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The Synthesis, Molecular Structures, and Supramolecular Architecture of Amine Adducts of Bis(pentafluorophenyl)zinc

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A series of eight adducts of the form $(RR'R''N)_2\cdot Zn(C_6F_5)_2$ have been prepared through treatment of the Lewis acid $Zn(C_6F_5)_2$ with 2 equiv of the corresponding amine (R = ^tBu or CH_2Ph, R′ = R″ = H; R = R′ = Me or CH_2Ph, R″ = H; R = Me, R′ = CH_2Ph, R″ = H; RR′ = *cyclo*-C_4H_8 or *cyclo*-C_5H_{10}, R″ = H; R = R′ = Me, R″ = CH_2Ph). The solid-state structures of all eight compounds have been elucidated by single-crystal X-ray diffraction. In each case the geometry about the zinc atom is essentially tetrahedral. However, there is considerable variation in the supramolecular architectures in the solid state. A number of types of noncovalent interactions are observed including phenyl−pentafluorophenyl stacking, X−H···F−C contacts, and offset face-to-face contacts between pentafluorophenyl rings, giving rise to one-, two-, and three-dimensional supramolecular structures. In our examples we find that no one intermolecular interaction predominates.

Introduction

The widely accepted definition of supramolecular chemistry offered by Lehn describes "chemistry beyond the molecule, based on organized entities of higher complexity that result from association of two or more chemical species held together by intermolecular forces".[1] The dative bond has long been the intermolecular interaction of choice in supramolecular coordination chemistry.[2] However, recently a number of research groups have met with considerable success by utilizing supramolecular synthons familiar to organic chemists to assemble supramolecular organometallic structures without recourse to dative bonds.[3−11] A series of observations by research groups including our own that metal−pentafluorophenyl fragments participate in a variety of intermolecular interactions prompted us to investigate the supramolecular assembly of these organometallic species through the attractive forces unique to such compounds.

Organofluorine has a special place in supramolecular chemistry.[12] Our interest is primarily in three key intermolecular interactions in which pentafluorophenyl groups participate: stacking interactions with aryl groups; as hydrogen bond acceptors; and in offset face-to-face arrangements with other perfluoroaryl rings (**I**−**III** in Chart 1). The first is perhaps the best known attraction and results from the opposing quadrupoles of the perfluorophenyl and phenyl groups.[13] Since the original discovery by Patrick and Prosser, it has been employed in a number of elegant studies to influence supramolecular assembly.[14−17] Though not as numerous as the organic examples, solid-state structures of organometallic compounds that exhibit aryl−perfluoroaryl stacking have been reported.[18,19]

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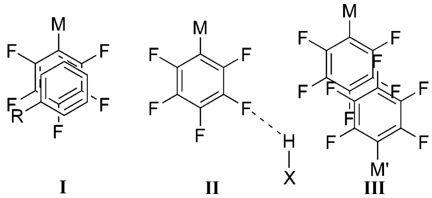
Chart 1



I **II** **III**

Since the seminal papers by Dunitz[20] and O'Hagan and Howard,[21] there has been increased interest in hydrogen bonding to weak organofluorine acceptors.[22,23] We and others have recently reported intramolecular bifurcated N−H···F···H−N hydrogen bonding in a number of neutral and anionic adducts of $B(C_6F_5)_3$.[24,25] Intermolecular X−H···F interactions have been found in the solid-state structures of a number of transition and main group organometallics with perfluorophenyl substituents.[24d,e,26]

Despite their opposite quadrupole moment the offset-face-to-face (*off*) interaction between perfluoroaromatic groups is comparable to the often observed supramolecular motif in which hydroaromatics form *off* pairs or stacks.[27,28] Such *off* interactions between pairs or stacks of C_6F_5 groups have been reported for organometallic and coordination compounds with pentafluorophenyl substituents.[18c,29] Dance surveyed the crystallographic structure database for the groups $E(C_6F_5)_3$ and $E(C_6F_5)_4$ (where E is an element from groups 13−15) and found a number of examples of both 4-fold and 6-fold perfluorophenyl "embraces" comprised of both *off* and edge-to-face (*ef*) interactions.[27]

Bis(pentafluorophenyl)zinc was chosen for this investigation because we reasoned that the one-to-one correspondence between the number of C_6F_5 groups and Lewis acidic sites would favor the formation of infinite supramolecular assemblies involving interactions of types **I**−**III**. Supramolecular architectures constructed using the coordination chemistry of zinc are well-known and have been considered for applications in nonlinear optics[30] and as gas storage materials.[31,32] There is also increasing interest in the combination of dative and other noncovalent interactions.[33] The supramolecular assembly of zinc complexes solely by truly intermolecular interactions is a somewhat less developed field.[34] Here we report the synthesis,

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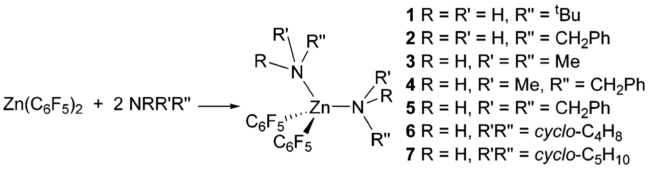
Scheme 1



1-8

Table 1. δ(N*H*) for the Free Amines and Zinc Adducts

	δ(N*H*)/ppm		
compound	free amine	adduct	$\Delta\delta$ (δ_H adduct − δ_H amine)
1	0.77	2.52	1.75
2	0.86	1.61	0.75
3	0.23	1.40	1.17
4	0.71	2.29	1.58
5	1.09	2.90	1.81
6	0.87	2.07	1.20
7	0.87	2.24	1.37

molecular geometry, and intermolecular interactions of eight amine adducts of $Zn(C_6F_5)_2$.

Results and Discussion

Treatment of $Zn(C_6F_5)_2$ with 2 equiv of the amines $^tBuNH_2$, $PhCH_2NH_2$, Me_2NH, $PhCH_2(Me)NH$, $(PhCH_2)_2NH$, *cyclo*-C_4H_8NH, *cyclo*-$C_5H_{10}NH$, or $PhCH_2NMe_2$ in toluene results in the formation of the adducts **1**−**8** in excellent yield (Scheme 1). The elemental analyses were all in good agreement with the expected compositions.

The ^1H and ^{19}F NMR data indicated that adduct formation had taken place. Addition of further amine to NMR samples did not result in duplication of ^1H NMR resonances but did produce a chemical shift change, whereas cooling the samples to −80 °C led only to a slight broadening of the resonances. These observations suggest that the thermodynamics strongly favor the adduct formation in solution but that the amine ligands are labile. Table 1 gives the δ(N*H*) resonances for the free amines and corresponding adducts. Where present, the ^1H NMR resonance of the NH group is shifted significantly downfield on adduct formation. It is not clear to what extent this is the result of the electronic influence of adduct formation or an indicator for intramolecular N−H···F−C interaction in solution.[35]

There is little variation between the ^{19}F NMR spectra of the adducts. The *ortho*-fluorine resonances are all within a 3 ppm chemical shift range at −116.5 (±1.5) ppm, and the *para*- and *meta*-fluorine resonances vary even less, −158 (±0.5) and −162 (±0.5) ppm, respectively. We have previously reported on the intramolecular N−H···F−C hydrogen-bonding interactions of a number of tris(pentafluorophenyl)borane adducts related to **1**−**7**.[24] The room-temperature ^{19}F NMR spectra of secondary-amine borane adducts exhibit a distinctive high-field shift for the *o*-F's engaged in bifurcated intramolecular hydrogen-bonding interactions (C−F···H···F−C) between amino hydrogens and *ortho*-fluorine atoms.[24d] The ^{19}F NMR spectra of **3**−**7** provide no such evidence for solution-phase N−H···F−C interactions even on cooling to −80 °C.

Intramolecular Interactions. Single crystals of **1**, **3**, **5**, and **6** suitable for X-ray diffraction were obtained by layering light petroleum over dichloromethane solutions of the crude products and cooling to −25 °C overnight. For compounds **2**, **4**, **7**, and **8**, X-ray quality crystals were afforded by cooling concentrated toluene solutions to −25 °C. The solid-state structures of **1**−**8** were determined by X-ray crystallography and are described below. No evidence for the formation of more than one type of crystalline product was observed in any of the samples examined.

