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Pyridine and benzonitrile adducts of bis(4-nonafluorobiphenyl)zinc

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ABSTRACT

Treatment of $(Ar'_F)_2Zn(OEt_2)_2$ (Ar'_F = 4-$C_6F_5C_6F_4$) with 2 equiv. of benzonitrile, 4-(phenyl)benzonitrile, 4-(pyrrolyl)benzonitrile, pyridine, 4-(phenyl)pyridine or 4-(pyrrolyl)pyridine in dichloromethane afforded the corresponding adducts $(Ar'_F)_2ZnL_2$ in near quantitative yield. The 2,2′-bipyridine adduct was prepared similarly. Multinuclear NMR spectroscopy indicated that zinc's four-coordinate character was maintained in solution. The pyridine complex crystallized from dichloromethane with a solid-state structure free of face-to-face aryl–aryl interactions. In contrast, the 4-(pyrrolyl)pyridine adduct crystallized from both dichloromethane and 1,2-difluorobenzene, with solvent of crystallization, but otherwise essentially identical supramolecular architectures assembled through aryl–aryl synthons, including a face-to-face pentafluorophenyl–pyrrole interaction.

1. Introduction

Most examples of metal–organic supramolecular architectures are assembled through dative bonds [1–3]. The supramolecular assembly of metal complexes without recourse to the dative bond synthon depends upon the same set of intermolecular interactions available to the organic crystal engineer [4–6]. The compensations for forgoing the relatively strong and highly directional dative bond include improved processability and physical properties that closely resemble the isolated monomer. A number of groups have investigated the supramolecular architectures of organometallic compounds, with appended functional groups proven to facilitate the assembly of metal-free molecules through intermolecular interactions such as hydrogen bonding [7–23].

We have focused on bis(pentafluorophenyl)zinc adducts because closely related complexes have been shown to function as non-linear optical materials [24,25]. At a molecular level the fluorine substituents serve to withdraw electron density inductively from the phenyl ring and, in turn, the zinc centre.

The perfluoroaryl ring has a well-established and remarkably rich supramolecular chemistry [26]. In the absence of a better acceptor, the organofluorine will form weak hydrogen bonds with strongly acidic heteroatom-bonded hydrogen atoms [27,28]. The (multipolar) charge distribution on the perfluorophenyl ring is complementary to that of a perhydro-aromatic [29–33]. This is the basis for the enhanced attractive interaction between hydro- and fluoro-aryl groups, which has been used to direct supramolecular assembly in a number of elegant studies [34–43]. If a (single, non-interpenetrated) network could be engendered with tetrahedral zinc nodes and asymmetric intermolecular links of the aryl-perfluoroaryl type then the crystal structure would be non-centrosymmetric and the resulting crystals polar [25a,44].

Initial investigation of the supramolecular architecture of adducts between bis(pentafluorophenyl)zinc and Lewis bases with hydrocarbon aromatic groups (Chart 1) revealed that offset face-to-face phenyl···phenyl (**A,** Chart 2) and pentafluorophenyl···pentafluorophenyl (**B**) interactions predominated and there were few examples of phenyl···pentafluorophenyl (**C**) directed assembly [45]. These observations were attributed to steric interference from the zinc substituent disfavouring the potentially stronger hetero-aryl interaction over the more flexible offset homo-aryl and homo-perfluoroaryl synthons [46–48].

The 4-nonafluorobiphenyl ligand can be regarded as an attractive derivative because of the similar cone angle to the pentafluorophenyl group and rigid projection from the metal centre. Furthermore, the insulation of the pentafluorophenyl ring from the electropositive zinc and relief in steric hindrance with increasing distance from zinc were both expected to further favour aryl-perfluoroaryl interactions. The labile diethyl ether adduct of bis(4-nonafluorobiphenyl)zinc (**1**) was recently described [49]. Herein the synthesis and characterization of a series of adducts between **1** and *para*-substituted benzonitrile and pyridine donor ligands are reported.

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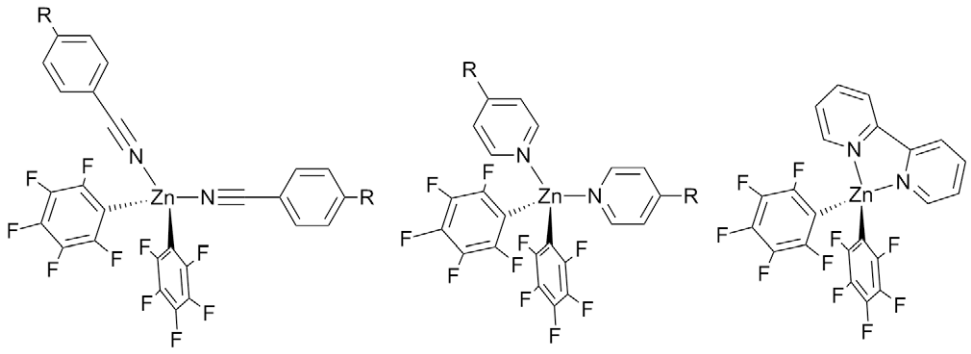
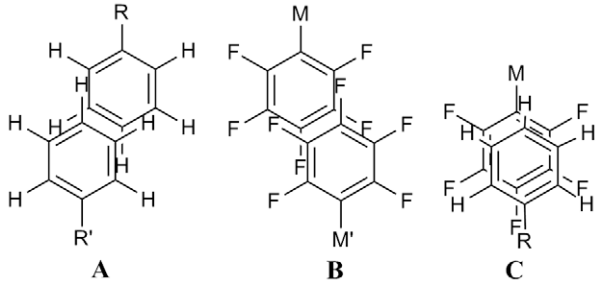


II: R = H;
III: R = Ph;
IV: R = *N*-Pyrrolyl

V: R = H;
VI: R = Ph;
VII: R = *N*-Pyrrolyl

VIII

Chart 1.



