9-7-2009

Manipulating Self-Assembly in Silver(I) Complexes of 1,3-Di-*N*-pyrazolylorganyls

Brendan J. Liddle
Marquette University

Daniel Hall
Marquette University

Sergey V. Lindeman
Marquette University, sergey.lindeman@marquette.edu

Mark D. Smith
University of South Carolina

James R. Gardinier
Marquette University, james.gardinier@marquette.edu

Accepted version. *Inorganic Chemistry*, Vol. 48, No. 17 (September 7, 2009): 8404-8414. DOI.

Inorganic Chemistry, Vol. 48, No. 17 (2009): 8404-8414. DOI. This article is © American Chemical Society and permission has been granted for this version to appear in e-Publications@Marquette. American Chemical Society does not grant permission for this article to be further copied/distributed or hosted elsewhere without the express permission from American Chemical Society.

Manipulating Self-Assembly in Silver(I) Complexes of 1,3-Di-*N*-pyrazolylorganyls

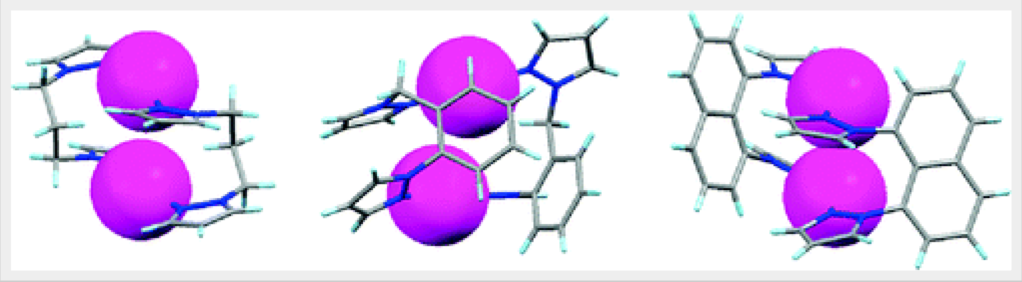
Brendan J. Liddle
Department of Chemistry, Marquette University, Milwaukee, WI
Daniel Hall
Department of Chemistry, Marquette University, Milwaukee, WI
Sergey V. Lindeman
Department of Chemistry, Marquette University, Milwaukee, WI
Mark D. Smith
Department of Chemistry and Biochemistry, University of South Carolina, Columbia, SC
James R. Gardinier
Department of Chemistry, Marquette University, Milwaukee, WI

Synopsis

Three di-*N*-pyrazolylorganyls with different conformational flexibilities in the three-atom organyl spacers have been prepared, and the self-assembly properties with $AgBF_4$ have been studied both in solution and in the solid state. All ligands give low-coordinate silver(I) centers that are capable of participating in multiple noncovalent interactions, but only the rigid 1,8-dipyrazolylnaphthalene ligand promotes very short Ag−Ag contacts.

-

Abstract



A series of ligands with two pyrazolyls (pz) linked by either a propyl (pz_2prop), a benzyl (pz_2Bn or pzBnpz*, where Bn = benzyl and pz* = 3,5-dimethylpyrazolyl), or a 1,8-naphthyl (pz_2naphth) spacer and their silver(I) tetrafluoroborate complexes have been prepared with the intent of evaluating how the conformational flexibility of the ligands would affect the supramolecular assembly of the 1:1 [Ag(ligand)](BF_4) complexes and their capacity for promoting short Ag⋯Ag interactions. The noncoordinating nature of the tetrafluoroborate anion ensured low coordination numbers to the silver(I) centers, thereby allowing the metal ion to participate in multiple noncovalent interactions that dictate the ligand conformations and supramolecular isomerism observed in the solid state. In the solid state, the complex [Ag(CH_3CN)(pz_2prop)](BF_4) forms a cyclic bimetallic cation that assembles into one-dimensional chains as a result of Ag−π and CH⋯F noncovalent interactions, in a manner distinct from the known nitrate derivative. With [Ag(pz_2Bn)](BF_4), either cyclic bimetallic cations or coordination polymers can be formed depending on the solvents used for crystallization, where acetone promotes the formation of the former while acetonitrile gives the latter. The complex [Ag(pzBnpz*)](BF_4) forms two different one-dimensional coordination polymers in the same flask during crystallization from acetone/Et_2O, where the presence or absence of the included solvent dictates the differences in the secondary coordination sphere of (and noncovalent interactions involving) silver(I). In all the above cases, neighboring silver atoms are separated beyond van der Waals contact. In contrast, the complex [Ag(pz_2naphth)](BF_4)·2CH_3CN forms discrete cyclic bimetallic cations where the rigid ligand enforces a short (3.19 Å) Ag⋯Ag contact. All complexes are extensively dissociated in a CH_3CN solution, as indicated from a combination of ^1H NMR and positive-ion electrospray ionization mass spectral data.

Introduction

Self-assembling “wirelike” systems are desirable to circumvent the highly (sometimes prohibitively) demanding synthetic efforts required to traverse various size regimes (from the molecular scale to the nanoscale and beyond) warranted in emerging technological applications such as those found in the areas of molecular electronics[1] or even solar energy conversion.[2] Simple, multinucleating ligand scaffolds with the capacity for enforcing discrete metal–metal interactions and extending these (or other) interactions over multiple metal centers via noncovalent self-assembly are enticing candidates for this prospect. For a given multinucleating ligand, the various structural factors influencing the controlled molecular and supramolecular organization of metal complexes can be most conveniently studied by an initial examination of their silver(I) coordination chemistry.[3] Appropriately designed silver(I) complexes are known to participate in either intra- or intermolecular closed-shell

d^{10}–d^{10} metallophilic interactions.[4] Moreover, the possibility of exploiting well-documented Ag^+–π interactions[5] to promote supramolecular assembly may provide an alternative means for mediating electronic communication within assemblies in the absence of intermolecular metallophilic interactions. Other advantages of exploring silver(I) systems include the synthetic simplicity of complex preparation, the favorable solubility of the complexes, the ease of obtaining high-quality crystalline products, the accessibility of desirable linear or T-shaped metal coordination geometries that permit the metal's involvement in noncovalent interactions, and, finally, their potential utility as reagents for subsequent chemistry.

As illustrated in Figure 1, dinucleating ligands constructed of monodentate heterocycles connected by three-atom or longer (but structurally flexible) spacers[6] can adopt desirable geometries that support short "intramolecular" Ag···Ag contacts (i.e., with an Ag···Ag separation less than twice the van der Waals radius of silver, 3.44 Å);[7] however, ligand scaffolds with one- or two-atom spacers do not possess the correct geometries for short "intramolecular" metal−metal contacts. The strategy of using heterocycles tethered to three-atom spacers to promote intramolecular argentophilic contacts in silver(I) complexes has been successfully demonstrated for a number of such ligands like 1,3-di-4-pyridyltetramethyldisiloxane,[8] bis(thioimidazolyl)methane,[9] among others.[10]

Figure 1. Expected geometries for metals (M) binding to tethered monodentate heterocycles with unspecified Lewis donor atoms (black spheres) containing one-atom (left), two-atom (center), and three-atom spacers (right).

