), and a C–H–O angle of 170.5°. This interaction builds up chains that run along the body diagonal of the unit cell.

$\{[HC(pz)_3]_2Ag_2\}(OTf)_2$ (3). Crystallization from an acetone–diethyl ether system of this compound produced crystals of **3**, a discrete bimetallic complex, rather than a coordination polymer as in other cases with this tris(pyrazolyl)methane ligand.[3] The ligand to metal ratio is 1 to 1, the compound is a dimer, built up by two ligands κ^2–κ^1 bonding to the same two silvers as seen with compound **2** (Fig. 4). Each ligand chelates a different silver using two pyrazolyl rings, while the third ring has κ^1-bonding to the silver κ^2-bonded to the other ligand. The distance between the silver atoms is 2.86 Å, considerably shorter than the sum of silver–silver van der Waals radii.[10] Each silver is equatorially surrounded by three nitrogen atoms. The sum of the Ag–N angles around the silver is 358.54°, thus placing it in a slightly distorted trigonal planar geometry. In addition, the triflate counterions are in close proximity to the metallic centers, with an Ag–O secondary bonding distance of 2.821(2) Å. If the triflate anions and the second silver atom are considered along with the three equatorial nitrogen atoms, the geometry around each silver becomes trigonal bipyramidal.

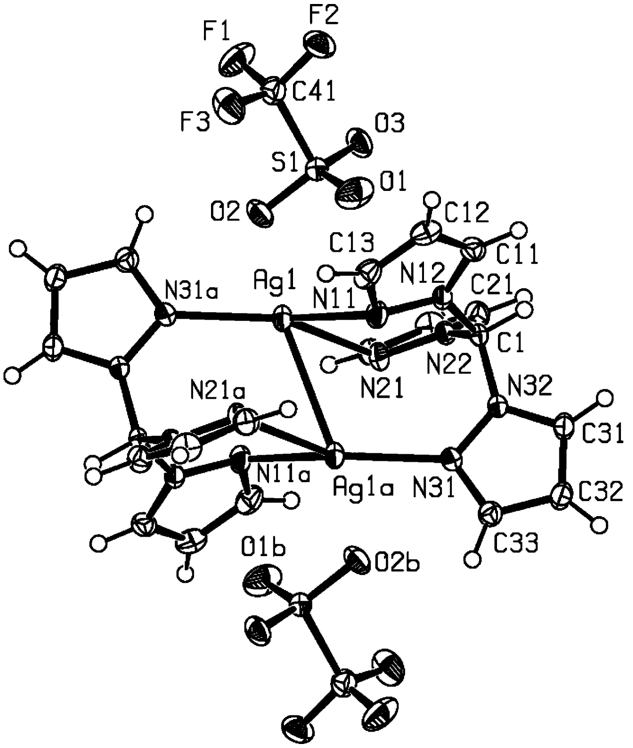


Fig. 4 ORTEP diagram of the formula unit of $\{[HC(pz)_3]_2Ag_2\}(OTf)_2$ (**3**). Displacement ellipsoids drawn at the 50% probability level.

These dimeric building blocks self-assemble into chains *via* the quadruple pyrazolyl embrace synthon–an interaction that we substantiated in other papers.[3k,11] In other cases involving tris(pyrazolyl)methane donor units, the interaction consist of two adjacent Cpz_2 units involved in a cooperative π–π stacking and two C–H···π interactions between the four pyrazolyl rings, with two pyrazolyl rings stacked one on top of another with their 4-position hydrogen atom oriented toward the other pyrazolyl rings, not involved in the π–π stacking motif. Fig. 5 depicts three $\{[HC(pz)_3]_2Ag_2\}^{2+}$ building blocks linked by the pyrazolyl embrace synthon, but in this case the interaction is unique. Instead of taking place between two κ^2-bonded Cpz_2 units, in **3** the π–π stacking interaction comes from pyrazolyl rings in two κ^2-bonded Cpz_2 units and the acceptor rings in the C–H···π interactions are the pyrazolyl rings κ^1-bonded to silver in the adjacent dimeric unit. These chains are further associated by the triflate anions (Fig. 6, blue lines) that link the units *via* a combined Ag···O/CH···O interaction. The Ag–O distances are 2.82 Å and the H···O distances are 2.14 Å (C···O distance = 3.1 Å), with a C–H–O angle of 161.1°. All these interactions build up sheets shown in Fig. 6.