A **B** **C**

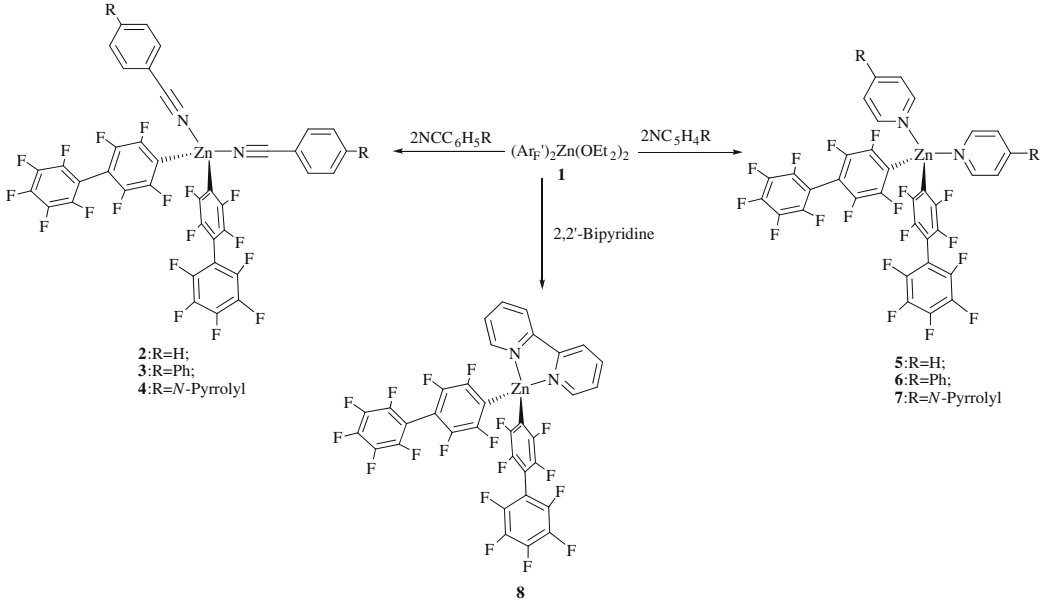
Chart 2.

2. Results and discussion

Bis(4-nonafluorobiphenyl)zinc can be isolated in good yield as the poorly soluble diethyl ether adduct (**1**) following the reaction of zinc dichloride with 2 equiv. of the Grignard reagent $C_6F_5C_6F_4MgBr$ [49]. The diethyl ether ligands are readily displaced by more basic donors, generating adducts of the form $(Ar'_F)_2ZnL_2$ (Ar'_F = 4-$C_6F_5C_6F_4$). Treatment of a dichloromethane solution of **1** with 2 equiv. of benzonitrile, 4-(phenyl)benzonitrile or 4-(pyrrolyl)benzonitrile afforded the corresponding adducts **2**–**4** (Scheme 1) in near quantitative yield. The reaction between **1** and pyridine, 4-(phenyl)pyridine or 4-(pyrrolyl)pyridine proceeded very similarly, giving complexes **5**–**7**, respectively. In each case the elemental analysis results were entirely consistent with formulation as bis(ligand) complexes. Satisfactory analysis was also obtained for the adduct with the 2,2′-bipyridine ligand, **8**.

At room temperature the solution-phase spectra show only one set of ^1H resonances for the coordinated donor ligand and one set of ^{19}F resonances for the Ar'_F groups (Table 1). The addition of excess ligand does not result in a change to the ^{19}F NMR spectrum but the ^1H resonances shift towards those of the free ligand. We interpret these changes, along with the fact that the ^{19}F resonances for the 2,2′-bipyridine adduct (**8**) are almost identical to those of the bis(pyridine) adduct (**5**), as evidence that these complexes exist predominantly as four-coordinate adducts in solution but undergo facile ligand exchange according to equilibrium (1) [50].

$$Ar'_FZnL_2 \rightleftharpoons (Ar'_F)_2ZnL + L \quad (1)$$



Scheme 1.

Table 1
Comparison of the ^{1}H NMR data.

Compound Pentafluorophenyl analogue Free ligand	^{1}H (C_6D_6, 293 K) NMR δ (ppm)			
2	7.07–7.03	6.78	6.58	
II	6.90	6.73	6.51	
C_6H_5CN	7.03	6.89	6.73	
3	7.34–7.30	7.21–7.20,	7.07–7.05	
III	7.12–7.07	7.03	6.90	
$C_6H_5C_6H_4CN$	7.12–7.10	7.01	6.94	
4	6.96	6.57	6.48	6.26
IV	6.91	6.56	6.43	6.28
$C_4H_4NC_6H_4CN$	6.85	6.60	6.48	6.30
5	8.51	6.80	6.51–6.47	
V	8.16–8.13	6.82–6.75	6.46–6.42	
C_5H_5N	8.51	7.01	6.68	
6	8.48	7.14–7.08	6.87	
VI	7.12–7.09	7.03	6.89	
$C_6H_5C_5H_4N$	5.82	5.70–5.66	5.57	
7	8.19	6.63	6.33	6.25
VII	8.08	6.61	6.33	6.23
$C_4H_4NC_5H_4N$	8.36	6.74	6.51	6.30
8	8.88	6.88–6.85	6.60–6.55	
VIII	8.74	6.73–6.76	6.48–6.44	
2,2′-Bipyridine	8.74	6.73–6.76	6.48–6.44	