Of particular relevance to this study, several silver complexes of ligands with pyrazolyls spaced three atoms apart have been structurally characterized but argentophilic interactions were found in only one of these cases.[11] The 1:1 silver nitrate complex of tetrakis(pyrazolylmethyl)ethane-1,2-diamine (with two C−N−C spacers) adopted a cyclic bimetallic geometry with a short Ag−Ag distance of 3.160 Å,[11] while the closely related 1:1 silver(I) nitrate complex of tetrakis(pyrazolylmethyl)methane was found to exist as polymeric chains of cyclic bimetallic $[Ag(\mu^2,\kappa^2,\kappa^1\text{-}L)]_2^{2+}$ moieties connected via bridging NO_3^- anions, without discrete Ag···Ag interactions.[12] Similarly, with 1,1′,3,3′-tetrapyrazolylpropanes, each end of two bridging ligands binds silver in a μ-κ^2,κ^2-coordination mode, forming cyclic bimetallic species in solution and the solid state when anions are noncoordinating (BF_4^- and PF_6^-) but forming linear oligomers or polymers with nitrate anions; no short Ag···Ag contacts were found owing to the high coordination number of silver.[13] The silver nitrate complex of the simpler 1,3-dipyrazolylpropane ligand (pz_2prop) did not exhibit short intramolecular Ag···Ag contacts.[14] Instead, a remarkable structure with two supramolecular isomers was found in the same crystal lattice, having both cyclic bimetallic [Ag(μ-κ^1,κ^1-pz$_2$prop)(NO$_3$)]$_2$ units and polymeric sheets comprised of one-dimensional chains of [Ag(μ-κ^1,κ^1-pz$_2$prop)]$^+$ units connected in a second dimension by μ^2-NO$_3^-$ anions. One aspect of the current study is to determine whether replacement of the nitrate in “[Ag(pz$_2$prop)](NO$_3$)” with a noncoordination anion would promote the exclusive formation of cyclic species as in the case of 1,1′,3,3′-tetrapyrazolylpropanes above and, if so, whether the ligand conformation and/or change in the silver coordination sphere would permit short Ag···Ag contacts.

In this study, the ligands in Chart 1 each possess *N*-pyrazolyl heterocycles linked through three carbon atom chain spacers with differing degrees of rotational freedom, consisting of a propyl group (pz$_2$prop), a benzyl group (pz$_2$Bn and pzBnpz*), or a naphthyl group (pz$_2$naphth). These ligands were chosen or designed in an effort to ascertain the various factors (including the relative rigidity of organyl backbones as well as the steric demand of pyrazolyl substituents in the case of pz$_2$Bn versus pzBnpz*) that might promote or hinder the formation of argentophilic contacts and/or, by subtle changes in ligand conformations, that could influence the relative stabilities of possible supramolecular isomers such as those depicted in Figure 2. Furthermore, in this current study, only those silver(I) complexes of the noncoordinating tetrafluoroborate anion[15] were examined with the intention of maintaining consistency in the role of the anion[10c,15] in determining the supramolecular organization of the structures (potentially limiting any organizing forces to weak Ag···F or CH···F noncovalent interactions). A more thorough examination of the anion dependence on the supramolecular organization of these and related complexes will be the subject of a future publication by our group.

Chart 1. Dipyrazolylorganyl Ligands Investigated in This Study

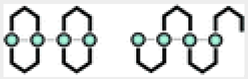
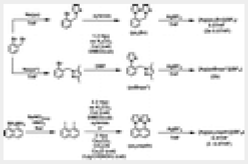


Figure 2. Possible supramolecular isomers of 1:1 metal complexes of bridging multinucleating ligands (ligands are in black and metals in gray). Left: Cyclic structures. Right: Polymeric structures.

Results

Syntheses

As mentioned in the Introduction, the ligand pz$_2$prop and its silver nitrate complex have been prepared previously.[14] In this contribution, we prepared [Ag(pz$_2$prop)](BF$_4$) (**1**) in a manner similar to that of the nitrate complex by mixing solutions of the ligand and silver salt but using tetrahydrofuran (THF) as a solvent to afford a precipitate of **1** as a colorless powder. The synthetic methodology to the various new ligands and silver(I) complexes in this study is found in Scheme 1. The key step in the syntheses of benzyl or naphthyl derivatives was a copper-catalyzed amination reaction between the appropriate aryl halides and pyrazole in the presence of a Brönsted base by adopting modifications[16] of the reaction conditions first outlined by Taillefer et al.[17] and Buchwald et al.[18] The potency of this approach is highlighted by the mild conditions in which the products are formed and by the isolation of the relatively sterically encumbered pz$_2$naphth. It is noted that, regardless of the reaction conditions (base, copper catalyst, chelating ligand cocatalyst, and solvent), the reaction times increased and yields of the product decreased with increasing steric bulk of the substituents proximal to the halide group of the starting haloarene, as might be expected. Similar to **1**, the silver tetrafluoroborate complexes of other dipyrazolylorganyls ([Ag(pz$_2$Bn)](BF$_4$) (**2a**), [Ag(pzBnpz*)](BF$_4$) (**2b**), and [Ag(pz$_2$naphth)](BF$_4$) (**3**); Scheme 1) were prepared in good yield by mixing equimolar amounts of the desired ligand and AgBF$_4$ in THF, which resulted in precipitation of the desired 1:1 complexes. For **2a** and **3**, 0.5 equiv of THF is retained even upon prolonged heating under vacuum, as indicated from mass measurements and NMR spectral data. Elemental analyses of dried single crystals also indicate that the solvent is tightly retained in these complexes (vide infra). The complexes are soluble in Lewis base solvents more polar than THF [acetone, CH$_3$CN, *N*,*N*-dimethylformamide (DMF), and dimethyl sulfoxide (DMSO)] and are insoluble in halo- and hydrocarbon solvents. Given the known propensity for solvents to effect changes in the supramolecular organization of silver(I) complexes,[3] we made every attempt to crystallize samples from the same solvent system (CH$_3$CN/Et$_2$O or acetone/Et$_2$O); however, X-ray diffraction quality crystals could not be obtained for the complete series using any one solvent system (vide infra).



Scheme 1. Syntheses of Dipyrazolylorganyls and Their Silver(I) Complexes

Solid-State Structures

To facilitate the discussion of the structural details of the complexes, it will be useful to define two torsion angles, τ_{N4} and τ_{NC} (Figure 3), that are independent of the three-atom spacer connecting the two pyrazolyls and that help to describe the conformation of the ligands.

Figure 3. Two spacer-independent torsion angles, τ_{N4} ($N^2N^1{-}N^{1\prime}N^{2\prime}$, pink) and τ_{NC}($N^1C^1{-}C^3N^{1\prime}$, green), for describing the relative conformations of pyrazolyls using pz_2Bn with coplanar pyrazolyls as an example (two views of the molecule are given for each conformation): (a) eclipsed, *syn*-$\tau_{N4} = \tau_{NC} = 0°$; (b) eclipsed, *anti*-$\tau_{N4} = 125°$, $\tau_{NC} = 0°$; (c) staggered, *anti*-$\tau_{N4} = 180°$, $\tau_{NC} = 60°$. See the text for comments on the carbon hybridization.