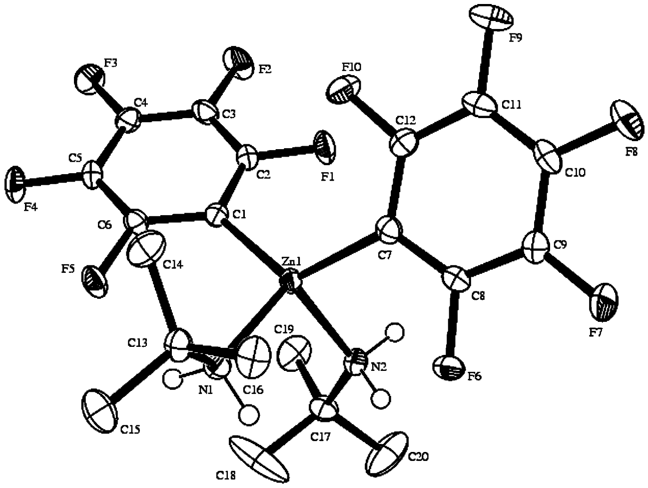


Figure 1. Molecular structure of **1**. Thermal ellipsoids are shown at the 50% probability level. H atoms on carbons have been omitted for clarity.

Compound **1** has the expected essentially tetrahedral geometry about the zinc center (Figure 1). Selected bond lengths and angles for this and other members of the series are collated in Table 2. To date, there are only five structures containing the $Zn(C_6F_5)_2$ fragment in the Cambridge Structural Database[36] including that of $Zn(C_6F_5)_2$ itself.[37] The Zn−C and Zn−N bond lengths are very similar to these reported examples. In all our compounds the single most significant distortion from ideal tetrahedral geometry is the opening of the C−Zn−C angle. For **1** the 123.05(7)° C1−Zn1−C7 bond angle is compensated by an asymmetric arrangement, which leads to smaller C7−Zn1−N2 (98.84(6)°) and N1−Zn1−N2 (101.26(6)°) angles. This asymmetry appears to result from the supramolecular structure adopted in the solid state, which is discussed below. There are two long intramolecular N−H···F−C contacts (Table 3).

The molecular structure of compound **2** is depicted in Figure 2. Here the distortion from tetrahedral to accommodate the C_6F_5 groups is more evenly distributed in a pseudosymmetric arrangement, with two very similar angles for C15−Zn1−N2 (102.66(18)°) and C21−Zn1−N1 (102.68(17)°), while N2−Zn1−N1 (110.09(17)°) is near ideal. The conformation aligns the C_6H_5 (Ph_H) and C_6F_5 (Ph_F) rings parallel to one another, but there is no overlap. The only intramolecular N−H···F−C contact of note is N1−H1c···F5, at 2.46 Å.

At the molecular level the structure of the Me_2NH adduct **3** (Figure 3), which has a 2-fold symmetry axis, is distinguished

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(34) (a) De Cires-Mejias, C.; Tanase, S.; Reedjik, J.; González-Vílchez, F.; Vilaplana, R.; Mills, A. M.; Kooijman, H.; Spek, A. L. *Inorg. Chim. Acta* **2004**, *357*, 1494. (b) Bareberio, G.; Bellusci, A.; Crispini, A.; Ghedini, M.; Golemme, A.; Prus, P.; Pucci, D. *Eur. J. Inorg. Chem.* **2005**, 181.

(35) The protic amine adducts of $B(C_6F_5)_3$ in which there is a strong bifurcated hydrogen-bonding interaction exhibit substantial downfield shifts δ(N*H*) versus the free amine: see ref 24d.

(36) Fletcher, D. A.; McMeeking, R. F.; Parkin, D. J. *Chem. Inf. Comput. Sci.* **1996**, *36*, 746.

(37) (a) Sun, Y.; Piers, W. E.; Parvez, M. *Can. J. Chem.* **1998**, *76*, 513. (b) Weidenbruch, M.; Herrndorf, M.; Schäfer, A.; Pohl, S.; Saak, W. *J. Organomet. Chem.* **1989**, *361*, 139. (c) Day, V. W.; Campbell, D. H.; Michejda, C. J. *J. Chem. Soc., Chem. Commun.* **1975**, 118. (d) Garratt, S.; Guerrero, A.; Hughes, D. L.; Bochmann, M. *Angew. Chem., Int. Ed.* **2004**, *43*, 2166.

Table 2. Bond Lengths and Angles (in Å and deg) about the Zinc Atom, with esd's in Parentheses

compound	Zn−C	Zn−N	C−Zn−C	N−Zn−N
1	2.030(2), 2.041(2)	2.1121(14), 2.1331(15)	123.05(7)	101.26(6)
2	2.025(5), 2.020(5)	2.108(4), 2.106(4)	122.48(19)	110.09(17)
3	2.0374(16)	2.1147(14)	120.22(9)	105.01(8)
4	2.0294(19), 2.028(2)	2.1038(17), 2.1133(16)	120.91(8)	101.11(6)
5	2.0301(17), 2.0277(17)	2.1874(14), 2.1504(14)	133.72(7)	112.50(5)
6	2.028(2)	2.0972(18)	125.02(12)	100.69(10)
7	2.032(5), 2.044(5)	2.094(4), 2.102(4)	120.05(18)	108.09(17)
8	2.0442(16)	2.1626(13)	117.93(9)	110.14(7)

Table 3. Hydrogen−Fluorine Contacts (in Å and deg)[a]

D−H···A	d(D−H)	d(H···A)[b]	d(D···A)	∠(DHA)	symmetry operation
1					
N1−H1a···F5	0.92	2.39	3.014(2)	125	
N2−H2b···F6	0.92	2.44	3.070(2)	125	
N2−H2a···F1	0.92	2.32	3.197(2)	159	* $1-x, 2-y, 1-z$
2					
N1−H1c···F5	0.92	2.46	3.014(5)	119	
N1−H1c···F5	0.92	2.48	3.380(5)	166	* $-x+1, -y, -z+2$
N2−H2a···F6	0.92	2.37	3.278(5)	171	* $-x, -y, -z+1$
3					
N1−H1···F1	0.93	2.42	3.0388(18)	124	$-x, y, \frac{1}{2}-z$
N1−H1···F2	0.93	2.41	3.0995(17)	131	* $x+\frac{1}{2}, y-\frac{1}{2}, z$
4					
N1−H1N···F3	0.83(2)	2.30(3)	3.119(2)	168(2)	* $x+1, y, z$
5					
N1−H1···F1	0.93	2.21	2.9402(17)	134	
N2−H2···F10	0.93	2.48	3.1266(17)	126	
6					
N1−H1···F1	0.93	2.39	2.991(2)	122	
8					
C8−H8b···F5	0.98	2.31	3.164(2)	145	
C7−H7a···F2	0.98	2.46	3.174(2)	129	* $-x+1, y-1, -z+3/2$

[a] An asterisk indicates an intermolecular interaction; esd's are in parentheses. [b] Only those contacts less than 2.50 Å are listed.

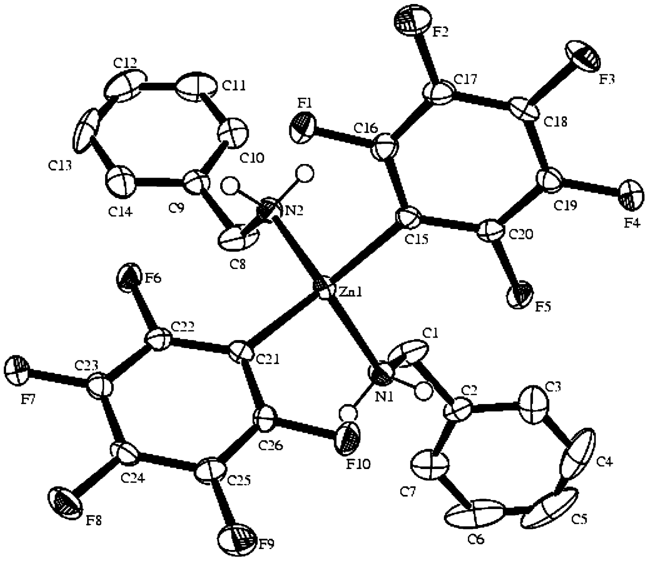

Figure 2. Molecular structure of compound **2**. Thermal ellipsoids are shown at the 50% probability level. H atoms on carbons have been omitted for clarity.

only by a symmetry-related pair of intramolecular N−H···F−C contacts (Table 3).

The molecular structure of compound **4** (Figure 4) lacks the precise symmetry of the closely related adducts **3** and **8**. Each benzyl group is orientated to reduce steric interaction with the methyl substituent. The distortion from tetrahedral geometry is largely confined to an opening of the C17−Zn1−C23 (120.91(8)°) and closing of the N1−Zn1−N2 angle (101.11(6)°). In this instance there are no noteworthy intramolecular N−H···F−C contacts.