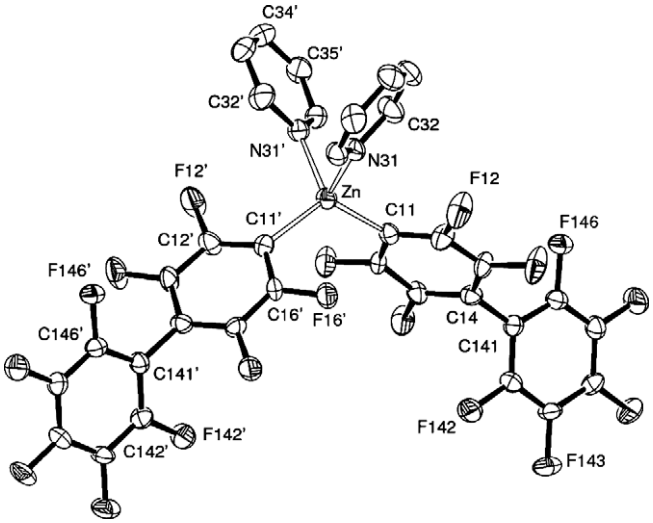


Fig. 1. Molecular structure of **5**. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. The zinc atom lies on a crystallographic C_2 axis.

The 4-nonafluorobiphenyl ligand presents essentially the same cone angle as the pentafluorophenyl ligand, meaning that their steric influence at the zinc centre is likely to be very similar. In consideration of the electronic properties of the two ligands, the Hammett constants, σ_p, for the F and C_6F_5 substituents at the 4-position, 0.06 and 0.27, respectively [51], suggest that the 4-$C_6F_5C_6F_4$ ligand should be more electron-withdrawing than C_6F_5. The ^{1}H NMR resonances for the ligand peaks of $(Ar'_F)_2ZnL_2$ (**2–8**) are consistently found at higher frequency than in the case of the corresponding $(Ar_F)_2ZnL_2$ adducts (Ar = C_6F_5). This is consistent with the assertion that the $(Ar'_F)_2Zn$ unit is indeed more Lewis acidic than $(Ar_F)_2Zn$.

Since the primary objective of this study was to look for patterns in the supramolecular architecture of this class of complex, we invested considerable effort in obtaining crystalline samples. However, only the pyridine and the 4-(*N*-pyrrolyl)pyridine adducts**, 5** and **7**, yielded crystals suitable for X-ray diffraction analysis. In the case of compound **7**, two sets of crystals were obtained, from dichloromethane and 2-difluorobenzene solutions,

Table 2
Selected distances (Å) and angles (°) of **5** and **7** and their analogous bis(pentafluorophenyl)zinc adducts.

Compound	Zn–C	Zn–N	C–Zn–C	N–Zn–N
V	2.0292(16) 2.0209(15)	2.0660(14) 2.1206(15)	123.55(6)	95.75(6)
5	2.011(4)	2.080(3)	119.2(2)	91.82(19)
VII	2.018(3)	2.099(3)	117.45(15)	87.59(13)
7·$C_6H_4F_2$	2.028(5) 2.053(5)	2.106(4) 2.100(5)	125.8(2)	98.96(17)
7·CH_2Cl_2	2.015(7) 2.048(8)	2.102(6) 2.084(7)	127.7(3)	102.0(2)