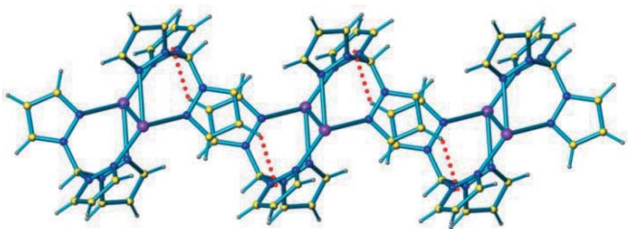


Fig. 5 Chain formation in **3** *via* the pyrazolyl embrace synthon; the π–π stacking component of the interaction in clearly shown for two pairs of pyrazolyl rings in the middle of the figure and the red dotted lines show the C–H···π interactions.

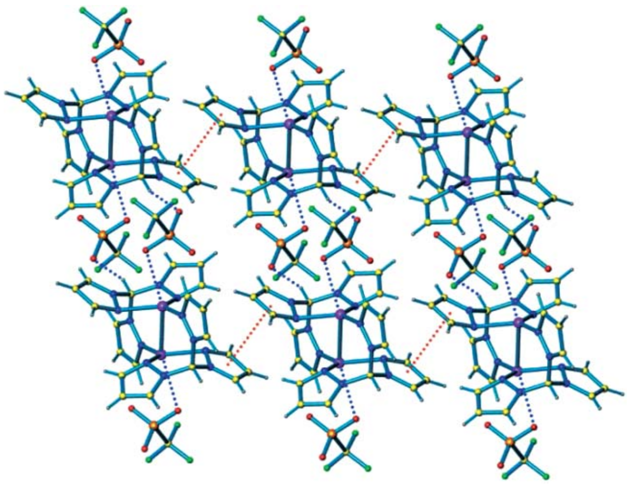


Fig. 6 The sheet like architecture of **3**.

$\{[Ph_2(O)POCH_2C(pz)_3]_2Fe\}(BF_4)_2{\cdot}2[(CH_3)_2CO]$ ($4{\cdot}2[(CH_3)_2CO]$). Vapor phase diffusion of diethyl ether into an acetone solution of the compound produced crystals suitable for X-ray diffraction. Both tris(pyrazolyl)methane ligands shows the κ^3-tripodal coordination mode, thus placing the Fe(II) center in an octahedral environment (Fig. 7). The structural parameters of the $\{[C(pz)_3]_2Fe\}^{2+}$ core are similar to those reported previously by us.[12] The Fe–N bond distances that average 1.94 Å clearly demonstrate that the iron(II) is in the low spin electronic state.[12] In contrast to compounds **1** and **2** described earlier, the P=O

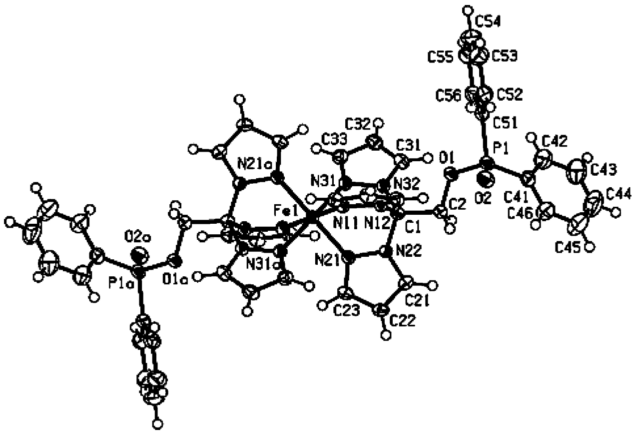


Fig. 7 ORTEP diagram of $\{[Ph_2(O)POCH_2C(pz)_3]_2Fe\}(BF_4)_2{\cdot}2[(CH_3)_2CO]$ ($\mathbf{4}{\cdot}2[(CH_3)_2CO]$).

