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Full Paper

Synthesis of Sterically Demanding Bis(phosphinimine) Dibenzofuran Ligands and Subsequent Zinc Metalation*

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In light of previous success surrounding the use of bis(phosphinimine)dibenzofuran ligands for zinc-mediated lactide polymerization, a series of sterically demanding P=N pincer compounds have been prepared with important steric and electronic modifications at both *P*- and *N*-sites (L, **3a**–**d**). These systems are highly crystalline and have been extensively characterized using multinuclear NMR spectroscopy, elemental analysis, and X-ray diffraction. The ligands can be transformed into their protonated analogues [HL][$BAr^F{}_4$] (**4a**–**d**, [$BAr^F{}_4$] = [B(*m*-$(CF_3)_2$-$C_6H_3)_4$]) by reaction with Brookhart's acid, and subsequently coordinated to zinc via an alkane elimination reaction with [$ZnEt_2$] at ambient temperature to afford the corresponding [LZnEt][$BAr^F{}_4$] cationic complexes **5a**–**d**. In addition, an unusual chloridozinc species [LZnCl][$BAr^F{}_4$] (**5c′**) has been isolated and structurally characterized, providing comparisons to previously established ligand sets with similar geometries.

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Introduction

Zinc is the 24th most abundant element in the Earth's crust,[1] and finds many uses in everyday life, from pigments in paint, to fire retardants,[2] wood preservatives,[3] laser outputs,[4] and antioxidant supplements.[5] In addition to the commercial application of this element, zinc salts have been used as catalysts in organic synthesis for decades owing to their abundance, low cost, non-toxicity, and environmentally benign properties. In particular, divalent Zn complexes find prevalent use in processes including hydrolysis of Si–H bonds,[6] C–C, C–N, and C–O bond formation,[1] enantioselective aldol reactions,[7] as well as the oxidative desulfurization of fuel.[8]

In addition to the aforementioned synthetic uses of catalytic zinc, our recent interest has been focussed on this element as a means to facilitate the polymerization of lactide.[9] Polylactide (PLA), derived from renewable plant feedstocks, may be a viable option for future plastic manufacturing amidst growing concerns over the economic and environmental sustainability of petrochemical-derived plastics.[9a,10] As a result of the recent popularity of PLA, numerous Zn lactide polymerization catalysts supported by monoanionic ligands (L_n), i.e. [$L_nZn^{II}R$] (R = alkyl, amide, or alkoxide) have been reported to compliment much of the work facilitated by rare earth metals in this domain. Of particular note is the seminal work conducted by Coates et al.[11] For several years, this framework served as the de facto infrastructure for zinc lactide polymerization catalysts.[12] Shortly thereafter, our group began exploring organozinc chemistry wherein we initiated a focus on *neutral* ligands to generate cationic Zn^{II} complexes, which we expected might exhibit unique chemical properties, such as enhanced activity, in lactide polymerization compared with systems supported by more typical anionic scaffolds.

Although the shift from anionic to neutral ligands served as an important development in PLA catalysis, pioneering developments by Bochmann established that *protonated* ligand variants ($[HL_n]^+[X]^-$) could be used to form *cationic* Zn species of the form $[L_nZn^{II}R]^+[X]^-$, bearing weakly coordinating anions.[13] Using a similar protocol, we were able to prepare Zn lactide polymerization catalysts that were coordinatively and electronically unsaturated,[14] and since then our research has focussed upon further developing electropositive zinc species.

Recently we reported a highly active cationic zinc catalyst supported by a finely tuned bis(phosphinimine)dibenzofuran framework (Fig. 1).[15] Although this complex was shown to be highly active in the generation of PLA, catalysis was hampered by intra- and intermolecular transesterification. In order to inhibit this competitive process of 'back-biting', we rationalized that systematically permuting substituents attached to the phosphinimine (P=N) moieties could afford a catalyst system which prevents large molecules (i.e. oligomers and growing polymer chains) from approaching the metal centre, while still readily permitting coordination and insertion of the desired lactide monomer. Specifically, we aimed to install substantial steric bulk onto our ligand system distal to the site of a coordinated

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*Dedicated to the bright memory of Professor Richard F. Langler, a true inspiration for countless young scientists.
'A free radical is a lot like a gorilla with a knife. It's going to get what it wants.'