The first torsion angle, τ_{N4} ($N^2N^1{-}N^{1\prime}N^{2\prime}$, pink lines in Figure 3), describes the relative orientation of the metal-binding nitrogen atoms and provides an alternative, more quantitative description of cases where these nitrogen atoms reside on the same (syn) or opposite (anti) faces of a given ligand. The second torsion angle, τ_{NC} ($N^1C^1{-}C^3N^{1\prime}$, green lines in Figure 3), enumerates whether the 1- and 3- carbons of the three-atom spacer are in pseudo eclipsed, staggered, or gauche conformations (whether these atoms are actually sp^3-hybridized or are hypothetically modeled as such). An ideal conformation for promoting Ag···Ag interactions would be eclipsed,syn ($\tau_{N4} = \tau_{NC} = 0°$) and with coplanar stacking of the pyrazolyl rings. Such a geometry could allow Ag···Ag separations as short as 2.55 Å based on the C−C separation of the respective organic linker.

The solid-state structures of pz_2naphth (see the Supporting Information for full details) as well as solvated and/or nonsolvated forms of the various silver(I) complexes (**1**·CH_3CN, **2a**·0.5acetone, **2b**, **2b**·acetone, and **3**·$2CH_3CN$) were characterized by single-crystal X-ray diffraction. A summary of the data collection and structure refinements as well as additional details regarding the structure solutions is provided in the Supporting Information. The structures and atom labeling of cyclic dications in **1**·CH_3CN, **2a**·0.5acetone, and **3**·$2CH_3CN$ or the monomeric units of coordination polymers **2a**, **2b**, and **2b**·acetone are depicted in Figure 4, while a summary of the pertinent structural features of these and related complexes is provided in Table 1.

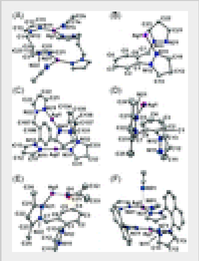


Figure 4. ORTEP diagrams (thermal ellipsoids drawn at the 50% probability level) and atom labeling of cyclic disilver dications or monomeric cation units of silver coordination polymers. (A) **1**·CH_3CN; (B) **2a**; (C) **2a**·0.5acetone; (D) **2b**; (E) **2b**·acetone; (F) **3**·$2CH_3CN$.

Table 1. Summary of the Structural Features of Silver(I) Complexes

compound	CN[a]	Ag–N$_{avg}$(Å)	N–Ag–N (deg)	Ag–Ag[b](Å)	τ_{N4}[c](deg)	τ_{NC}[c](deg)	conformation	form
[Ag(pz$_2$prop)](NO$_3$)[14]	3	2.171	161.8	5.334	75.0	133.9	gauche,syn	cyclic
	4	2.276	111.4	5.502	11.1	123.8	staggered,anti	polymer
[Ag(pz$_2$prop)](BF$_4$)	3	2.194	152.5	3.682	19.1	17.9	gauche,syn	cyclic
[Ag(pz$_2$Bn)](BF$_4$)	2	2.134	169.9	5.434	59.1	60.2	staggered,anti	polymer
[Ag(pz$_2$Bn)](BF$_4$)·0.5 acetone[d]	2	2.125	176.8	3.767	20.3	145.4	gauche,syn	cyclic
	2	2.098	174.0		51.7	53.4	staggered,syn	
	2	2.119	177.1	3.775	20.8	145.5	gauche,syn	cyclic
	2	2.110	174.3		51.3	52.7	staggered,syn	
[Ag(pzBnpz*)](BF$_4$)	2	2.125	166.3	6.167	173.1	52.9	staggered,anti	3_1polymer
[Ag(pzBnpz*)](BF$_4$) ·acetone	2	2.133	168.7	6.695	165.5	50.6	staggered,anti	polymer
[Ag(pz$_2$naphth)](BF$_4$)	3	2.175	152.4	3.187	4.1	0.1	eclipsed,syn	cyclic
	3	2.213	147.6		2.6	5.8	eclipsed,syn	

[a] Primary coordination no. about Ag.

[b] Closest Ag···Ag distance.

[c] See Figure 3 for the definition.

[d] Two independent dications in the asymmetric unit.

The structure of **1**·CH_3CN (Figure 4A) is remarkably different from its previously reported nitrate counterpart “[Ag(pz$_2$prop)](NO_3)”[14] (both being obtained by vapor diffusion of Et_2O into a CH_3CN solution of the complex), underscoring the influence of the anion on the molecular and supramolecular architecture of silver(I) complexes.[10c,15] The new derivative **1**·CH_3CN consists of discrete cyclic bimetallic $\{[Ag(CH_3CN)]_2(\mu\text{-}pz_2prop)_2\}^{2+}$ dications centralized on inversion centers where two pz$_2$prop ligands bridge two silver(I) centers to form a 16-membered ring system. The primary coordination geometry about silver is distorted T-shaped with a planar (sum of angles about silver = 360°) AgN_3 kernel derived from two shorter Ag−N(pz) bonds (2.181 and 2.207 Å, with average 2.194 Å) and one longer Ag−N(CH_3CN) bond (2.393 Å). The ligands adopt a gauche,syn conformation with two torsion angles, τ_{N4} = 19.1° and τ_{NC} = 17.9°, with slipped cofacial arrangement of the pyrazolyls [centroid (N11)−centroid (N12) distance of 3.505 Å with dihedral, slip, and tilt angles: α = 17.1°, β = 13.8°, and γ = 24.6°]. As such, the Ag···Ag distance of 3.682 Å within the dication is longer than twice the van der Waals radius (3.44 Å) of silver, precluding metallophilic interactions.

A closer inspection of the structure reveals a number of noncovalent interactions that support the geometry of the dication and the overall layered supramolecular structure. A view of the extended coordination sphere around silver in **1**·CH_3CN is given in the top of Figure 5. In addition to the planar AgN_3 kernel described above, there are two close contacts that occur between silver and atoms of the nearby pyrazolyl groups, specifically between Ag···N21 (3.237 Å) and Ag···C22 (2.938 Å), which are nearly collinear (N21−Ag−C22 = 171°) and are orthogonal to the AgN_3 plane (red and pink dashed lines in Figure 5B−D). These contact distances are longer than those typically found in more familiar $Ag^+\cdots\pi$ complexes of aromatic hydrocarbons (2.4−2.9 Å),[5] but each is less than the sum of the van der Waals radii of the respective elements ($\sum_{vdw}$(Ag,N) = 3.27 Å; $\sum_{vdw}$(Ag,C) = 3.42 Å). Given the paucity of known Ag···π complexes of N-heterocycles,[19] it remains unclear whether these long contacts are due to very weak Ag···π interactions or are simply a consequence of the numerous CH···F interactions[20] that both bolster the “intradicationic” geometry and dictate the overall supramolecular structure. The various weak CH···F interactions involving the dication hydrogen donors and the tetrafluoroborate acceptor of **1**·CH_3CN are summarized in Table 2. Of the fluorine groups, all except F2 are involved in bifurcated hydrogen-bonding interactions. Briefly, F1 is involved in bifurcated hydrogen-bonding interactions with H21 of a pyrazolyl of one dication and with H3b of the propyl backbone of an adjacent dication (green dashed lines in Figures 5C,D). The inversion center in the middle of the dications gives rise to a polymeric chain that propagates along the *b* axis. The longer interdicationic Ag···C contacts also support the chain. The bifurcated CH···F interactions involving F3 (with a pyrazolyl hydrogen, H13, of one chain and an acetonitrile hydrogen, H2S2, of an adjacent chain) and F4 (with propyl hydrogens of adjacent chains, H1A and H2B) serve to link the chains into sheets in the *ab* plane. Although not shown, the sheets are stacked along the *c*direction, with the closest contacts occurring between F3 and an acetonitrile hydrogen of a neighboring sheet, H2S3 (C2s−H2S3 = 0.979 Å, H2S3−F3 = 2.595 Å, and C2s−H2S3−F3 = 129.4°).