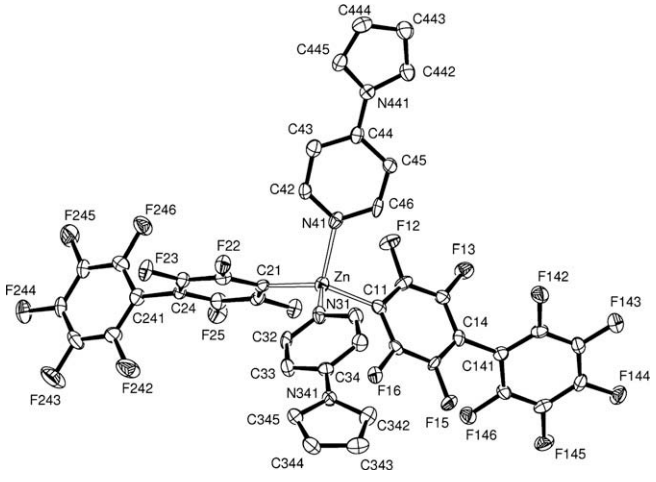
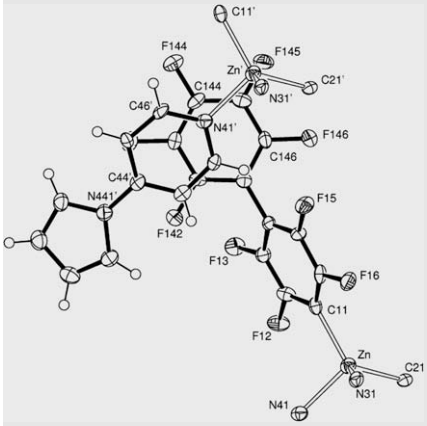
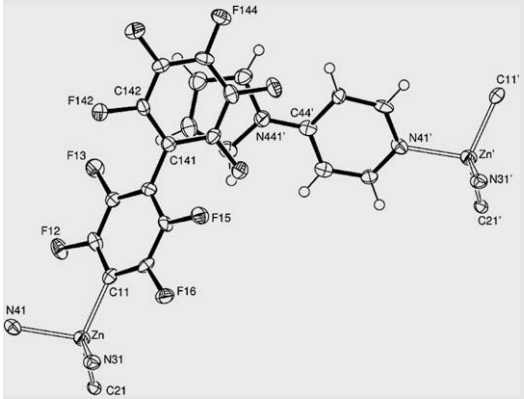
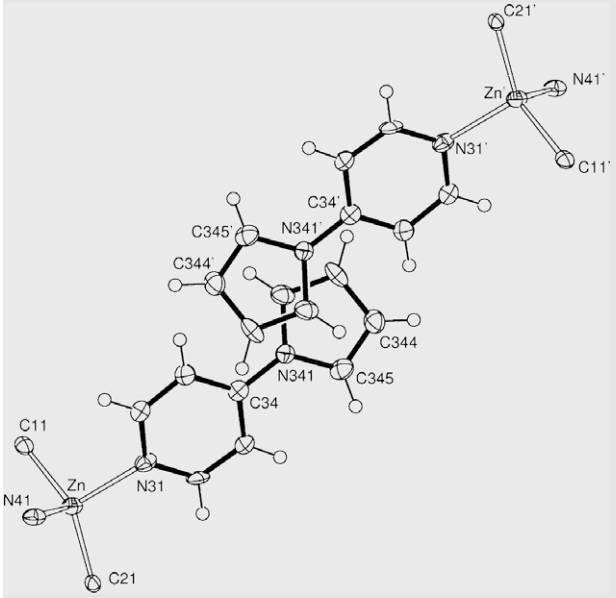


Fig. 2. Molecular structure of **7** in its $C_6H_4F_2$ solvate. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. The structure and geometry in the CH_2Cl_2 solvate are very similar.

Table 3
Summary of the face-to-face interactions between aryl rings present in **7**·$C_6H_4F_2$. Very similar interactions are found in **7**·CH_2Cl_2. Ct represents a ring centroid.

Diagram	Rings	Symmetry operation	Ct···Ct distance (Å)	Ct···plane distance (Å)	Interplanar angles (°)
	C141–C146 and N41′–C46′	*x*, *y* + 1, *z*	3.98	Ct(pyr): 3.71 Ct(C_6F_5): 3.59	19.2
View along the normal to the C_6F_5 plane					
	C141–C146 and N441′–C445′	*x* + 1, *y* + 1, *z*	3.83	Ct(pyrrole): 3.24 Ct(C_6F_5): 3.64	14.6
View along the normal to the pyrrole ring plane					
	N341–C345 and N341′–C345′	−*x*, 2 − *y*, 1 − *z*	3.73	3.31	0
View along the normal to the plane of the rear pyrrole ring					

and in both cases solvent molecules are present in the crystal structure.

The geometry about the zinc centre in the solid-state structure of **5** is distorted tetrahedral (Fig. 1). The molecular structure of **5** resembles that of the analogous bis(pentafluorophenyl)zinc complex **V** and the Zn–C and Zn–N bond lengths are quite similar (Table 2). For the somewhat less distorted **V** the only aryl–aryl interaction of note is an offset face-to-face (*off*) interaction between centrosymmetrically related pyridine ligands.

The distorted tetrahedral solid-state molecular structures of **7** (Fig. 2) are similar in the dichloromethane and difluorobenzene solvates. The geometry in four-coordinate zinc complexes of this type is known to deform readily to accommodate intermolecular interactions [52], and, as is discussed below, the similarity in molecular structure does reflect a conserved supramolecular architecture. By comparison, the C–Zn–C and N–Zn–N angles are significantly different from those observed for **VII**, the pentafluorophenyl analogue of compound **7**. The most striking feature of **VII** was the anomalously small N–Zn–N angle, which was explained by an *off* pairing of the 4-(*N*-pyrrolyl)pyridine ligands, whereby each pyridine ring was located over an *N*-pyrrolyl ring and *vice versa*; this interaction is not present in **7** and as a consequence the N–Zn–N angle is more than 10° larger and within the normal range for these adducts. It is these differences in the supramolecular