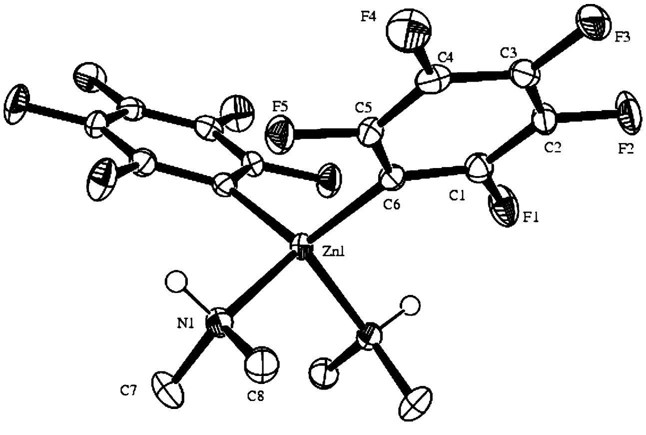

Figure 3. Molecular structure of **3** with a 2-fold symmetry axis approximately vertical in the plane of the page. Thermal ellipsoids are shown at the 50% probability level. The methyl group hydrogen atoms have been omitted for clarity.

The molecular structure of **5** (Figure 5) exhibits the only examples of intramolecular aryl−aryl interactions found in this series. Each of the two Ph_F groups associates with a benzyl substituent through a pairing interaction with one of the Ph_H rings, and the remaining pair of Ph_H rings are overlapping in an *off* fashion. The centroid···centroid distances (3.60 and 3.56 Å) and centroid···plane separations of 3.41 and 3.35 Å for the first interaction and 3.57 and 3.46 Å for the second with interplanar dihedral angles of 12.4° and 8.0° describe good alignment of associated rings. As a consequence of accommodating these ring-pairing interactions, the greatest C−Zn−C angle in the series is observed in compound **5** (133.72(7)°). In addition to the intramolecular aryl-pairing interactions there is

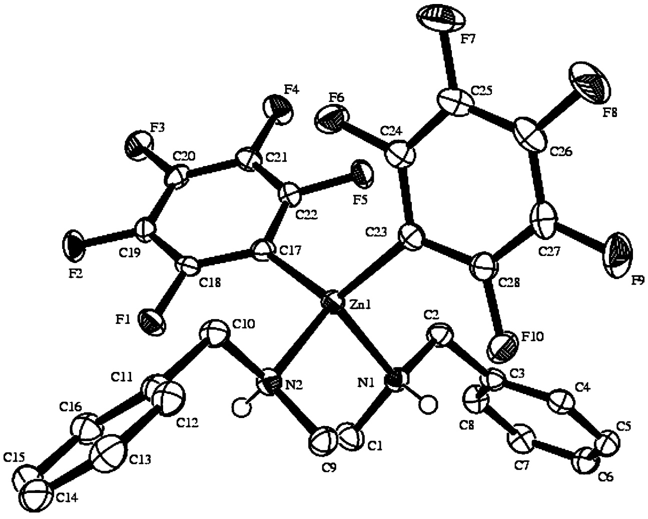

Figure 4. Molecular structure of compound **4**. Thermal ellipsoids are shown at the 50% probability level. H atoms on carbons have been omitted for clarity.

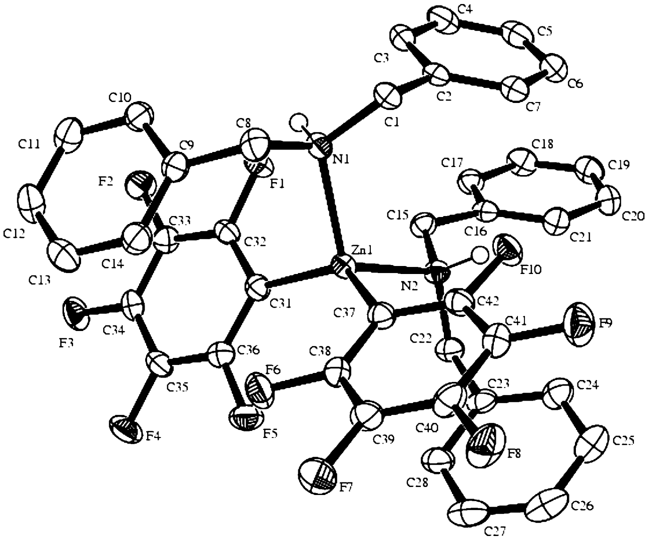

Figure 5. Molecular structure of compound **5**. Thermal ellipsoids are shown at the 50% probability level. H atoms on carbon have been omitted for clarity.

one medium length N1$-$H1$\cdots$F1 (2.21 Å) and one long N2$-$H2$\cdots$F10 (2.48 Å) contact.

The molecular structure of **6** (Figure 6) has 2-fold symmetry. The pyrrolidine group adopts an orientation to minimize steric interactions with the C_6F_5 groups, which results in a relatively large C$-$Zn$-$C (125.02(12)°) and a small N$-$Zn$-$N (100.69(10)°) angle. There is a pair of symmetry-related, long, intramolecular N$-$H$\cdots$F$-$C contacts (Table 3).

Compound **7** crystallizes with pseudo-2-fold symmetry but with a quite different orientation of the piperidine group from that of the pyrrolidine group in **6** (Figure 7). Consequently, the C$-$Zn$-$C and N$-$Zn$-$N angles at 120.05(18)° and 108.09(17)°, respectively, are much closer to the tetrahedral ideal. There are no X$-$H$\cdots$F$-$C interactions substantially shorter than the van der Waals' radii in the solid-state structure of **7**.

Compound **8** is the only adduct of a tertiary amine in this study and crystallizes with 2-fold molecular symmetry (Figure 8). As a consequence of the match between the steric bulk of the tertiary amine group and the pentafluorophenyl groups, we see the least distorted tetrahedral geometry in the series. Although **8** has no amino hydrogens, each of the methyl groups provides a hydrogen donor in either an intra- or an intermolecular C$-$H$\cdots$F$-$C interaction. The intramolecular interaction C8$-$H8b$\cdots$F5 (2.31 Å, C$-$H$\cdots$F 145°) is reminiscent of the C$-$H$\cdots$F$-$C contact we reported for the borane adduct *cyclo*-$C_4H_8N(H)\cdot B(C_6F_5)_3$ (2.20 Å, C$-$H$\cdots$F 151°).[23a,b,f,24c]

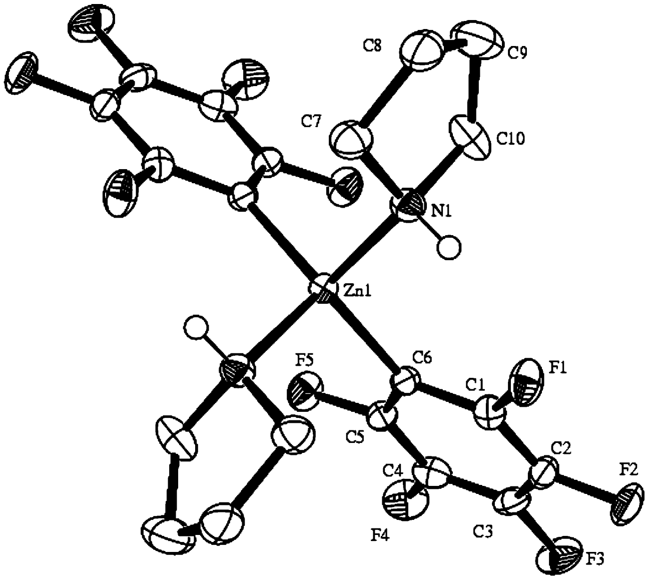

Figure 6. Molecular structure of **6** viewed down the 2-fold symmetry axis. Thermal ellipsoids are shown at the 50% probability level. The hydrogens, except for the amine H atoms, have been omitted for clarity.

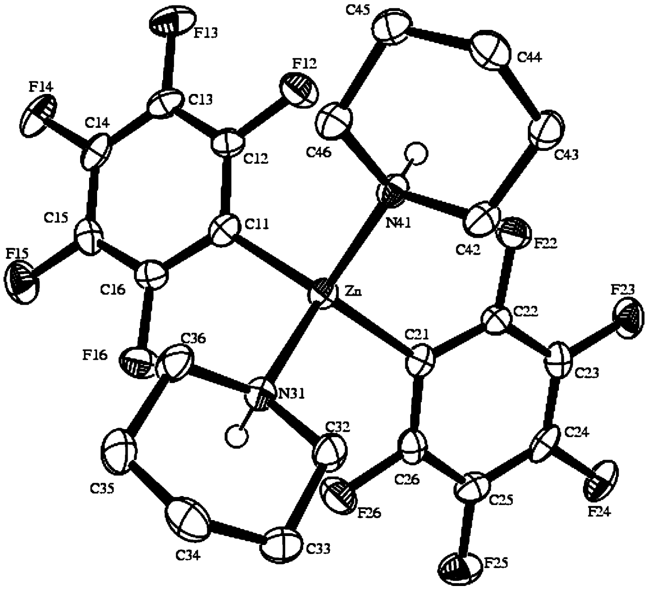

Figure 7. Molecular structure of **7** viewed down the pseudo-2-fold symmetry axis. Thermal ellipsoids are shown at the 50% probability level. The pyrrolidine group hydrogens have been omitted for clarity.