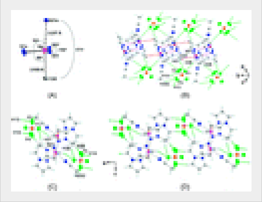


Figure 5. Supramolecular structure of **1**·CH_3CN. (A) Extended coordination sphere around Ag1. (B) View of the polymeric chain along the *b* axis, supported by CH···F (green dashed lines) and Ag···π (red and pink dashed lines) noncovalent interactions. (C) View of the chain down the *b* axis. (D) View down the *b* axis of a sheet in the *ab* plane.

Table 2. Geometries of Various CH···F Interactions in 1·CH_3CN

donor (D)−H···acceptor (A)	D−H (Å)	H···A (Å)	D···A (Å)	D−H···A (deg)
C1−H1a···F4	0.99	2.54	3.406(3)	146
C2−H2b···F4	0.99	2.51	3.291(3)	135
C2s−H2s2···F3	0.98	2.40	3.209(3)	139
C13−H13···F3	0.95	2.25	3.179(2)	165
C3−H3b···F1	0.99	2.44	3.374(2)	157
C21−H21···F1	0.95	2.46	3.184(2)	133

Two different supramolecular isomers of **2a** can be obtained by altering the solvents for crystallization. Vapor diffusion of Et_2O into an acetonitrile solution of the complex affords a solvent-free coordination polymer (Figures 4B and 6), **2a**, whereas substitution of acetonitrile for acetone affords a cyclic bimetallic species (Figure 4C), **2a**·0.5 acetone, which crystallizes with 0.5 equiv of acetone included in the lattice (but not bound to silver). In both cases, the primary coordination geometry around silver is nearly linear, as indicated by the short Ag−N bonds that average 2.134 Å for **2a** (with N−Ag−N of 169.9°) and 2.113 Å (average of two crystallographically independent dications) for **2a**·0.5 acetone (with an average N−Ag−N of 175.6°). The ligand in solvent-free **2a**adopts a staggered,anti conformation, indicated by the two torsion angles τ_{N4} = 59.1° and τ_{NC} = 60.2°, with proximal pyrazolyl rings that deviate modestly from coplanarity by a dihedral angle between the mean planes, α, of 11.3° and that also have large slip angles β of 36.9° and γ of 39.1°, giving a centroid−centroid distance of 3.88 Å and an average perpendicular distance between the mean planes of 3.00 Å; these geometric features are outside the accepted values for a normal π···π stacking interaction.[21] As such, the bridging ligands separate silver centers beyond any reasonable metallophilic considerations (5.43 Å).

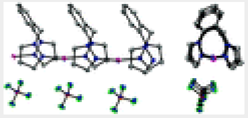


Figure 6. Two views of the coordination polymer chain of **2a**. Left: Chain propagating along the *b* axis. Right: View of the chain down the *b* axis.

In each of the two nearly identical crystallographically independent cyclic dications in **2a**·0.5acetone (Table 1 and Figure 7), two ligands span silver centers in such a manner that one silver (Ag2 or Ag4) connects the aryl pyrazolyl of each ligand while the other silver (Ag1 or Ag3) connects the benzylic pyrazolyl of each ligand. The two ligands in each cyclic dication exhibit different conformations (Table 1). One ligand adopts a staggered,syn conformation (average τ_{N4} = 51.5° and τ_{NC} = 53.1°) with offset and fairly coplanar pyrazolyls (α = 16°, β = 31°, and γ = 26° with an average centroid−centroid distance of 3.54 Å and with a perpendicular separation of 3.16 Å), whereas the second ligand adopts a gauche,syn conformation (average τ_{N4} = 20.5° and τ_{NC} = 145.5°) that places pyrazolyl rings further apart and closer to orthogonality (the angle between the mean pyrazolyl planes is 128° in each dication). The two ligands in each dication are skewed with respect to each other such that the two bound silver centers are well-separated (Ag1···Ag2 of 3.767 Å and Ag3···Ag4 of 3.775 Å) excluding any Ag−Ag interactions. In both **2a** and **2a**·0.5acetone, the ligand conformations are secured by multiple noncovalent interactions that also organize the overall supramolecular structures (see the Supporting Information for complete details).

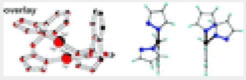


Figure 7. Overlay of two crystallographically independent cyclic dications in **2a**·0.5acetone (left) with views of gauche,syn (center) and staggered,syn (right) ligand conformations that occur within each cyclic dication.

When the analytically pure sample of **2b** was subject to vapor diffusion of Et_2O into an acetone solution of the complex, two types of crystals formed in the same vial, the majority being small bar-shaped crystals of solvent-free **2b** (Figure 4D) and a few larger colorless blocks of an acetone solvate **2b**·acetone (Figure 4E), where both were coordination polymers. As indicated in Table 1, the silver centers in each **2b** and **2b**·acetone are nominally two-coordinate with short Ag−N distances and nearly linear N−Ag−N bonds ($Ag{-}N_{avg}$ = 2.125 Å, N−Ag−N = 166.3° for **2b** and $Ag{-}N_{avg}$ = 2.133 Å, N−Ag−N = 168.7° for **2b**·acetone) where the metal centers connect the arylpyrazolyl arm of one ligand to the benzylic dimethylpyrazolyl arm of a neighboring ligand. As indicated later, in **2b**·acetone, the acetone is very weakly associated with silver and can only be considered as a secondary interaction. As can be seen in Figure 8 and as summarized in Table 1, there are relatively small but significant differences in the staggered,anti ligand conformations in each **2b** and **2b**·acetone (with τ_{N4} = 173.1° and τ_{NC} = 52.9° for the former and τ_{N4} = 165.5° and τ_{NC} = 50.6° for the latter) that arise, in part, by differences in the secondary coordination sphere of silver and the noncovalent interactions organizing the supramolecular structures.

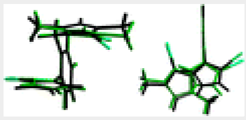


Figure 8. Overlay of cationic monomer units in **2b** (black) and **2b**·acetone (green) with silver in cyan.