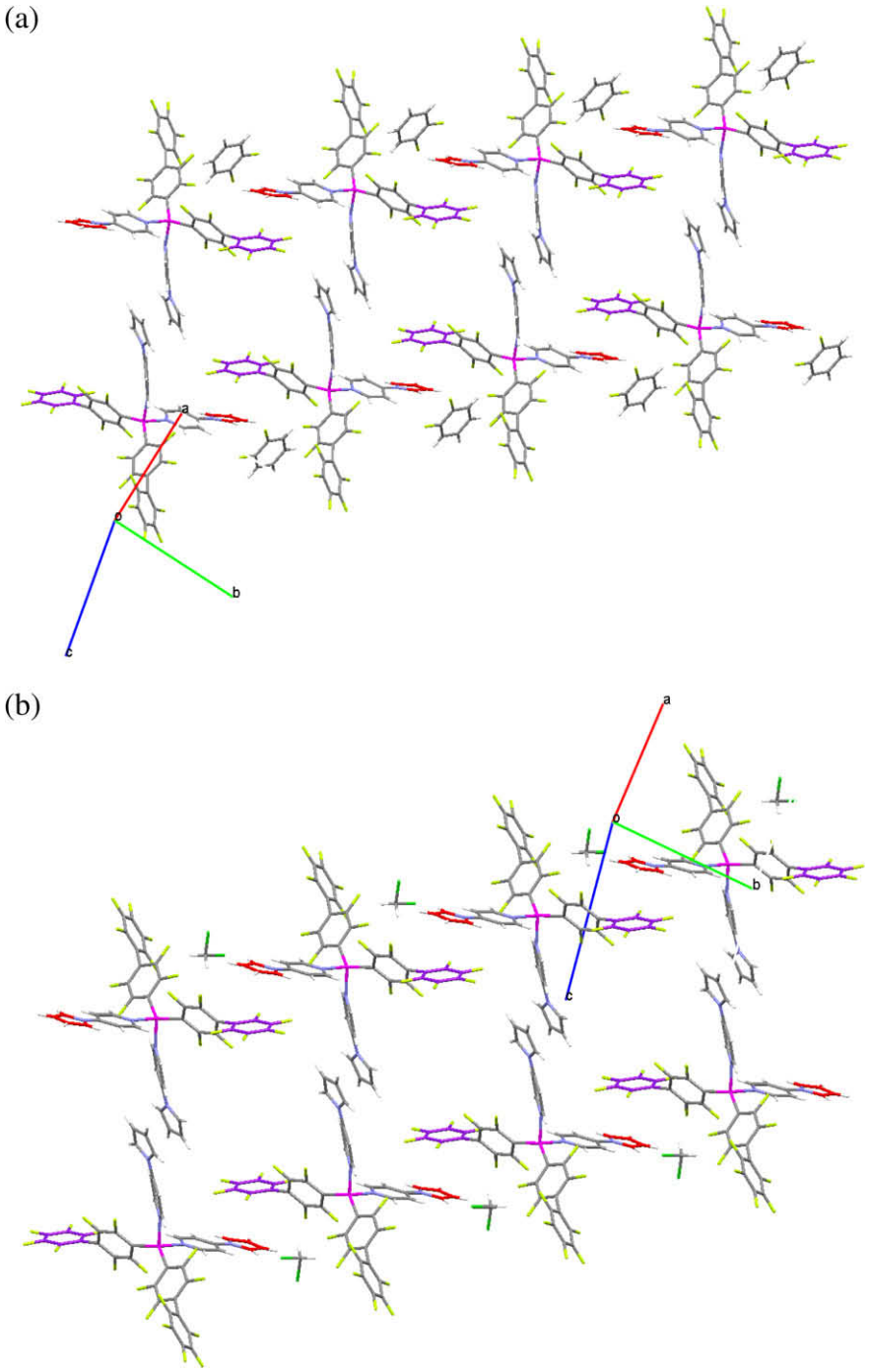


Fig. 3. Supramolecular architecture of (a) **7**·$C_6H_4F_2$ and (b) **7**·CH_2Cl_2. The pentafluorophenyl rings in purple interact face-to-face with the red pyrrole rings.

architectures, rather than a molecular effect, that provides an explanation for the rather large differences between angles in **5** and **7** and their analogues.

The supramolecular architecture of **5** is noteworthy for the absence of face-to-face aryl–aryl interactions. Whereas the pentafluorophenyl groups of the analogous complex, **V**, did not participate in face-to-face aryl–aryl interactions, in that instance there was an *off* interaction between centrosymmetrically related pyridine ligands [45b].

In contrast, molecules of **7** do assemble in the solid-state through aryl–aryl interactions. In **7**·$C_6H_4F_2$ (Table 3) there is a face-to-face interaction between a pentafluorophenyl group and the pyrrole ring from an equivalent molecule related by a [1 1 0] translation, generating infinite chains along the *ab* face diagonal direction (Fig. 3a). This pentafluorophenyl substituent also engages, on its other face, in a face-to-face interaction with the pyridine ring of a donor ligand, generating chains propagating parallel to the *b* axis (not shown). The second pyrrole ring is part of an infinite *off* ($C_4H_4N\cdots C_4H_4N$) arrangement constructed from centrosymmetrically related adjacent rings. Together, these chain-like motifs describe a complex three-dimensional supramolecular architecture.

The supramolecular architecture of **7**·CH_2Cl_2 (Fig. 3b) is very similar to that of **7**·$C_6H_4F_2$. The two structures differ significantly only in the identity of the solvent of crystallisation, which occupies essentially the same position in both cases.

3. Conclusions

The Et_2O donors of the (4-C_6F_5-C_6F_4)$_2$Zn(OEt_2)$_2$ complex are readily displaced by pyridine and benzonitrile bases to form four-coordinate Lewis adducts of the form (4-C_6F_5-C_6F_4)$_2$ZnL_2. The observation of ^{1}H NMR resonances for the basic ligands in adducts of (4-C_6F_5-C_6F_4)$_2$Zn at higher frequency than those of the corresponding (C_6F_5)$_2$Zn complexes is consistent with the 4-nonafluorobiphenyl group being more electron-withdrawing than the pentafluorophenyl group, thus rendering the zinc centre more Lewis acidic.