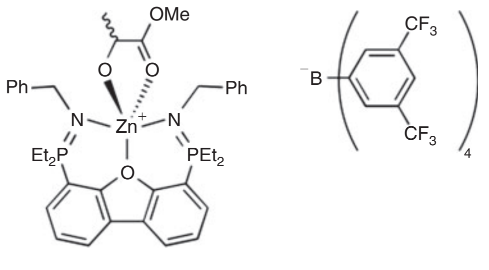


Fig. 1. Recently reported cationic zinc lactide polymerization catalyst.

metal centre; the catalytic implications of such modifications will be studied in due course. Herein we report the synthesis, structure, and characterization of our new ligands, as well as their ability to stabilize zinc alkyl complexes.

Results and Discussion

Sites of Modification

In order to generate sterically demanding analogues of our previously reported dibenzofuran ligand (exhibited in Fig. 1), we chose to systematically modify both the *N*- and *P*-sites of the phosphinimine moiety. Installation of phosphine groups on positions 4 and 6 of dibenzofuran (**1**) can be facilitated by deprotonation at these positions, followed by reaction with a halophosphine to generate compounds **2-R** (R = Ph or ^{i}Pr) (Scheme 1). Subsequently, transformation of the phosphines to desired phosphinimine functionalities under Staudinger conditions generates ligands **3**. In the first two ligands reported below, standard phenyl groups were bound to the phosphorus atoms, while *meta*-xylyl (*m*-Xy, 3,5-dimethylphenyl) and *para*-tritylphenyl (*p*-TrPh, 4-(triphenylmethyl)phenyl) groups were installed on the nitrogen atoms (**3a** and **3b**, respectively). These alterations allowed for facile structural comparison with other previously reported *P*-phenyl-substituted analogues,[16] isolating the effect of altering the substituents on the nitrogen centers, which typically employ *N*-Pipp groups (Pipp = *para*-isopropylphenyl). In addition, we prepared even bulkier versions of **3a** and **3b** by replacing the phenyl groups at the phosphorous atoms with isopropyl moieties (**3c** and **3d**, respectively). While the isopropyl groups were expected to exert greater pressure on the *N*-aryl substituents, thereby forcing them closer to the metal centre, it is worthwhile to note that they should also create a more electron-rich phosphinimine moiety.

Ligand Synthesis and Characterization

As previously reported,[14,15] efficient synthesis of the diphosphine compound **2** can be accomplished via addition of 2.0 equiv. of ^{t}BuLi to dibenzofuran (**1**), followed by subsequent treatment with the appropriate chlorophosphine (Scheme 1). These diphosphine compounds exhibit one sharp signal in the ^{31}P{^{1}H} NMR spectrum (benzene-d_6) at δ −14.3 and 11.1 for the *P*-phenyl (**2-Ph**) and *P*-isopropyl (**2-^{i}Pr**) analogues, respectively. The ^{1}H NMR and ^{13}C{^{1}H} spectra of these compounds agree well with earlier reports.[17] The *P*-phenyl-substituted phosphinimine ligands **3a**,**b** can be generated in high yield by reaction of **2-Ph** with *m*-XyN$_3$ (**3a**) or *p*-TrPhN$_3$ (**3b**) at 55°C for 17.5 h in toluene solvent; while the more bulky *P*-isopropyl species can be generated in similar yields by the reaction of the aforementioned azides with **2-^{i}Pr** (**3c** and **3d**, respectively), as indicated in Scheme 1.

The transformation of compounds **2** to the new ligands **3** was confirmed using multinuclear NMR spectroscopy. A single, sharp ^{31}P{^{1}H} NMR signal was apparent for all ligands (**3a**, δ −4.9; **3b**, δ −0.3; **3c**, δ 8.2; **3d**, δ 20.2). Characteristic shifts at ~δ 8.21 and 7.63, corresponding to the 1,9- and 3,7-positions of the dibenzofuran backbone, respectively, can be observed in the ^{1}H{^{31}P} NMR spectra of **3a**–**d**. In addition, a diagnostic *m*-Xy methyl signal is present at ~δ 2.21 for **3a** and **3c**, while **3c** and **3d** contain typical resonances for isopropyl methine (~δ 2.60) and methyl groups (~δ 1.21 and 0.93). As outlined in the *Experimental* section of this manuscript, compounds **3** also exhibit the expected resonances in their respective ^{13}C{^{1}H} NMR spectra.