The extended structure of solvent-free **2b** reveals a helical coordination polymer formed as a result of the divergent disposition of nitrogen donors on the pz and pz* groups and the large dihedral angle between the mean planes of the pz and pz* rings, α, of 30°. This large dihedral angle combined with and two large slip angles β of 36° and γ of 31° gives a centroid−centroid distance of 3.93 Å, parameters that are outside the accepted ranges for a π···π-stacking interaction.[21] The Ag···Ag separation of 6.17 Å in **2b** is substantially longer than 5.43 Å found in **2a** (mainly because of the discrepancy in τ_{N4} in each complex, as above). In the crystal structure of **2b**, the coordination polymer adopts a right-handed 3_1 helical arrangement along the crystallographic *c* axis (Figure 9a). It is likely that the bulk crystalline sample contains equal quantities of crystals from each of the enantiomorphous space groups $P3_1$ and $P3_2$ and that it was fortuitous that the crystal selected was from the former, composed of right-handed helices, rather than the latter, presumably composed of left-handed helices. In the right-handed helix, the angle between three adjacent silvers, Ag−Ag−Ag, is 147°, and by the plotting of centroids between three neighboring silver centers, which represent the loci of the helix, the pitch and rise were found to be 17.47 and 5.825 Å, respectively. Examination of the supramolecular structural features shows that the extended coordination sphere [$\sum_{vdw}$(Ag,X) = 0.2 Å] of silver is distorted octahedral as a result of Ag···π and Ag···F interactions (Figure 9c,d and Table 3). Specifically, silver is sandwiched between aryl rings with Ag1−C6 = 2.90 Å and Ag−C1 = 3.05 Å where the C1−Ag−C6 angle is 121°, at the upper end of the range found for other Ag···π interactions. The tetrafluoroborate is anchored to silver in an asymmetric κ^2 mode with Ag−F1 = 2.77 Å and Ag−F2 = 2.99 Å.[22] As such, 3-fold symmetry of various CH···F interactions (green lines in Figure 9) with the metrical parameters given in Table 3 gives a close-packed arrangement of helices, completing the three-dimensional supramolecular structure.

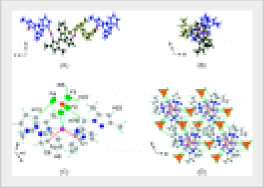


Figure 9. (A) View of **2b** along the *a* axis of the 3_1 helical coordination polymer chain. (B) View of the helical chain along the *c* axis. (C) View of the extended coordination sphere around silver in the helical chain emphasizing Ag···F (cyan dashed lines), Ag···π (red dashed lines), and CH···F (green dashed lines) interactions. (D) View down the *c* axis of four chains assembled by CH···F interactions of tetrafluoroborate anions (orange tetrahedra).

Table 3. Geometries of Various Noncovalent Interactions in 2b[a]

B−F ···Ag interactions	**B−F (Å)**	**F···Ag (Å)**	**B−F···Ag (deg)**
B1−F1···Ag1	1.399	2.765(4)	106
B1−F2···Ag1	1.385	2.985(3)	96

Ag···π (shortest contact, X)	**Ag−X (Å)**	**Ag−Ct (Å)**	**⊥ Dist (Å)**	**β (deg)**	**rs (Å)**
Ag1···C6	2.898(4)	3.201	2.875	26	1.408
Ag1···C1	3.048(5)	3.568	2.987	33	1.952

donor (D)–H···acceptor (A)	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (deg)
C7–H7b···F2	0.99	2.52	3.485(6)	166
C5–H5···F3	0.95	2.27	3.214(7)	173
C22–H22···F3	0.95	2.40	3.307(5)	161
C13–H13···F4	0.95	2.54	3.485(7)	171

[a] Ct(*i*) = centroid of the ring-containing atom *i*; β = angle between the Ct(*i*)–Ag vector and normal to the plane containing Ct(*i*); rs = ring slippage; ⊥ = projection of a heavy atom on the least-squares mean plane of the ring and centroid.

The subtle differences in the ligand geometry imposed by the secondary coordination sphere of silver differentiate the 3_1 helical chains in nonsolvated **2b** in Figure 9 from that of the nonhelical polymeric structure of **2b**·acetone in Figure 10. In **2b**·acetone, the individual “**2b**·acetone” moieties of the chain are related via a *c*-glide operation, as can be seen in Figure 10B,C; the repeat positions of the acetone and tetrafluoroborate groups signify that the chain does not propagate along a 2_1-screw axis (the latter symmetry operation is coincident with the *b* axis in Figure 10D). As indicated earlier, the ligand conformation in **2b**·acetone is similar to that in **2b**, but in **2b**·acetone, the pz and pz* rings are closer together and more coplanar relative to those in **2b**. That is, the centroid–centroid distance of 3.67 Å, the dihedral angle between the mean planes, α, of 21°, and the slip angles β of 28° and γ of 26° are all smaller in magnitude in **2b**·acetone than in **2b** (vide supra), yet these values are still outside the accepted ranges for an effective π–π interaction. Moreover, while the nitrogen donors of the pz and pz* groups are divergent in each complex, the angle between N–Ag bond vectors within the ligand is more obtuse in **2b**· acetone (86°) than in **2b** (70°). The metrical parameters of the noncovalent interactions in **2b**·acetone are listed in Table 4. The coordination geometry about silver including secondary interactions can be described as square pyramidal with an AgN_2OFC kernel as a result of a presumably weak interaction between silver and oxygen atoms of acetone (with a long Ag···O distance of 2.815 Å; violet dashed lines in Figure 10), κ^1F coordination of tetrafluoroborate (Ag···F1 = 2.993 Å; cyan dashed lines in Figure 10), and a weak Ag···π interaction with the carbon meta to the aryl-bound pyrazolyl and ortho to the benzylic pyrazolyl (Ag···C5 = 3.00 Å; red dashed lines in Figure 10). Two types of noncovalent interactions secure the one-dimensional chain. First, a CH···π interaction[24] (solid pink lines in Figure 10) occurs between a methyl hydrogen donor of the coordinated acetone and the pyrazolyl acceptor of a neighboring ligand. Second, the tetrafluoroborate anion, which is anchored to silver, also participates in a bifurcated CH···F interaction (green dashed lines in Figure 10) involving F2 and a benzylic hydrogen [C5–H5···F2 (2.45 Å, 158°)] along with an aryl hydrogen ortho to the benzylic pyrazolyl [C7–H7A···F2 (2.56 Å, 159°)]. Two additional CH···F interactions involving F3 and F4 organize the chains into a three-dimensional supramolecular structure.

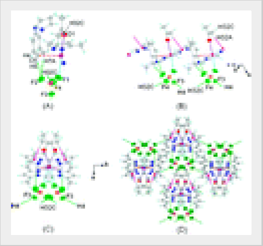


Figure 10. Molecular and supramolecular structures of **2b**·acetone. (A) ORTEP diagram of the asymmetric unit (thermal ellipsoids drawn at 50% probability). (B) View of the polymeric chain with an extended coordination environment around the silver. (C) View of the chain along the *c* axis. (D) View of three-dimensional packing along the *c* axis.

Table 4. Geometries of Various Noncovalent Interactions in 2b·acetone

B–F ···Ag interaction	**B–F (Å)**	**F···Ag (Å)**	**B–F···Ag (deg)**
B1–F1···Ag1	1.360	2.9965(17)	136

C–O ···Ag interaction	**C–O (Å)**	**O···Ag (Å)**	**C–O···Ag (deg)**
C31–O1···Ag1	1.216	2.8120(16)	133

Ag···π (shortest contact, X)	**Ag–X (Å)**	**Ag–Ct (Å)**	**⊥ Dist (Å)**	**β (deg)**	**rs (Å)**
Ag1···C5	2.9996(17)	3.410	2.881	32	1.824

donor (D)–H···acceptor (A)	**D–H (Å)**	**H···A (Å)**	**D···A (Å)**	**D–H···A (deg)**	**γ (deg)**
C32–H32A···[Ct(N21)]	0.98	2.83		157	17

donor (D)–H···acceptor (A)	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (deg)	γ (deg)
C4–H4···F3	0.95	2.51	3.410(3)	159	
C5–H5···F2	0.95	2.45	3.345(3)	158	
C7H7A···F2	0.99	2.56	3.501(3)	159	
C32–H32C···F4	0.98	2.39	3.221(3)	142	

Ct(*i*) = centroid of the ring-containing atom *i*; β = angle between the Ct(*i*)–Ag vector and normal to the plane containing Ct(*i*); γ = angle CH–Ct(*i*) and normal to plane containing Ct(*i*); rs = ring slippage;⊥ = projection of a heavy atom on the least-squares mean plane of the ring and centroid.