By comparison to the previously characterised (C_6F_5)$_2$ZnL_2 series, these complexes proved to be poorly crystalline and we were successful in structurally characterising only the pyridine and 4-*N*-pyrrolylpyridine adducts. The lack of crystallinity in the majority of these (4-C_6F_5-C_6F_4)$_2$ZnL_2 complexes and the absence of a substantial aryl–aryl interaction in the solid-state structure of **5** would suggest that this system shows little promise for controlled supramolecular assembly. However, complex **7** crystallises in chains assembled through a pyrrole-pentafluorophenyl intermolecular synthon, which is conserved in both the dichloromethane and difluorobenzene solvates. The structure of **7** thus provides a tantalising confirmation that the aryl-pentafluoroaryl intermolecular synthon does indeed have at least the potential to direct the supramolecular assembly of this class of organometallic compound. Although complex **7** crystallizes in chains assembled from the asymmetric intermolecular links discussed in the introduction these propagate in only one dimension and the structure is centrosymmetric. Since none of the structures reported herein crystallise in non-centrosymmetric space groups the solid-state NLO properties have not been investigated.

The 4-nonafluorobiphenyl group is not ideal because of the steric encumbrance to efficient aryl-perfluoroaryl overlap, inherent in a biphenyl derivative. These results suggest that the successful direction of supramolecular assembly will require a perfluorinated ligand with similar steric and electronic character to the 4-nonafluorobiphenyl ligand but substituted in such a fashion as to eliminate steric impediments to efficient aryl overlap.

4. Experimental

Syntheses were performed under anhydrous oxygen-free nitrogen using standard Schlenk techniques. Solvents were distilled over sodium-benzophenone (diethyl ether, tetrahydrofuran), sodium (toluene), sodium-potassium alloy (light petroleum, b.p. 40–60 °C), or CaH_2 (dichloromethane, 1,2-difluorobenzene). NMR solvents ($CDCl_3$, C_6D_6, C_7D_8) were dried over activated 4 Å molecular sieves and degassed by several freeze–thaw cycles. NMR spectra were recorded using a Bruker DPX300 spectrometer. Chemical shifts are reported in ppm and referenced to residual solvent resonances (^{1}H, ^{13}C); ^{19}F is relative to $CFCl_3$. The atom numbering scheme is given in Chart 3. Elemental analyses were performed at the Department of Health and Human Sciences, London Metropolitan University. Compound **1**, (4-$C_6F_5C_6F_4$)$_2$Zn(OEt_2)$_2$, was prepared according to the recently published literature procedure [49]. 4-(*N*-pyrrolyl)pyridine and 4-(*N*-pyrrolyl)benzonitrile were prepared according to the literature procedures [53]. The remaining benzonitrile and pyridine derivatives were purchased from Aldrich or Lancaster, dried over 4 Å molecular sieves and used without further purification.

4.1. General procedure for the preparation of compounds *2*–*8*

Two equivalents of the appropriate ligand were added to a solution of **1** in dichloromethane. The resulting solutions were stirred at room temperature for 30 min before the solvent was removed under vacuum. The residues were washed with light petroleum and the crude product purified by dissolution in dichloromethane and precipitation with light petroleum. In the cases of **5** and **7** only, X-ray quality crystals were obtained by the slow diffusion of light petroleum into those dichloromethane solutions. Crystals suitable for X-ray analysis were also obtained following slow diffusion of light petroleum into a difluorobenzene solution of **7**.

4.2. ($C_6F_5C_6F_4$)$_2$Zn(NCC_6H_5)$_2$ (*2*)

Benzonitrile (80 μL, 1.2 mmol) and **1** (0.5 g, 0.6 mmol) were combined in CH_2Cl_2 (10 mL) according to the procedure outlined above, affording **2** as a colourless solid (0.47 g, 87%). *Anal.* Calc. for $C_{38}H_{10}F_{18}N_2Zn$: C, 50.61; H, 1.12; N, 3.11. Found: C, 50.42; H, 1.08; N, 3.00%. ^{1}H NMR (300 MHz, 293 K, C_6D_6): δ 7.05 (m, 4H, *o-H*), 6.78 (t, 2H, J = 6.4 Hz, *p-H*), 6.58 (m, 4H, *m-H*). ^{19}F NMR (282 MHz, 293 K, C_6D_6): δ −117.8 (dd, 4F, J = 28 and 16 Hz, *F2*), −138.7 (m, 4F, *F3 or 2′*), −139.3 (m, 4F, *F3 or 2′*), −152.0 (t, 2F, J = 21 Hz, *F4′*), −161.5 (m, 4F, *F3′*).

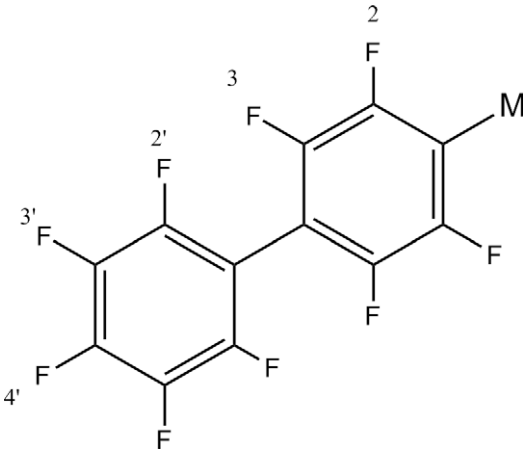


Chart 3.

Table 4
Crystallographic data.