Intermolecular Interactions. The frequency, nature, and extent of the intermolecular interactions (possible with pentafluorophenyl groups and introduced above) vary greatly in the solid-state structures of compounds **1**$-$**8**. That of **6** is distinguished by the absence of either *off* interactions between Ph_F rings or short intermolecular N$-$H$\cdots$F distances. The shortest contacts to neighboring molecules are between *m*-F atoms and N$-$H groups but with H$\cdots$F distances corresponding

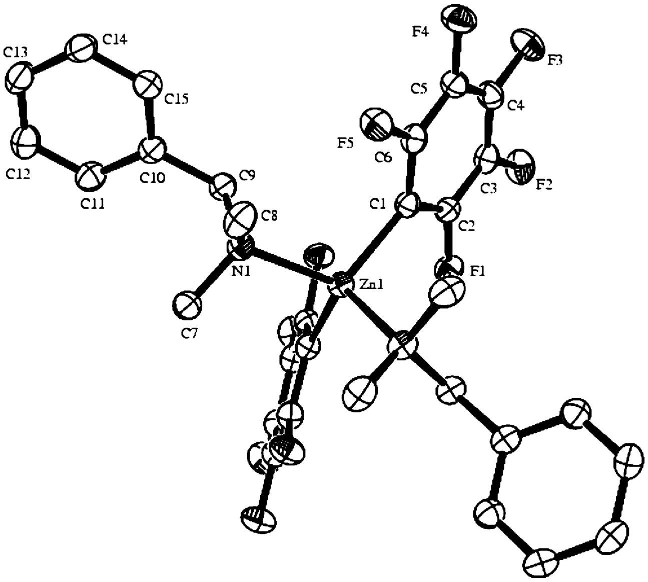

Figure 8. Molecular structure of compound **8**. Thermal ellipsoids are shown at the 50% probability level. H atoms have been omitted for clarity.

to the sum of the van der Waals' radii (2.55 Å). The intermolecular interactions in the remaining structures are discussed below in order of increasing complexity.

Compound **7** has a supramolecular structure consisting of one-dimensional chains running parallel to the *b*-axis (Figure 9). Molecules are linked by *off* interactions between pairs of Ph$_{F}$ rings that are not symmetry-related. The centroid···centroid distance between adjacent Ph$_{F}$ rings is 3.84 Å, the centroid···plane distances are ca. 3.4 Å, while the offset between centroids is 1.88 Å.[38]

The supramolecular structure of compound **3** is depicted in Figure 10. Each molecule engages in N−H···F−C interactions with four neighbors (two as donor molecules, two as acceptors). Collectively they define a supramolecular structure consisting of infinite sheets parallel to the *a*−*b*-plane. Neighboring sheets are aligned to each other through *off* Ph$_{F}$···Ph$_{F}$ interactions similar to those in **7**; the interplanar distance in **3** is 3.299 Å (the extent of overlap is illustrated in Figure 17c). The two sets of interactions cooperate to give a three-dimensional network in which every group bonded to zinc participates in a significant intermolecular interaction.

The supramolecular structure of **1** (Figure 11) is assembled from the same types of intermolecular interaction as **3** but has no molecular symmetry and does not realize the bonding potential of every group. While shorter (2.32 Å) than the contacts in **3**, only one of the amino-H's in each molecule of **1** participates in an intermolecular interaction; this leads to pairing of molecules by two such interactions about a center of symmetry. Also, one of the two Ph$_{F}$ groups interacts with that of a second molecule (also related by a center of symmetry); while the distance between the two parallel rings is 3.190 Å, the degree of overlap is small. Together these interactions link molecules in chains parallel to the *b*-axis.

The supramolecular architectures of **1**, **3**, and **7** are thus shaped by H···F and/or offset Ph$_{F}$···Ph$_{F}$ stacking interactions. The introduction of benzyl substituents in adducts **2**, **4**, **5**, and **8** provides for further potential intermolecular associations, namely, the well-documented Ph$_{H}$···Ph$_{F}$ motif and *off* Ph$_{H}$···Ph$_{H}$ stacking interactions.

In compound **8**, in addition to the intramolecular C−H···F−C interaction as described above, the second methyl group is engaged in an, albeit rather weak, C−H···F−C intermolecular interactions with a *m*-F on a neighboring molecule (H···F 2.46 Å, C−H···F 129°). In this way each molecule is associated with two of its neighbors, forming infinite chains (Figure 12) that are linked via offset homoaryl stacking interactions of the pentafluorophenyl rings. We note that no Ph$_{F}$···Ph$_{H}$ interactions are seen in the crystal structure of **8**. The *off* Ph$_{F}$···Ph$_{F}$ stacks afford one-dimensional chains that zigzag in a direction parallel to the crystallographic *c*-axis (Figure 13). The extent of the overlap of the pentafluorophenyl rings and the subsequent centroid···plane distance at 3.171Å are similar to that in **1**. There is the suggestion of a Ph$_{H}$···Ph$_{H}$ offset stack in the crystal lattice of **8**, but the centroid···plane distances at 3.706 and 4.089 Å are much greater than those calculated by Dance (ca. 3.4 Å) for the binding pair $(C_6H_6)_2$ in an *off* motif, so we conclude there is no significant interaction.[27]

The most readily apparent intermolecular interactions in **4** are H···F contacts (2.30 Å, N−H···F 168°) between NH and *p*-F atoms linking molecules in chains parallel to the *a*-axis. Less obvious is the association of adjacent molecules through Ph$_{H}$···Ph$_{H}$ vertex-to-face (*vf*) interactions. There are four distinct *vf* contacts: one Ph$_{H}$···Ph$_{F}$ ring with an H···centroid distance of 2.51 Å, two Ph$_{H}$···Ph$_{H}$ with H···centroid distances of 2.71 and 2.99 Å, and one methylene···Ph$_{H}$ with an H···centroid distance of 2.80 Å; Ph$_{H}$···Ph$_{H}$ contacts thus link four phenyl rings in a cyclic arrangement about a center of symmetry (Figure 14), and the methylene···Ph$_{H}$ contacts link pairs of benzyl groups about another center of symmetry. This packing is distinct from the 4-fold phenyl embrace described by Dance, which associates pairs of adjacent molecules.[39]

In the crystal lattice of **5**, there are two types of stacked ring systems, first a stack of four C_6H_5 rings and second a stack of

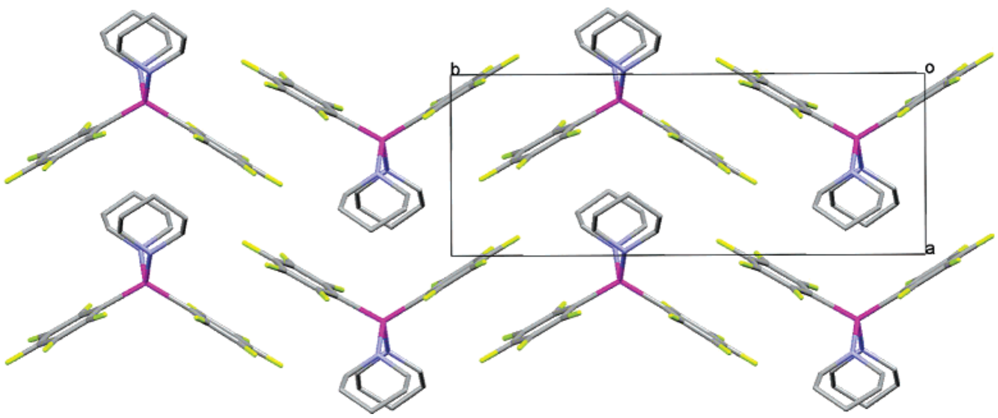

Figure 9. Packing diagram illustrating the one-dimensional chains in **7** formed by a Ph$_{F}$···Ph$_{F}$ stacking motif.