Diffusion of a layer of Et_2O into an acetonitrile solution of **3**·0.5THF resulted in a species best described by the formula $\{[Ag(CH_3CN)](\mu\text{-}cis\text{-}pz_2naphth)_2[Ag(CH_3CN)_2]\}(BF_4)_2\cdot CH_3CN$ (Figure 4F), which, for simplicity, will be referred to as **3**·$2CH_3CN$. The complex contains a discrete cyclic bimetallic dication, where both ligands adopt desirable eclipsed,syn conformations (one with τ_{N4} = 4.1° and τ_{NC} = 0.1° and one with τ_{N4} = 2.6° and τ_{NC} = 8.5°). The ligands sandwich two silver(I) centers in such a manner as to give a pseudochair conformation to the 16-membered $Ag_2N_8C_6$ring, where the naphthyl rings of the ligands are directed in opposite directions away from the mean N_4 plane formed by the silver-bound nitrogen atoms of the pyrazolyl groups (N11, N21, N31, and N41). Interestingly, the primary coordination sphere around the silver atoms is nominally three-coordinate (slightly distorted T-shaped) as a result of coordinating two nearly linear N(pyrazolyl) donors (Ag1–N_{avg} = 2.175 Å, N11–Ag1–N31 = 152.4° and Ag2–N_{avg} = 2.213 Å, N21–Ag2–N41 = 147.6°) and one acetonitrile (Ag1–N71 = 2.446 Å and Ag2–N81 = 2.398 Å) to give a sum of angles of about Ag1 = 353.4° and about Ag2 = 353.0°. For Ag2, there is an additional rather long Ag···N contact for a weakly bound acetonitrile (Ag1–N71 = 2.519 Å), which is probably best described as a secondary interaction given its length[10b] and the apparent sensitivity of the Ag–N(pyrazolyl) bond distances to the metal's primary coordination geometry (two-coordinate Ag–$N_{avg.}$ ~ 2.10–2.14 Å, three-coordinate 2.2–2.3 Å, and four-coordinate 2.3–2.4 Å). It should be noted that the fourth acetonitrile is not associated with any silver centers and that the overall dication geometry may be influenced, in part, by crystal packing forces that afford the overall three-dimensional supramolecular structure (see the Supporting

Information). Nonetheless, the two metal atoms in **3**·2CH_3CN are constrained to an Ag1−Ag2 separation of 3.19 Å, the shortest such distance of all of the new compounds reported here. This Ag−Ag distance is less than twice the sum of the van der Waals radii minus 0.2 Å and is intermediate between 2.78 Å found in the silver complex of 1,2,4,5-tetrakis(pyrazol-1-ylmethyl)benzene[23] and 3.37 Å found in $\{[Ph_2P(O)CH_2C(pz)_3Ag]_2(THF)_2\}(BF_4)_2$,[19] where Ag−Ag interactions were proposed (supported by semiempirical Fenske−Hall calculations, in the latter case). It is noted that vacuum-dried single crystals lose acetonitrile molecules of solvation and the sample absorbs atmospheric moisture because elemental analyses are consistent with the formula **3**·3H_2O·0.5CH_3CN.

Solution Properties

The solution and solid-state structures of ionic silver(I) coordination compounds are generally thought to be quite different from one another, given the labile nature of the d^{10} metal centers in Lewis basic solvents (in which the complexes are soluble). As such, solution spectroscopic data can be deceptively simple (or ambiguous), requiring a combination of techniques such as NMR and positive-ion electrospray ionization mass spectrometry [ESI(+)-MS] to glean any useful information about possible solution structures. For example, the ^1H NMR spectra in CD_3CN for each silver(I) complex examined here showed only a downfield shift in resonances relative to those obtained in spectra of the free ligands. For complexes of pz_2prop, pz_2Bn, and pzBnpz*, the methylene hydrogen atoms would be inequivalent if the solid-state structures and ligand conformations were retained in solution. As such, additional resonances characteristic of AB splitting patterns (in addition to other ^3J couplings for the propyl derivative) are expected. In these cases, such splitting patterns of resonances were not observed, indicating a stereochemically nonrigid ligand environment due to either rapid conformational averaging (where silver remains bound to pyrazolyls), dissociative processes, or both. It was not possible to slow any potential dynamic process occurring in CD_3CN upon cooling to −35 °C so as to be distinguished by NMR. Clearly, ESI(+)-MS data (vide infra) provide more insight into the structural nature in solution in all of the above cases.

ESI-MS data are thought to accurately reflect the solution structures of coordination complexes and coordination polymers.[25] The ESI(+)-MS data obtained from either crystals or the as-isolated powders of the silver complexes dissolved in CH_3CN were nearly identical, with only the relative intensities of the peaks changing (vide infra). Taken altogether, the ESI(+)-MS data suggest that all of the present complexes are predominantly dissociated in solution. Peaks for solvated silver ions $[Ag(CH_3CN)_n]^+$ (n = 2−4) and protonated ligands $[HL]^+$ were present, those of dimeric bimetallic ions such as $[Ag_2L_2]^{2+}$ were only sometimes observed, but those for higher oligomers $[Ag_2L_3]^+$, $[Ag_3L_3]^{2+}$, etc., were never observed. It is noteworthy that the ESI(+)-MS spectra of silver(I) coordination polymers of more strongly donating multitopic ligands have shown peaks for higher-order oligomeric species.[9]

In every case reported here, the major peaks in the ESI(+)-MS spectrum (see the data for **3**·CH_3CN in Figure 11 as an example) correspond to $[AgL_2]^+$, $[AgL(CH_3CN)]^+$, $[AgL]^+$, $[Ag(CH_3CN)_2]^+$ ($m/z = 189$), $[HL]^+$, [HL-pz (or pz* for **2b**)]$^+$, and $[Ag(CH_3CN)]^+$ ($m/z = 148$), a pattern consistent with that observed for other silver(I) complexes of poly(pyrazolyl)organyls.[26] Interestingly, for **1** or **2a**, peaks for dimeric bimetallic ions such as $[Ag_2L_2]^{2+}$ or $\{[Ag_2L_2](BF_4)\}^+$were absent even though the solid-state structure contained such an ion. Surprisingly, in the case of **2b**, minor peaks (ca. 1% intensity) for dimeric bimetallic ions $\{[Ag_2L_2](X)\}^+$ ($X = BF_4^-$, Cl^-, and formate$^-$; the latter two anions arise from the nature of the MS experiments) were observed, even though the solid-state structure showed a coordination polymer. For **3**, similar peaks for $\{[Ag_2L_2](X)\}^+$ [$X = Cl^-$ ($m/z = 771$), formate$^-$ ($m/z = 781$), and BF_4^- ($m/z = 823$)] ions were observed. In addition, there was an unusual peak at $m/z = 517$, which appears to correspond to the $[NaAgL(CH_3CN)(BF_4)]^+$ ion, where the sodium originates from a common impurity in the MS experiments rather than from the crystals that were examined. All of these data are indicative of substantial dissociative processes occurring in solution and, perhaps, also of the relative efficacy for self-assembly processes to occur during the desolvation phase of the MS experiment.