Crystal	**5**	**7**·CH_2Cl_2	**7**·$C_6H_4F_2$
Empirical formula	$C_{34}H_{10}F_{18}N_2Zn$	$C_{42}H_{16}F_{18}N_4Zn$, CH_2Cl_2	$C_{42}H_{16}F_{18}N_4Zn$, $C_6H_4F_2$
Formula (wt/g mol^{-1})	853.8	1068.9	1098.1
Crystal system, space group	monoclinic, *C*2/*c*	triclinic, $P\bar{1}$	triclinic, $P\bar{1}$
a (Å)	20.503(7)	8.9517(8)	9.3752(3)
b (Å)	8.196(3)	10.3603(8)	10.2612(3)
c (Å)	18.852(6)	22.4328(15)	22.3817(7)
α (°)	90	97.696(6)	95.920(2)
β (°)	93.850(4)	99.202(6)	100.250(2)
γ (°)	90	98.119(7)	94.517(2)
V (Å^3)	3160.8(19)	2006.9(3)	2097.08(11)
Z, calc density (Mg m^{-3})	4, 1.794	2, 1.769	2, 1.739
Absorption coefficient μ (mm^{-1})	0.914	0.870	0.718
Colour, habit	colourless plates	colourless plates	colourless rods
Crystal dimensions (mm^3)	0.06 × 0.06 × 0.02	0.18 × 0.10 × 0.03	0.06 × 0.03 × 0.02
θ range (°)	4.7–27.5	3.2–20.5	2.9–22.5
No. of reflections collected/unique/observed	7021/2530/1817	13 871/3992/1895	23 645/5452/3977
R_{int}	0.053	0.147	0.083
Absorption T_{min}/T_{max}	0.71/1.00	0.93/1.09	0.79/1.00
No. of data/parameters	2530/249	3992/568	5452/658
Final *R* indices [$F^2 > 2\sigma(F^2)$]: R_1, wR_2	0.046, 0.093	0.048, 0.045	0.059, 0.102
R indices (all data): R_1, wR_2	0.077, 0.102	0.141, 0.061	0.099, 0.115
Largest difference peak and hole (e Å^{-3})	0.26 and −0.38	0.47 and −0.47	0.34 and −0.39

4.3. $(C_6F_5C_6F_4)_2Zn(NCC_6H_4C_6H_5)_2$ (**3**)

4-(Phenyl)benzonitrile (0.21 g, 1.2 mmol) was treated with **1** (0.5 g, 0.6 mmol) in CH_2Cl_2 (10 mL), yielding **3** as a colourless solid (0.52 g, 81%). *Anal.* Calc. for $C_{50}H_{18}F_{18}N_2Zn$: C, 56.98; H, 1.72; N, 2.66. Found: C, 57.14; H, 1.91; N, 2.55%. ^{1}H NMR (300 MHz, 293 K, C_6D_6): δ 7.32 (m, 6H), 7.20 (m, 4H), 7.06 (m, 8H). ^{19}F NMR (282 MHz, 293 K, C_6D_6): δ −116.8 (m, 4F, *F*2), −138.5 (m, 4F, *F3 or* 2′), −139.6 (m, 4F, *F3 or* 2′), −152.5 (t, 2F, *J* = 21 Hz, *F4*′), −161.7 (m, 4F, *F3*′).

4.4. $(C_6F_5C_6F_4)_2Zn(NCC_6H_4NC_4H_4)_2$ (**4**)

Following the procedure outlined above, to a solution of 4-(*N*-pyrrolyl)benzonitrile (0.20 g, 1.2 mmol) in CH_2Cl_2 (10 mL) was added **1** (0.5 g, 0.6 mmol). Precipitation resulted in the isolation of **4** as a colourless solid (0.48 g, 79%). *Anal.* Calc. for $C_{46}H_{16}F_{18}N_4Zn$: C, 53.54; H, 1.56; N, 5.43. Found: C, 53.71; H, 1.64; N, 5.51%. ^{1}H NMR (300 MHz, 293 K, C_6D_6): δ 6.96 (d, 4H, *J* = 7.0 Hz, *H* benzonitrile), 6.57 (t, 4H, *J* = 2.1 Hz, *H* pyrrole), 6.48 (d, 4H, *J* = 7.0 Hz, *H* benzonitrile), 6.26 (t, 4H, *J* = 2.1 Hz, *H* pyrrole). ^{19}F NMR (282 MHz, 293 K, C_6D_6): δ −117.3 (dd, 4F, *J* = 29 and 16 Hz, *F*2), −138.7 (m, 4F, *F3 or* 2′), −139.3 (m, 4F, *F3 or* 2′), −152.0 (t, 2F, *J* = 19 Hz, *F4*′), −161.5 (m, 4F, *F3*′).

4.5. $(C_6F_5C_6F_4)_2Zn(NC_5H_5)_2$ (**5**)

Pyridine (0.1 mL, 1.2 mmol) and compound **1** (0.5 g, 0.6 mmol) were dissolved in CH_2Cl_2 (10 mL). The resulting adduct, **5**, was successfully crystallised through the slow diffusion of light petroleum into a dichloromethane solution at −27 °C, giving colourless plates (0.48 g, 94%). *Anal.* Calc. for $C_{34}H_{10}F_{18}N_2Zn$: C, 47.83; H, 1.18; N, 3.28. Found: C, 48.11; H, 1.64; N, 3.44%. ^{1}H NMR (300 MHz, 293 K, C_6D_6): δ 8.51 (d, 4H, *J* = 4.1 Hz, *o-H*), 6.80 (t, 2H, *J* = 7.2 Hz, *p-H*), 6.51 to 6.47 (m, 4H, *m-H*). ^{19}F NMR (282 MHz, 293 K, C_6D_6): δ −115.4 (m, 4F, *F*2), −138.8 (m, 4F, *F3 or* 2′), −139.2 (m, 4F, *F3 or* 2′), −152.1 (t, 2F, *J* = 22 Hz, *F4*′), −161.5 (m, 4F, *F3*′).