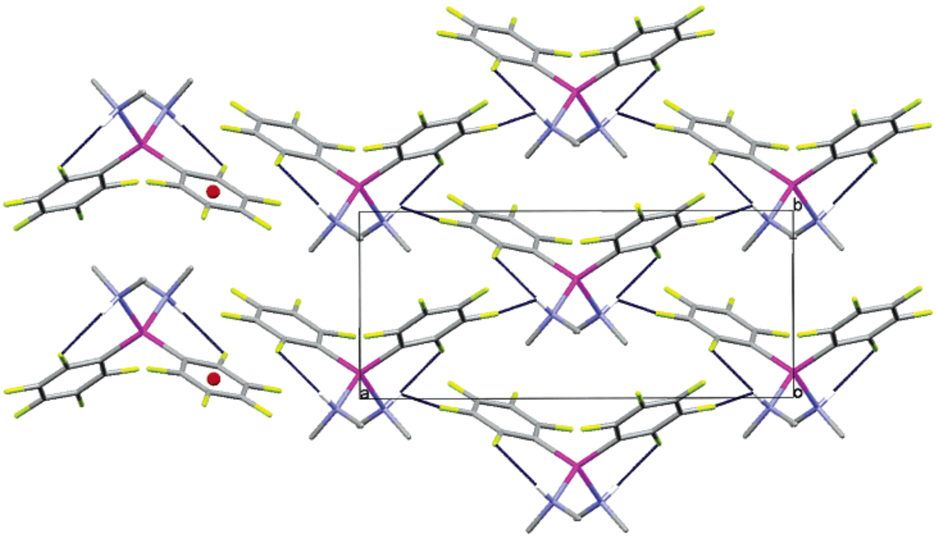

Figure 10. Sheet of molecules of **3** connected through the illustrated N−H⋯F interactions. The two ligands labeled ● are of a neighboring sheet and have parallel overlapping $Ph_F \cdots Ph_F$ ring interactions with groups of the first sheet.

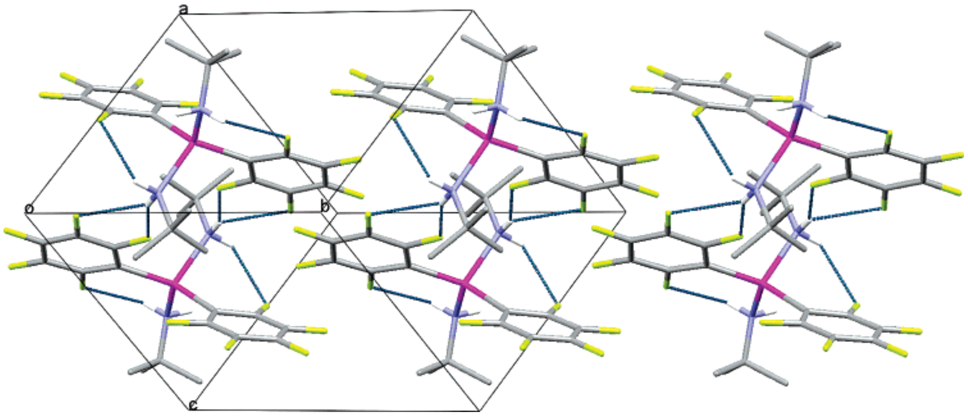

Figure 11. Molecules of **1** viewed down a cell diagonal. Molecules are connected in pairs by short N2−H2a⋯F1′ interactions, and these pairs are linked in chains by overlap of Ph_F rings.

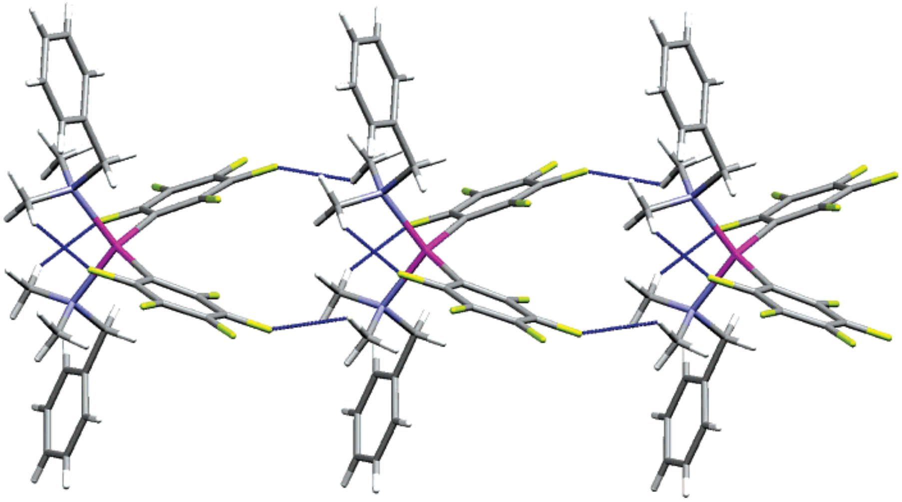

Figure 12. Packing diagram illustrating the formation of a chain through C−H⋯F−C interactions in compound **8**.

eight rings with a sequence $Ph_F \cdots Ph_H \cdots Ph_F \cdots Ph_H \cdots Ph_H \cdots Ph_F \cdots Ph_H \cdots Ph_F$. The angles between the normals in adjacent rings vary from 0° (about a center of symmetry) to 24.1° in the longer stack, and 0° (also about an inversion center) and 11.6° in the shorter stack. In the *off* stacking of $Ph_H \cdots Ph_H$ rings, in

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[38] There are two slightly different centroid (cg)⋯plane distances (3.452 and 3.351 Å (cg (C21−C26)⋯plane (C11−C16) and cg (C11−C16)⋯plane (C21−C26), respectively); the planes lie at an angle of 4.96° to each other).

[39] Dance, I.; Scudder, M. *Chem. Eur. J.* **1996**, *2*, 481. Density functional calculations for the *vf* and *ef* supraisomers of the gas-phase benzene pair $(C_6H_6)_2$ concluded that both structures exhibit near identical pair-binding energies, with the *ef* structure only slightly less favorable: see ref 27.

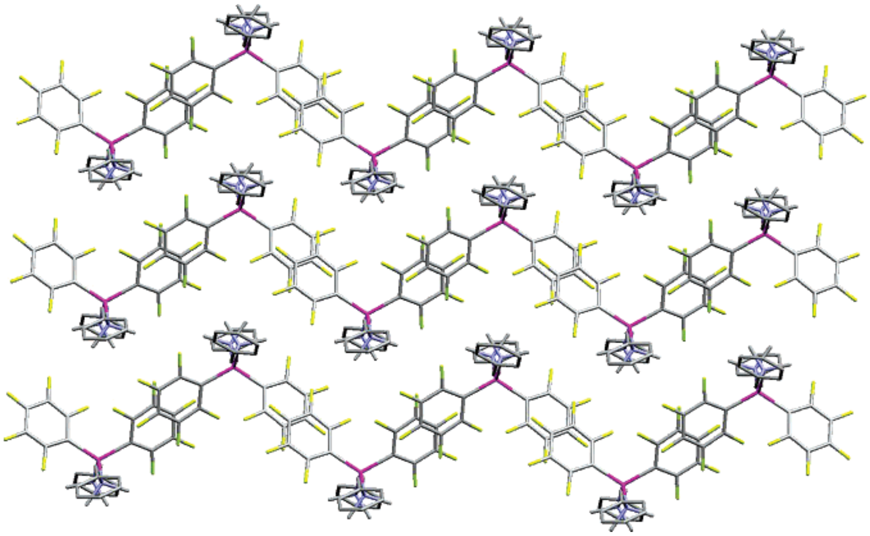

Figure 13. Zigzag pattern afforded by overlapping Ph_F substituents in the crystal lattice of **8**.

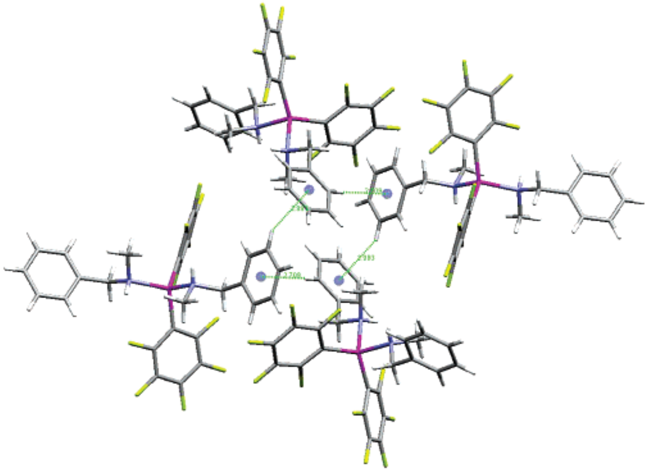

Figure 14. Packing diagram showing the edge-to-face and vertex-to-face arrangements of the Ph_F rings in **4**.

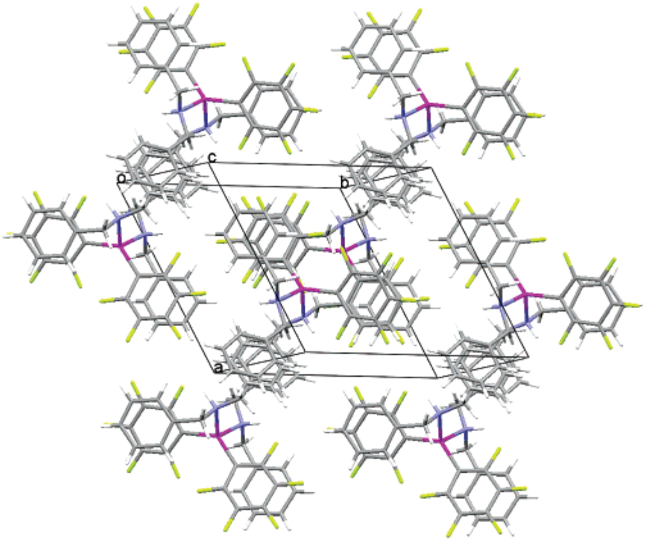

Figure 15. View close to the crystallographic *c*-axis showing the staggered aryl···aryl and eclipsed pentafluoroaryl···aryl stacking interactions in the crystal lattice of **5**.