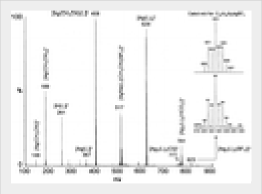


Figure 11. Representative ESI(+)-MS of **3**·0.5THF in acetonitrile.

Summary

Four di-*N*-pyrazolylorganyl ligands, one known and three new derivatives with pyrazolyls spaced three atoms apart by carbon backbones with differing degrees of conformational flexibility, have been prepared in order to delineate the ligand design factors most likely to afford metallophilic interactions in coordination complexes. The copper-catalyzed amination reactions described by Taillefer et al. and Buchwald et al. provide an alternative, convenient means for obtaining *N*-pyrazolylaryls with respect to nucleophilic aromatic substitution reactions that have been traditionally used to access such derivatives. Reactions of the various ligands with $AgBF_4$ afforded 1:1 complexes that contain low-coordinate silver(I), a requisite feature that allows the metal center to participate in a variety of noncovalent secondary [$Ag{-}\pi$, $Ag\cdots X$ ($X = F, N, O$), and $d^{10}{-}d^{10}$] interactions. The results presented here along with extensive work on related systems by other groups[13,19,26] show that Ag−N(pyrazolyl) bond distances are sensitive to the primary coordination number of the metal with $Ag{-}N_{avg} \sim 2.10{-}2.14$ Å for two-coordinate silver, $Ag{-}N_{avg} \sim 2.2{-}2.3$ Å for three-coordinate silver, and $Ag{-}N_{avg} \sim 2.3{-}2.4$ Å for four-coordinate silver. The striking difference in structures between the 1:1

silver/dipyrazolylpropane complexes with the coordinating nitrate and noncoordinating tetrafluoroborate anions is noteworthy. With the nitrate, a complicated structure with two types of silver centers is obtained. When silver is three-coordinate, a cyclic bimetallic species is formed, whereas when silver is four-coordinate, a polymeric sheet is formed. In both cases, the secondary coordination sphere is dominated by Ag⋯O−NO_2 contacts, and the ligand conformations (perhaps dictated by extensive CH⋯O noncovalent interactions[27]) are such that neighboring silver centers are greatly separated (Ag⋯Ag > 5.3 Å). When the noncoordinating tetrafluoroborate is employed instead of nitrate, a simple structure with three-coordinate silver is obtained (with a coordinated acetonitrile solvent) that contains a cyclic bimetallic species with shorter intracationic Ag−Ag separation (3.7 Å), but this distance is still outside twice the sum of the van der Waals radii of silver. In this latter case, the silver is involved in intra- and intercationic Ag−π secondary interactions that assemble cations into one-dimensional chains. The ligand conformation and supramolecular structure are bolstered by various CH⋯F interactions involving the ligands and the tetrafluoroborate anion. With the relatively more rigid pz_2Bn ligand, both cyclic bimetallic dications (Ag⋯Ag > 5.3 Å) and one-dimensional coordination polymers (Ag⋯Ag > 5.3 Å), each with two-coordinate silver, are formed, depending on the solvent of crystallization. With the relatively less polar and less donating solvent, acetone, the former is obtained, but with the more polar and more strongly donating solvent, acetonitrile, the latter is obtained; in neither case is solvent bound to the silver center in the solid state, but acetone fills channels available by crystal packing of the former. Interestingly, by replacement of the benzylic pyrazolyl in pz_2Bn with a dimethylpyrazolyl, a mixture of two different coordination polymers, each with two-coordinate silver and with Ag−Ag separations greater than 6.1 Å, is obtained under crystallization conditions: a solvent-free 3_1-helical chain and an acetone solvate with a nonhelical chain. In these two cases, differences in the secondary coordination sphere (the former contains two Ag−π and two Ag⋯F interactions, while the latter has one Ag−π, one Ag⋯F, and one Ag⋯O interaction) likely dictate the ligand conformations in each of the two forms. Finally, the rigid 1,8-dipyrazolylnaphthalene ligand (pz_2naphth) was successfully used to enforce a short intracationic Ag⋯Ag contact (3.19 Å) in a cyclic bimetallic $[Ag_2(pz_2\text{naphth})_2]^{2+}$ framework. This Ag⋯Ag contact distance is intermediate in length compared to other related systems that were proposed to exhibit argentophilic interactions. In all cases, the combined NMR and ESI(+)-MS data indicate that the solid-state structures are not retained in a CH_3CN solution because extensive dissociation likely occurs in this solvent.

Conclusions

While the short metal−metal contacts in the $[Ag_2(pz_2\text{naphth})_2]^{2+}$ framework did not bestow any unusual photophysical properties to this complex in either the solid state or solution, the structural result is an important first step toward the longer term goal of discovering the design features that would promote self-assembled, extended metallophilic contacts. In this regard, it can be conjectured that more strongly donating ligands (such as negatively charged species) built upon the 1,8-naphthyl spacer (and perhaps even the other more flexible spacers) would be better equipped to confer greater solution stability to the self-assembled systems. More importantly, more electron-rich or anionic systems may also offset any electrostatic repulsion between proximal silver(I) centers (allowing shorter contacts) and could render a closer energy separation between the metal's filled $4d^{10}$ and virtual 5s orbitals that may bestow interesting photophysical properties in the resulting complexes. Synthetic efforts toward these goals are currently underway in our laboratory.

-

Acknowledgment

J.R.G. thanks Marquette University and the Petroleum Research Fund for financial support.

-

References

[1] In *Molecular Electronics*; Jortner, J. and Ratner, M., Eds.; Blackwell Science, Ltd.: Malden, MA, **1997**.

[2] For example, see: (a) Fukuzumi, S., Honda, T., Ohkubu, K., and Kojima, T. *Dalton Trans.* **2009**,3880 (b) Rybtchinski, B., Sinks, L. E., and Wasielewski, M. R. *J. Am. Chem. Soc.* **2004**, 126, 12268

[3] (a) See the special issue on silver(I) coordination polymers: *Aust. J. Chem.* **2006**, 59, 1. (b) Khlobystov, A. N., Blake, A. J., Champness, N. R., Lemenovskii, D. A., Majouga, A. G.,Zyk, N. V., and Schröder, M. *Coord. Chem. Rev.* **2001**, 222, 155 (c) Kalf, I.,Braun, M., Wang, Y., and Englert, U. *CrystEngComm* **2006**, 8, 916 (d)Feazell, R. P., Carson, C. E., and Klausmeyer, K. K. *Inorg. Chem.* **2006**, 45, 935 (e) Oh, M., Stern, C. L., and Mirkin, C. A. *Inorg. Chem.* **2005**, 44, 2647 (f) Mann, K. L. V., Jeffery, J. C., McCleverty, J. A., and Ward, M. D. *J. Chem. Soc., Dalton Trans.***1998**, 3029 (g) Schultheiss, N., Powell, D. R., and Bosch, E. *Inorg. Chem.* **2003**,42, 8886 and references cited therein. (h) Beloso, I., Castro, J.,García-Vázquez, J. A., Pérez-Lourido, P., Romero, J., and Sousa, A. *Inorg. Chem.* **2005**, 44, 336