4.6. $(C_6F_5C_6F_4)_2Zn(NC_5H_4C_6H_5)_2$ (**6**)

4-(Phenyl)pyridine (0.19 g, 1.2 mmol) and **1** (0.5 g, 0.6 mmol) were combined in CH_2Cl_2 (10 mL) and the product isolated according to the procedure outlined above as a colourless solid (0.46 g, 77%). *Anal.* Calc. for $C_{46}H_{18}F_{18}N_2Zn$: C, 54.92; H, 1.80; N, 2.78. Found: C, 54.90; H, 1.97; N, 2.84%. ^{1}H NMR (300 MHz, 293 K, C_6D_6): δ 8.48 (d, 4H, *J* = 4.9 Hz), 7.14 to 7.08 (m, 10H), 6.87 (dd, 4H, *J* = 4.9 and 1.7 Hz). ^{19}F NMR (282 MHz, 293 K, C_6D_6): δ −115.0 to −115.1 (m, 4F, *F*2), −138.8 (m, 4F, *F3 or* 2′), −139.1 (m, 4F, *F3 or* 2′), −152.1 (t, 2F, *J* = 22 Hz, *F4*′), −161.5 (m, 4F, *F3*′).

4.7. $(C_6F_5C_6F_4)_2Zn(NC_5H_4NC_4H_4)_2$ (**7**)

Compound **1** (0.5 g, 0.6 mmol) was treated with 4-(*N*-pyrrolyl)pyridine (0.17 g, 1.2 mmol) in CH_2Cl_2 (10 mL). The product crystallised from a dichloromethane solution following slow diffusion of light petroleum at −27 °C as colourless plates (0.54 g, 92%). *Anal.* Calc. for $C_{42}H_{16}F_{18}N_4Zn$: C, 51.27; H, 1.64; N, 5.69. Found: C, 51.45; H, 1.31; N, 5.76%. ^{1}H NMR (300 MHz, 293 K, C_6D_6): δ 8.19 (dd, 4H, *J* = 5.3 and 1.5 Hz, *H pyridine*), 6.63 (t, 4H, *J* = 2.3 Hz, *H pyrrole*), 6.33 (dd, 4H, *J* = 5.3 and 1.5 Hz, *H pyridine*), 6.25 (t, 4H, *J* = 2.3 Hz, *H pyrrole*). ^{19}F NMR (282 MHz, 293 K, C_6D_6): δ −115.2 (m, 4F, *F*2), −138.9 (m, 4F, *F3 or* 2′), −139.1 (m, 4F, *F3 or* 2′), −152.0 (t, 2F, *J* = 22 Hz, *F4*′), −161.4 (m, 4F, *F3*′).

4.8. $(C_6F_5C_6F_4)_2Zn(2,2'\text{-bipy})$ (**8**)

Following the procedure outlined above, 2,2-bipyridine (0.10 g, 0.6 mmol); and **1** (0.5 g, 0.6 mmol) were combined in CH_2Cl_2 (10 mL). The residue was precipitated from a CH_2Cl_2:light petroleum (1:1) mixture to afford **8** as a colourless solid (0.43 g, 86%). *Anal.* Calc. for $C_{34}H_8F_{18}N_2Zn$: C, 47.94; H, 0.95; N, 3.29. Found: C, 48.11; H, 0.78; N, 3.17%. ^{1}H NMR (300 MHz, 293 K, C_6D_6): δ 8.88 (d, 2H, *J* = 5.1 Hz), 6.87 (m, 4H), 6.63 (m, 2H). ^{19}F NMR (282 MHz, 293 K, C_6D_6): δ −116.2 (m, 4F, *F*2), −138.8 to −139.0 (m, 4F, *F3 or* 2′), −139.6 (m, 4F, *F3 or* 2′), −152.5 (t, 2F, *J* = 22 Hz, *F4*′), −161.8 (m, 4F, *F3*′).

5. Crystal structure analyses

Suitable crystals were selected and data for **7**·$C_6H_4F_2$ were measured at 120 K at the National Crystallography Service on a Bruker Nonius KappaCCD diffractometer equipped with a Bruker Nonius FR591 rotating anode ($\lambda_{Mo\text{-}K\alpha}$ = 0.71073 Å) driven by COLLECT [54] and data were processed by DENZO [55] software. Intensity data

for complex **5** were measured at the Synchrotron Radiation Source at Daresbury on a Bruker APEX2 diffractometer using thin-slice ω scans and data were processed using the Bruker SAINT program [56]. For **7**·CH_2Cl_2, data were collected at 140 K at UEA on an Oxford Diffraction Xcalibur-3 CCD diffractometer equipped with Mo Kα radiation and a graphite monochromator, and the data were processed using the CRYSALIS-CCD and -RED [57] programs. The structures were determined in SHELXS-97 and refined using SHELXL-97 [58]. Crystal data and refinement results for all samples are collated in Table 4.

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Appendix A. Supplementary data

CCDC 724580, 724581 and 724582 contain the supplementary crystallographic data for **5**, **7**·$C_6H_4F_2$ and **7**·CH_2Cl_2. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2009.06.018.

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