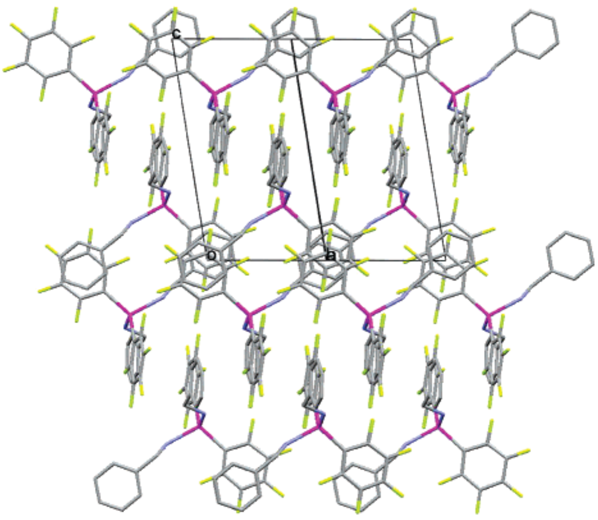

Figure 16. Packing in **2** showing columns of overlapping rings in two directions.

both stacks, an H atom of the adjoining methylene group is directed toward the center of the opposing Ph_H ring with H···centroid distances of 2.57 and 2.76 Å in the short stack and 2.75 Å in the central Ph_H···Ph_H contact in the longer stack. Laterally adjacent molecules are associated through the Ph_H···Ph_H interactions in a zigzag pattern, which combines with the heteroaryl stacks affording infinite sheets (Figure 15). For the heteroaryl stacks the intermolecular centroid···centroid separation (3.897 Å) is larger than the intramolecular value (3.579 Å (av)). The remaining aryl rings form an *off* stack in which the average centroid···plane separation between intramolecular *homo*-rings is 3.408 Å, while the intermolecular distance between the two symmetry-related rings is only slightly greater at 3.446 Å. The packing of **5** involves no intermolecular H···F contacts less than 2.50 Å.

The supramolecular structure of compound **2** is intriguing; each aryl ring has one homo- (to a symmetry-related ring) and one hetero-intermolecular *off*-type interaction. This overlap of aryl rings gives rise to columns, which are stacked in parallel arrays in layers in the crystallographic *a*−*b*-plane. In one layer the columns are directed along the [−110] vector; in the next, they are parallel to the [110] vector, at an angle of 100.1° to the first. The columns are linked by the zinc coordination bonds (Figure 16). Thus each molecule associates with two neighbors via four Ph_F···Ph_H interactions, facilitated by two pairs of essentially parallel phenyl and pentafluorophenyl rings within the molecular structure. Another four molecules share the homo-

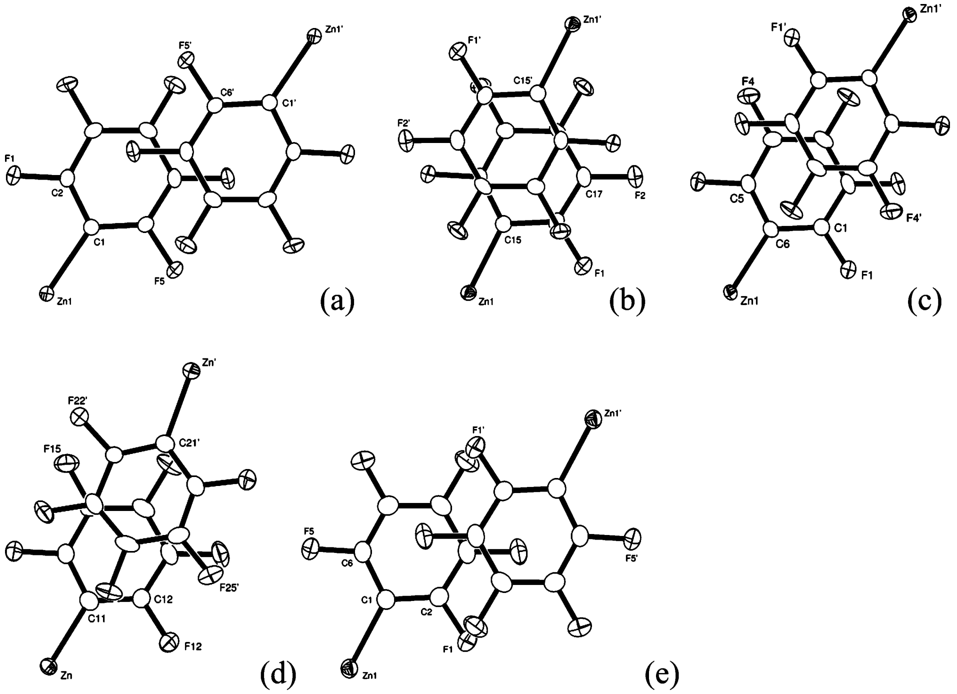

Figure 17. Projection of overlapping rings onto the plane of the lower ring for the *off* pentafluorophenyl rings in **1** (a), **2** (b), **3** (c), **7** (d), and **8** (e).

Table 4. Structural Parameters for the Homo- and Hetero-aryl Interactions in Compound 2

plane 1	plane 2	centroid···centroid distances (Å)	centroid···plane distances (Å)	angle (deg) between the normals to these planes
C2−C7 (Ph_H)	C15−C20 (Ph_F)	3.68	3.40, 3.41	3.00
C9−C14 (Ph_H)	C21−C26 (Ph_F)	3.73	3.38, 3.47	3.98
C2−C7 (Ph_H)	C2−C7 (Ph_H)	3.95	3.56	0
C9−C14 (Ph_H)	C9−C14 (Ph_H)	3.86	3.50	0
C15−C20 (Ph_F)	C15−C20 (Ph_F)	3.54	3.38	0
C21−C26 (Ph_F)	C21−C26 (Ph_F)	3.51	3.37	0

aryl interactions of each ring. The centroid···centroid and centroid···plane distances for each of these homo- and hetero-aryl interactions are collated in Table 4. In addition, there are two weak intermolecular H···F interactions.

Discussion

The effect of complexing a protic amine to the Lewis acidic zinc center in $Zn(C_6F_5)_2$ is to increase its potential as a hydrogen-bond donor. However, with the nitrogen lone pair now participating in a dative bond, the only possible hydrogen-bond acceptors are organofluorines. Furthermore, the length of the Zn−N bond (2.03 Å (av)) disfavors the formation of the bifurcated intramolecular hydrogen-bonding arrangements predicted by Etter's rules and consistently found in protic amine adducts of $B(C_6F_5)_3$ (B−N bond length 1.64 Å).[40] While there are a number of N−H···F−C contacts well within the van der Waals' radii (Table 3), few approach the Dunitz criteria for designation as hydrogen bonds.[20] Although interactions of this type are doubtless individually weak in the absence of stronger competing packing forces, they may play a significant role in the supramolecular assembly of crystal lattices.[23] The best example from this study is compound **3**, in which infinite sheets are constructed by each molecule donating two and accepting two N−H···F−C interactions. While significantly longer than the intermolecular interaction in $(H_2O)\cdot Al(C_6F_5)_3$,[26d] they are within the range we have observed for the related amine adducts of $Al(C_6F_5)_3$[24d] and are comparable to the H···F distances reported for *cis*-$(NH_3)_2\cdot Pd(C_6F_5)_2$.[26c]

There are relatively few reports of *off* interactions between pairs of metal-bonded C_6F_5 rings.[29b,37a] However, interrogation of the CSD yielded many further examples of crystal structures where such interactions are present but have not attracted comment by the authors. We were therefore not surprised to find *off* interactions in five of our eight adduct lattices. The centroid−plane distances (**1**, 3.19; **2**, 3.38 (av); **3**, 3.30 (av); **7**, 3.40 (av); and **8**, 3.17 Å) are in line with those observed for the base-free parent compound $Zn(C_6F_5)_2$ (3.26 Å (av)) and the dimeric aluminum complex $[AlMe(C_6F_5)(\mu\text{-}Me)_2]_2$ (3.39 Å (av)).[29b,37a] These values approach the centroid···plane distance for the *off* paired gas-phase dimer $(C_6F_6)_2$, in which the closest calculated contacts were 3.19 and 3.14 Å for C···C and C···F, respectively.[27] There is however, as illustrated in Figure 17, considerable variation in the degree of overlap (extent of offset) between instances of this interaction.