oxygen atom is involved in a hydrogen bond with H(55) situated in the *meta*-position on one of the diphenylphosphine rings from an adjacent cation. The O···H distance is 2.35 Å (O···C distance is 3.35 Å), and the corresponding C–H–O angle is 166°; a detailed view of the interaction is shown in Fig. 8. This symmetry related interaction builds up a sheet like overall supramolecular structure, pictured in Fig. 9, where the blue stars show where the interaction described in Fig. 8 takes place. The BF_4^- counterions are involved in hydrogen bonds with acidic hydrogen atoms from the methylene group; however, these interactions are intramolecular only and do not increase the dimensionality of the supramolecular structure.

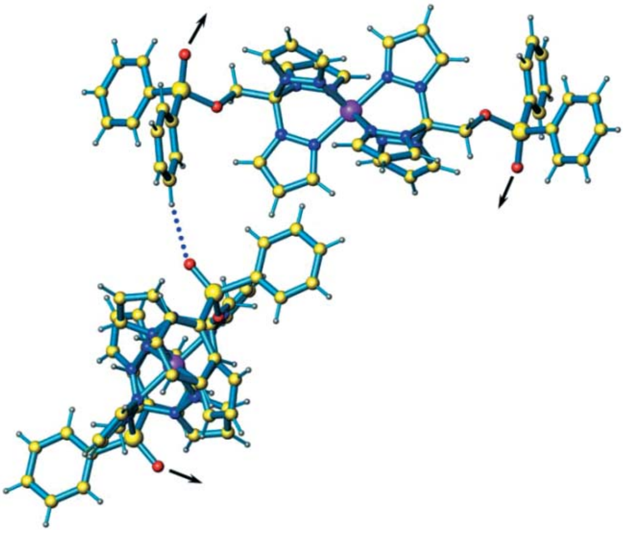


Fig. 8 Intermolecular forces that organize the supramolecular structure of $\mathbf{4}{\cdot}2[(CH_3)_2CO]$; arrows indicate the location of the additional C–H···O interactions.

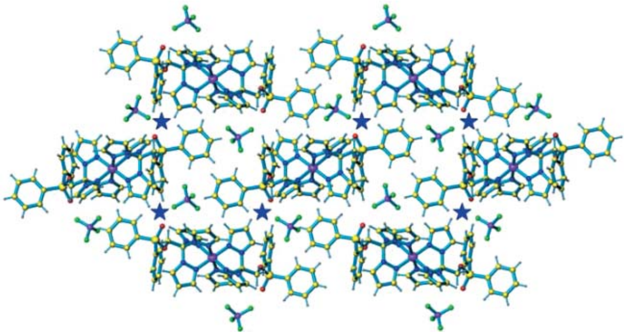


Fig. 9 Sheet supramolecular structure of $\mathbf{4}{\cdot}2[(CH_3)_2CO]$; stars indicate the locations of the C–H···O interactions.