[4] (a) Pyykko, P. *Chem. Rev.* **1997**, 97, 597 (b) For other leading references, see: Rasika Dias, H. V., Gamage, C. S. P., Keltner, J., Diyabalanage, H. V. K., Omari, I.,Eyobo, Y., Dias, N. R., Roehr, N., McKinney, L., and Poth, T. *Inorg. Chem.* **2007**, 46, 2979

[5] (a) Ma, N. L. *Chem. Phys. Lett.* **1998**, 297, 230 (b) Klippenstein, S. I. andDunbar, R. C. *J. Phys. Chem. A* **1997**, 101, 3338 (c) Munakata, M.,Wu, L. P., Ning, G. L., Kuroda-Sowa, T., Maekawa, M., Suenaga, Y., and Maeno, N. *J. Am. Chem. Soc.***1999**, 121, 4968

(d) Munakata, M., Wu, L. P., Sugimoto, K.,Kuroda-Sowa, T., Maekawa, M., Suenaga, Y., Maeno, N., and Fujita, M. *Inorg. Chem.* **1999**, 38, 5674 (e) Lindeman, S. V., Rathore, R., and Kochi, J. K. *Inorg. Chem.* **2000**, 39,5707 (f) Hubig, S. M., Lindeman, S. V., and Kochi, J. K. *Coord. Chem. Rev.* **2000**, 200–202, 831

[6] For instance, 1,2-bis(imidazolylmethyl)benzene with a four-atom spacer between imidazolyl rings was capable of adopting a desirable geometry for rectangular bimetallic complexes that exhibit short intracationic Ag···Ag contacts. See: (a) Zhou, T., Zhang, X., Chen, W., and Qiu, H *J. Organomet. Chem.* **2008**, 693,205 (b) Also see: Hartshorn, C. M. and Steel, P. J. *Inorg. Chem. Commun.* **2000**,3, 476.

[7] Bondi, A. *J. Phys. Chem.* **1964**, 68, 441

[8] Jung, O.-S., Kim, Y. J., Lee, Y.-A., Kang, S. W., and Choi, S. N. *Cryst. Growth Des.* **2004**, 4, 23

[9] Silva, R. M., Smith, M. D., and Gardinier, J. R. *Inorg. Chem.* **2006**, 45, 2132

[10] (a) Awaleh, M. O., Badia, A., and Brisse, F. *Cryst. Growth Des.* **2005**, 5, 1897 (b) Koizumi, T. and Tanaka, K. *Inorg. Chim. Acta* **2004**, 357, 3666 (c)Chen, C. Y., Zeng, J. Y., and Lee, H. M. *Inorg. Chim. Acta* **2007**, 360, 21

[11] Clegg, W., Cooper, P. J., Lockhart, J. C., and Rushton, D. J. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1994**, C50, 383

[12] McMorran, D. A., Pfadenhauer, S., and Steel, P. J. *Inorg. Chem. Commun.* **2002**, 5, 449

[13] (a) Reger, D. L., Gardinier, J. R., Semeniuc, R. F., and Smith, M. D. *Dalton Trans.* **2003**, 1712 (b) Reger, D. L., Gardinier, J. R., Grattan, T. C., Smith, M. R., and Smith, M. D. *New J. Chem.* **2003**, 27, 1670

[14] McMorran, D. A., Pfadenhauer, S., and Steel, P. J. *Aust. J. Chem.* **2002**, 55, 519

[15] The influence of BF_4^- and other anions on assisting to organize structures has been previously addressed. See: (a) Manzano, B. R., Jalón, F. A., Soriano, M. L., Carrión, M. C., Carranza, M. P., Mereiter, K.,Rodríguez, A. M., de la Hoz, A., and Sánchez-Migallón, A. *Inorg. Chem.* **2008**, 47, 8957 (b) Wei, K.-J., Ni, J., Liu, Y., and Liu, Q.-L. *Eur. J. Inorg. Chem.* **2007**, 3868 (c) Withersby, M. A., Blake, A. J., Champness, N. A., Hubberstey, P., Li, W.-S., andSchroder, M. *Angew. Chem., Int. Ed.* **1997**, 36, 2327

[16] Liddle, B. J., Silva, R. M., Morin, T. J., Macedo, F. P., Shukla, R., Lindeman, S. V., and Gardinier, J. R. *J. Org. Chem.* **2007**, 72, 5637

[17] (a) Taillefer, M., Xia, N., and Ouali, A. *Angew. Chem., Int. Ed.* **2007**, 46, 934 (b) Cristau, H.-J., Cellier, P. P., Spindler, J.-F., and Taillefer, M. *Eur. J. Org. Chem.* **2004**,695 (c) Christau, H.-J., Cellier, P. P., Spindler, J.-F., and Taillefer, M. *Chem.—Eur. J.* **2004**, 10, 5607

[18] Antilla, J. C., Baskin, J. M., Barder, T. E., and Buchwald, S. L. *J. Org. Chem.* **2004**, 69, 5578

[19] Reger, D. L., Semeniuc, R. F., Radu, F., and Smith, M. D. *Inorg. Chem.* **2005**, 44, 2995

[20] Grepioni, F., Cojazzi, G., Draper, S. M., Scully, N., and Braga, D. *Organometallics* **1998**, 17, 296

[21] Janiak, C. *J. Chem. Soc., Dalton Trans.* **2000**, 3885

[22] Beck, W. and Suenkel, K. *Chem. Rev.* **1988**, 88, 1405

[23] Hartshorn, C. M. and Steel, P. J. *Aust. J. Chem.* **1997**, 50, 1195

[24] Takahashi, H., Tsuboyama, S., Umezawa, Y., Honda, K., and Nishio, M. *Tetrahedron* **2000**, 56,6185

[25] (a) Miras, H. N., Wilson, E. F., and Cronin, L. *Chem. Commun.* **2009**, 1297
(b) Baytekin, B., Baytekin, H. T., and Schalley, C. A. *Org. Biomol. Chem.* **2006**, 4,2825

[26] (a) Reger, D. L., Wright, T. D., Semeniuc, R. F., Grattan, T. C., and Smith, M. D. *Inorg. Chem.* **2001**, 40,6212 (b) Reger, D. L., Semeniuc, R. F., and Smith, M. D. *Eur. J. Inorg. Chem.* **2002**, 543 (c) Reger, D. L., Semeniuc, R. F., and Smith, M. D. *Inorg. Chem. Commun.* **2002**, 5, 278 (d) Reger, D. L., Gardinier, J. R., andSmith, M. D. *Inorg. Chem.* **2004**, 43, 3825

[27] (a) Taylor, R. and Kennard, O. *J. Am. Chem. Soc.* **1982**, 104, 5063
(b)Steiner, T. and Saenger, F. *J. Am. Chem. Soc.* **1992**, 114, 10146

Supporting Information

Experimental procedures, analytical and spectral characterization data, expanded discussions of structural findings, and crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.