In principle, the Ph_H···Ph_F interaction is the most favorable supramolecular synthon for molecules containing a combination of these two rings but no other functional groups. However, in our study the hetero-aryl stacking motif is found only in **5**. Although we see intramolecular hetero-aryl pairing in **2**, it does not extend to intermolecular Ph_H···Ph_F···Ph_H···Ph_F stacks. The pattern in **5**, of intramolecular pairs combining to give intermolecular stacks, is very similar to that observed for the imine adduct of tris(pentafluorophenyl)borane, Z-Ph(H)C=N(CH_2Ph)·$B(C_6F_5)_3$ (**IV**), and the $PhCH_2NH_2$ adducts of $M(C_6F_5)_3$ (M = B, Al).[19b,24d] Like **5**, in **IV** the intramolecular centroid···centroid

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(40) Walker, D. A.; Woodman, T. J.; Hughes, D. L.; Bochmann, M. *Organometallics* **2001**, *20*, 3772.

distance (3.374 Å) is significantly shorter than the intermolecular separation (3.910 Å). Heteroaryl pairing or stacking was not found in **4** or **8**, where the supramolecular architectures rely upon homoaryl interactions. We ascribe the relative paucity of hetero-aryl stacking in this series of solid-state structures to steric hindrance from the metal preventing optimal $Ph_H\cdots Ph_F$ overlap, thus rendering other interactions more favorable.

Conclusion

Amine adducts of $Zn(C_6F_5)_2$ exhibit a rich supramolecular chemistry [X−H···F−C, where X = N or C, $Ph_F\cdots Ph_F$, $Ph_H\cdots Ph_F$, and $Ph_H\cdots Ph_H$ interactions]. However, within the series of related compounds reported here there are no indications for a preferred supramolecular motif. The rationalization, prediction, and ultimately direction of supramolecular structure in perfluoroaryl zinc complexes will require systems that do not exhibit such a finely balanced set of competing intermolecular interactions. We are currently exploring the effectiveness of targeted molecular modifications in favoring $Ph_H\cdots Ph_F$ pairing.

Experimental Section

General Procedures. All reactions were conducted under an atmosphere of dry nitrogen using standard Schlenk line techniques. All solvents were purified by distillation from molten sodium (toluene), sodium/potassium alloy (light petroleum), or calcium hydride (dichloromethane). NMR spectra were recorded at 300.1 (^{1}H), 75.5 (^{13}C), and 282.4 (^{19}F) MHz and at 24 °C unless otherwise stated. Elemental analyses were performed by the in-house service at the University of East Anglia. $Zn(C_6F_5)_2$·toluene was prepared according to the literature procedure.[40] The amines were purchased from Aldrich or Lancaster, dried over 4 Å molecular sieves, and used without further purification.

Crystal Structure Analyses. Suitable crystals were selected, and data for **1**−**6** and **8** were measured on a Bruker Nonius KappaCCD area detector equipped with a Bruker Nonius FR591 rotating anode ($\lambda_{\text{Mo−K}\alpha} = 0.71073$ Å) driven by COLLECT[41] and processed by DENZO[42] software at 120 K. The structures were determined in SHELXS-97 and refined using SHELXL-97.[43] The intensities for a crystal of **7** were measured on a Rigaku/MSC diffractometer with Mo radiation and a graphite monochromator at 140 K. Data were processed using MSC TeXsan/Process software.[44] Structure analysis was by the SHELX-97 software. The large residual electron density and high/hanging *R* factor indicate possible twinning in compound **2**; a twin law could not be found, and it occurs with all crystals.

Crystal data and refinement results for all samples are collated in Table 5.

Table 5. Crystal Data and Refinement Results for All Samples

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
empirical formula	$C_{20}H_{22}F_{10}N_2Zn$	$C_{26}H_{18}F_{10}N_2Zn$	$C_{16}H_{14}F_{10}N_2Zn$	$C_{28}H_{22}F_{10}N_2Zn$	$C_{40}H_{30}F_{10}N_2Zn$	$C_{20}H_{18}F_{10}N_2Zn$	$C_{22}H_{22}F_{10}N_2Zn$	$C_{30}H_{26}F_{10}N_2Zn$
fw/g mol^{-1}	545.77	613.79	489.66	641.85	794.03	541.73	569.79	669.90
cryst syst, space group	triclinic, $P\bar{1}$	triclinic, $P\bar{1}$	monoclinic, *C*2/*c*	monoclinic, $P2_1/c$	triclinic, $P\bar{1}$	orthorhombic, *Pccn*	monoclinic, $P2_1/n$	monoclinic, *C*2/*c*
a/Å	9.3604(2)	8.9718(10)	17.2494(3)	10.1667(3)	11.1400(3)	10.3253(2)	7.075(9)	22.8942(6)
b/Å	10.6617(2)	10.7059(14)	6.8268(2)	12.6768(2)	11.6904(3)	13.5674(3)	18.435(9)	8.7771(2)
c/Å	11.8605(2)	12.7667(10)	16.9013(4)	21.2601(6)	15.1739(4)	14.9591(3)	17.723(9)	16.1559(3)
α/deg	85.673(1)	95.767(9)	90	90	78.780(2)	90	90	90
β/deg	78.553(1)	96.916(8)	113.509(1)	90.659(1)	80.701(2)	90	93.84(8)	118.437(1)
γ/deg	75.044(1)	91.488(11)	90	90	62.503(1)	90	90	90
vol/Å^3	1120.44(4)	1210.3(2)	1825.07(8)	2739.85(12)	1713.52(8)	2095.58(7)	2306(3)	2854.73(11)
Z, calc density (Mg m^{-3})	2, 1.618	2, 1.684	4, 1.782	4, 1.556	2, 1.539	4, 1.717	4, 1.641	4, 1.559
abs coeff (mm^{-1})	1.188	1.111	1.448	0.985	0.805	1.270	1.159	0.949
crystal	colorless block	colorless plate	colorless prism	colorless blade	colorless shard	colorless block	colorless prism	colorless block
cryst dimens/mm^3	0.40 × 0.18 × 0.16	0.48 × 0.38 × 0.05	0.35 × 0.20 × 0.10	0.40 × 0.08 × 0.03	0.35 × 0.30 × 0.10	0.30 × 0.10 × 0.10	0.40 × 0.20 × 0.10	0.50 × 0.30 × 0.25
θ range/deg	3.13−27.50	2.93−27.50	3.25−25.03	3.19−27.50	3.11−27.50	3.00−25.03	2.21−22.50	3.14−27.50
no. of reflns collected/unique/obsd	19847/5088/4532	26076/5554/4894	3007/1596/1554	31806/6231/4831	34402/7846/6571	12001/1842/1643	4199/3009/2514	19251/3267/3081
R_{int}	0.0532	0.0788	0.0140	0.0578	0.0433	0.0629	0.0525	0.0588
no. of data/restraints/params	5088/0/305	5554/0/352	1596/0/134	6231/0/381	7846/0/479	1842/0/151	3009/0/316	3267/0/197
final *R* indices [$F^2 > 2\sigma(F^2)$]: R_1, wR_2	0.0314, 0.0729	0.0966, 0.2525	0.0197, 0.0534	0.0353, 0.0797	0.0333, 0.0733	0.0300, 0.0744	0.0434, 0.0977	0.0294, 0.0756
R indices (all data): R_1, wR_2	0.0378, 0.0761	0.1040, 0.2608	0.0206, 0.0539	0.0557, 0.0876	0.0460, 0.0782	0.0340, 0.0776	0.0552, 0.1011	0.0317, 0.0772
largest diff peak and hole/e Å^{-3}	0.447, −0.573	6.309, −1.059	0.257, −0.226	0.366, −0.578	0.360, −0.482	0.437, −0.322	0.540, −0.409	0.380, −0.280

Synthesis of Compounds 1−8. ($(^t\text{BuNH}_2)_2\cdot\text{Zn}(\text{C}_6\text{F}_5)_2$) (1). A sample of $Zn(C_6F_5)_2$·toluene (1.23 g, 2.5 mmol) was dissolved in toluene (10 mL) at room temperature and treated with *tert*-butylamine (0.37 g, 5.0 mmol). After 1 h the solvent was removed under reduced pressure, affording a sticky residue, which was washed with light petroleum. Colorless crystals were grown from a light petroleum/dichloromethane mixture cooled to −25 °C overnight (0.98 g, 72%). Anal. Found: C 43.90, H 3.85, N 5.05. Calc for $C_{20}H_{22}F_{10}N_2Zn$: C 44.01, H 4.06, N 5.13. ^{1}H NMR (C_6D_6): δ 2.52 (s, 4H, N*H*$_2$), 1.17 (s, 18H, C*H*$_3$). ^{13}C{^{1}H} NMR

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(C_6D_6): δ 51.4 ((CH$_3$)$_3$*C*), 31.0 (*C*H$_3$). ^{19}F NMR (C_6D_6): δ −118.0 (d, 4F, *J* = 19.6 Hz, *o*-F), −157.9 (t, 2F, *J* = 19.5 Hz, *p*-F), −161.9 (4F, m, *m*-F).