Discussion

It is interesting to note that in the three compounds of the new third generation $Ph_2(O)POCH_2C(pz)_3$ ligand (**L**) reported here there are three very different bonding arrangements. In **1**, with the formula of the cation being $\mathbf{L}_2Ag^+$, κ^2–κ^0 coordination is observed forming monomeric cationic units. In **2**, with the formula of the cation changing to $[\mathbf{L}_2Ag_2]^{2+}$, two ligands κ^2–κ^1 bond two silver(I) forming dimeric cationic units with close Ag···Ag distances. In **4**, with the formula of the cation being $\mathbf{L}_2Fe^{2+}$, changing the metal to iron(II), which prefers octahedral coordination, leads to κ^3 coordination again forming monomeric cationic units. In none of the compounds of this ligand do we observe the structural arrangement most prevalent for the -$C(pz)_3$ structural unit which is the formation of κ^2–κ^1 bonding where each unit bridges *different* silver(I) centers leading to a coordination polymer.[3i,6,13] Compound **3** is also an exception to this rule having a structure like **2**, in this case with a very short Ag···Ag distance.

The $Ph_2(O)POCH_2C(pz)_3$ ligand was designed with a secondary tecton, $P(O)Ph_2$, to support supramolecular structures. In both silver(I) structures **1** and **2** the electronegative oxygen of the $Ph_2P(O)$ secondary tectons interact in a cooperative pair of hydrogen bonds with the methylene groups situated on the neighboring building block so as to connect these cationic building blocks into chains. In contrast, in octahedral **4** this oxygen is involved in a hydrogen bond with a *meta*-position hydrogen on one of the diphenyl-phosphine rings from an adjacent cation. Overall, it appears that this secondary tecton does not influence structure in a predictable fashion.

In addition to the structural variation in metal complexes of **L**, an interesting feature of these compounds is the dimeric nature of $\{[Ph_2(O)POCH_2C(pz)_3Ag]_2(THF)_2\}(BF_4)_2$ (**2**) and $\{[HC(pz)_3]_2Ag_2\}(OTf)_2$ (**3**). In both structures the two silver(I) are bridged by κ^2–κ^1 bonding of two tris(pyrazolyl)methane ligands, a bonding arrangement that is unique to these two compounds. It is not clear whether this arrangement is a consequence of the Ag···Ag interaction or is the reason why the bridged metals are in such close proximity. This type of ligand bonding has been observed in tris(pyrazolyl)borate chemistry, but with smaller, hard metals that had no M···M interaction.[14] The Ag···Ag bond distances are surprisingly different with **3** being 0.5 Å shorter than in **2**. Another unusual structural feature of **3**, which could possibly account for the short Ag···Ag bond distance, is the unusual pyrazolyl embrace interaction where the acceptor ring

Table 3 AgN(n1)–N(n2)C(1) torsion angles (°)

Angle	2	3
Ag(1)N(11)–N(12)C(1)	89.5(2)	8.1(3)
Ag(1)N(21)–N(22)C(1)	42.3(3)	51.6(3)
Ag(1)N(31)–N(32)C(1)	18.6(3)	56.5(2)

Table 4 Coordination geometries and AgN_4C ring puckering parameters in various silver di(pyrazolyl)methane complexes

Cation	Coord. env.	Fold AgNN[a]	Fold CNN[b]	Ref.
$\{Ag(C_6H_5[C(pz)_2(2\text{-}py)])_2{}^+\}$	sq. pl.	135.4	130.4	17
$\{Ag[(pz)_2CPh_2]_2{}^+\}$ (190 K)	sq. pl.	136.4	127.9	16
$\{Ag(m\text{-}C_6H_4[C(pz)_2(2\text{-}py)]_2)_2{}^+\}$	sq. pl.	147.7	128.6	17
$\{[Ph_2(O)POCH_2C(pz)_3]_2Ag^+\}$ (**1**)	sq. pl.	152.3	121.8	[c]
$\{Ag[(pz)_2CHPh]_2{}^+\}$	tet.	160.3	124.8	16
$\{Ag_2(\mu\text{-}[(pz)_2CH]_2CH_2)_2{}^+\}$	tet.	160.4	126.9	18
$\{Ag[(pz)_2CHCH_2Ph]_2{}^+\}$[d]	tet.	164.1 165.4	121.4 123.0	16
$\{Ag_2(\mu\text{-}[(pz)_2CH]_2CH_2)_2{}^+\}$	tet.	167.6	121.1	18
$\{Ag[(pz)_2CMe_2]_2{}^+\}$[d]	tet.	172.4 173.4	121.4 120.9	19

[a] Fold AgNN is the angle defined by points connecting silver and the centroid between N(11) and N(21) and the centroid between N(12) and N(22), each of which lies on a plane bisecting AgN_4C chelate ring. [b] Fold CNN is similar but with the C atom replacing Ag as one point. [c] This work. [d] Two independent Ag sites.

in the C–H···π interaction is the pyrazolyl ring κ^1-bonded to silver in the adjacent dimeric unit rather than the other ring in a κ^2-bonded Cpz_2 unit.

In both dimeric structures, secondary bonding of an oxygen donor to the silvers is observed. In fact, **2** is formed from the crystallization of monomeric $\{[Ph_2(O)POCH_2C(pz)_3]_2Ag\}(BF_4)$ (**1**) from thf, so a radical change takes place in that process. In the case of **3**, although this compound forms directly in the reaction of AgOTf, the analogous reactions with $AgBF_4$ and $AgPF_6$ yield compounds that are "normal" coordination polymers in which each tris(pyrazolyl)methane ligand is bonded κ^2–κ^1 to two silvers that are over 4 Å apart.[6] This secondary bonding interaction of the oxygen donor appears to support the unusual κ^2–κ^1 bonded $[Ag_2\mathbf{L}_2]^{2+}$ arrangement.

Another unique feature of the bonding in both **2** and **3** involves the orientations of the pyrazolyl rings with respect to the metal. For maximum overlap with the lone pair on the nitrogen donor atom, the silver would lie in the plane of each pyrazole ring. Any deviation from this orientation can be measured by the AgN(n1)–N(n2)C(1) torsion angle, where *n* denotes the ring number, an angle that would have the value of 0° if the metal were in the pyrazolyl ring plane. The torsion angles are presented in Table 3. Large deviations down have been observed in several other cases, especially for large metallic centers (e.g. lead(II) and thallium(I)) where for $\{[HC(3,5\text{-}Me_2pz)_3]_2Tl\}(PF_6)$ the average is 49°.[15] The deviation to 89.5° for one angle in **2** and 51.6 and 56.5° for two of the angles in **3** indicate that the silver, a smaller metal cation, is coordinated more by π-type orbitals from the pyrazolyl rings than a conventional nitrogen based σ-type lone pair orbital in these cases.

Finally, the square planar structure of **1** is unusual. We have previously reported that silver(I) bis(pyrazolyl)methane complexes with two bulky substituents bonded to the central methine carbon atom, such as in $\{Ag[(pz)_2CPh_2]_2\}(PF_6)$ or $\{Ag(\kappa^2\text{-}m\text{-}C_6H_4[C(pz)_2(2\text{-}py)]_2)_2\}(PF_6)$ adopt square planar arrangements about silver(I) and argued that the steric constraints imposed by these aromatic groups enforce the unusual square planar conformation.[16] We also pointed out an indication that the steric bulk of the substituents will force the square planar arrangement is the AgN_4C chelate rings in the square planar complexes adopt a more boat-like configuration (lower fold angles, Table 4) when compared to analogous tetrahedral complexes, such as $\{Ag[(pz)_2CHPh]_2\}(PF_6)$, that contain bis(pyrazolyl)methane ligands with only one bulky substituents or $\{Ag[(pz)_2CMe_2]_2\}(ClO_4)$, that contains two smaller groups, bonded to the central methine carbon atom. Compound **1**, with one bulky substituent and one smaller substituent has a fold angle between these previously studied compounds, although more closely aligned with the square planar complexes. Apparently the steric bulk on the methine carbon is substantial enough to push the non-coordinated pyrazolyl rings over the silver center, favoring the square planar arrangement.

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