$(PhCH_2NH_2)_2 \cdot Zn(C_6F_5)_2$ (2). Compound **2** was isolated using the same general method described for **1**; benzylamine (0.29 g, 2.7 mmol) was added to $Zn(C_6F_5)_2 \cdot$toluene (0.67 g, 1.4 mmol). Colorless crystals were isolated from a saturated toluene solution cooled to −25 °C (0.63 g, 75%). Anal. Found: C 50.49, H 3.29, N 4.57. Calc for $C_{26}H_{18}F_{10}N_2Zn$: C 50.88, H 2.96, N 4.56. ^{1}H NMR (C_6D_6): δ 7.04−6.60 (m, 10H, C_6H_5), 3.07 (t, 4H, *J* = 7.3 Hz, CH_2), 1.61 (br, 4H, NH_2). ^{13}C{^{1}H} NMR (C_6D_6): δ 129.4, 129.1, 127.7, 127.5 (C_6H_5), 46.4 (CH_2). ^{19}F NMR (C_6D_6): δ −118.0 (d, 4F, *J* = 19.5 Hz, *o*-F), −157.2 (t, 2F, *J* = 18.0 Hz, *p*-F), −161.4 (m, 4F, *m*-F).

$(Me_2NH)_2 \cdot Zn(C_6F_5)_2$ (3). Compound **3** was prepared following a procedure similar to that for **1** by addition of dimethylamine (4.4 mmol, 1.8 mL of a 2.41 M solution in toluene) to $Zn(C_6F_5)_2 \cdot$toluene (1.09 g, 2.2 mmol). Recrystallization from a light petroleum/dichloromethane mixture led to isolation of the product as colorless crystals (1.20 g, 75%). Anal. Found: C 38.89, H 2.84, N 5.59. Calc for $C_{16}H_{14}F_{10}NZn$: C 39.25, H 2.88, N 5.72. ^{1}H NMR (C_6D_6): δ 1.58 (s, 12H, CH_3), 1.40 (br, 2H, NH). ^{19}F NMR (C_6D_6): δ −117.4 (d, 4F, *J* = 19.8 Hz, *o*-F), −157.3 (t, 2F, *J* = 19.8 Hz, *p*-F), −161.6 (m, 4F, *m*-F).

$(PhCH_2(Me)NH)_2 \cdot Zn(C_6F_5)_2$ (4). Compound **4** was prepared in a fashion similar to **1** by addition of *N*-benzylmethylamine (0.12 g, 1.0 mmol) to $Zn(C_6F_5)_2 \cdot$toluene (0.24 g, 0.5 mmol). X-ray-quality crystals were obtained from a light petroleum/dichloromethane mixture on cooling to −25 °C overnight (0.25 g, 78%). Anal. Found: C 55.81, H 4.27, N 5.86. Calc for $C_{28}H_{22}F_{10}N_2Zn$: C 52.40, H 3.45, N 4.36. ^{1}H NMR (C_6D_6): δ 7.32−7.07 (m, 10H, C_6H_5), 3.86 (br, 2H, NH), 2.29 (br, 4H, CH_2), 1.34 (s, 6H, CH_2). ^{13}C{^{1}H} NMR (C_6D_6): δ 129.6, 128.8, 126.2 (C_6H_5), 52.6 (CH_2), 24.6 (CH_3). ^{19}F NMR (C_6D_6): δ −118.5 (t, 4F, *J* = 19.9 Hz, *o*-F), −157.8 (t, 2F, *J* = 19.8 Hz, *p*-F), −161.8 (m, 4F, *m*-F).

$((PhCH_2)_2NH)_2 \cdot Zn(C_6F_5)_2$ (5). Compound **5** was prepared in a manner analogous to that for **1** using *N*,*N*-dibenzylamine (1.07 g, 5.4 mmol) and $Zn(C_6F_5)_2 \cdot$toluene (1.34 g, 2.7 mmol), yielding colorless crystals from a light petroleum/dichloromethane mixture cooled to −25 °C (1.89 g, 88%). Anal. Found: C 60.42, H 3.59, N 3.55. Calc for $C_{40}H_{30}F_{10}N_2Zn$: C 60.50, H 3.81, N 3.53. ^{1}H NMR (C_6D_6): δ 6.98−6.81 (m, 10H, C_6H_5), 3.40 (d, 4H, *J* = 6.6 Hz, CH_2), 2.90 (m, 2H, NH). ^{13}C{^{1}H} NMR (C_6D_6): δ 137.0, 129.1, 129.0 (C_6H_5), 52.6 (CH_2). ^{19}F NMR (C_6D_6): δ −115.2 (d, 4F, *J* = 20.0 Hz, *o*-F), −157.0 (t, 2F, *J* = 19.7 Hz, *p*-F), −161.2 (m, 4F, *m*-F).

(*cyclo*-$C_4H_8NH)_2 \cdot Zn(C_6F_5)_2$ (6). Compound **6** was isolated following the procedure outlined for **1** by addition of pyrrolidine (0.25 mL, 3.0 mmol) to $Zn(C_6F_5)_2 \cdot$toluene (0.74 g, 1.5 mmol). Colorless crystals suitable for X-ray crystallography were obtained by slow diffusion of light petroleum into a dichloromethane solution at −25 °C (0.67 g, 82%). Anal. Found: C 44.21, H 3.23, N 5.23. Calc for $C_{20}H_{18}F_{10}N_2Zn$: C 44.34, H 3.35, N 5.17. ^{1}H NMR (C_6D_6): δ 2.36 (br, 8H, C_4H_8), 1.13 (br, 8H, C_4H_8), 2.07 (m, 2H, NH). ^{13}C{^{1}H} NMR (C_6D_6): δ 47.8, 25.0 (C_4H_8). ^{19}F NMR (C_6D_6): δ −116.9 (d, 4F, *J* = 19.8 Hz, *o*-F), −157.9 (t, 2F, *J* = 19.8 Hz, *p*-F), −161.9 (m, 4F, *m*-F).

(*cyclo*-$C_5H_{10}NH)_2 \cdot Zn(C_6F_5)_2$ (7). Compound **7** was prepared according to the method described for **1** using piperidine (0.17 g, 2.0 mmol) and $Zn(C_6F_5)_2 \cdot$toluene (0.5 g, 1.0 mmol). Colorless crystals were afforded by cooling a saturated toluene solution to −25 °C overnight (0.53 g, 92%). Anal. Found: C 46.62, H 3.85, N 4.89. Calc for $C_{22}H_{22}F_{10}N_2Zn$: C 46.38, H 3.89, N 4.92. ^{1}H NMR (C_6D_6): δ 3.05 (br, 2H, NH), 2.54 (br, 4H, C_5H_{10}), 1.72 (br, 8H, C_5H_{10}), 1.48 (br, 8H, C_5H_{10}). ^{13}C{^{1}H} NMR (C_6D_6): δ 47.9, 27.5, 24.1 (C_5H_{10}). ^{19}F NMR (C_6D_6): δ −118.2 (d, 4F, *J* = 19.7 Hz, *o*-F), −158.0 (t, 2F, *J* = 19.3 Hz, *p*-F), −161.9 (m, 4F, *m*-F).

$(PhCH_2NMe_2)_2 \cdot Zn(C_6F_5)_2$ (8). Compound **8** was prepared in a manner analogous to that described for **1** using *N*-dimethylbenzylamine (0.77 g, 5.6 mmol) and $Zn(C_6F_5)_2 \cdot$toluene (1.39 g, 2.8 mmol). Colorless crystals were obtained from a minimum volume of toluene cooled to −25 °C overnight (1.74 g, 93%). Anal. Found: C 53.33, H 3.86, N 4.37. Calc for $C_{30}H_{26}F_{10}N_2Zn$: C 53.79, H 3.91, N 4.18. ^{1}H NMR (C_6D_6): δ 7.27−7.11 (m, 10H, C_6H_5), 3.56 (s, 4H, CH_2), 2.08 (s, 12H, CH_3). ^{13}C{^{1}H} NMR (C_6D_6): δ 130.7, 129.0, 128.9 (C_6H_5), 63.7 (CH_2), 45.1 (CH_3). ^{19}F NMR (C_6D_6): δ −115.5 (d, 4H, *J* = 18.8 Hz, *o*-F), −156.0 (t, 2H, *J* = 19.7 Hz, *p*-F), −161.2 (m, 4H, *m*-F).

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Supporting Information Available: CIF containing the crystallographic information for compounds **1**−**8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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