Structural Comparison

Single crystals of **3a** (Fig. 2) and **3b** (Fig. 3) were grown from concentrated ambient temperature solutions of toluene and

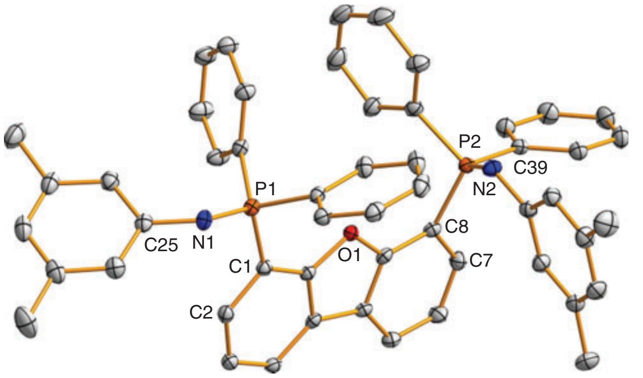
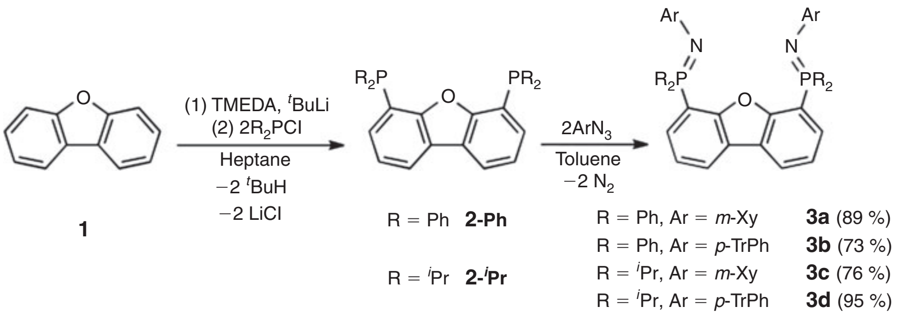


Fig. 2. Thermal ellipsoid plot (30 % probability) of the partial asymmetric unit of **3a**, with H-atoms omitted for clarity. Selected bond distances (Å) and angles (deg.): P1–N1 = 1.5622(18), P2–N2 = 1.5592(18), C25–N1 = 1.401(3), C45–N2 = 1.395(3); C25–N1–P1 = 131.36(15), C45–N2–P2 = 129.24(15).



Scheme 1. Synthesis of dbf bis(phosphinimine) ligands **3a**–**d**.

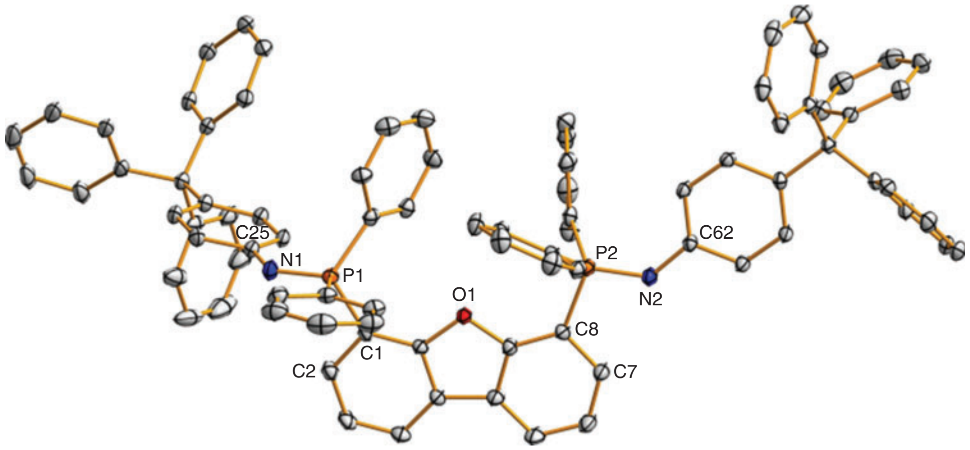


Fig. 3. Thermal ellipsoid plot (30 % probability) for the molecular structure of **3b**, with H-atoms and bromobenzene solvent molecules omitted for clarity. Selected bond distances (Å) and angles (deg.): P1–N1 = 1.5709(18), P2–N2 = 1.5663(17), C25–N1 = 1.390(3), C62–N2 = 1.381(3); C25–N1–P1 = 127.56(15), C62–N2–P2 = 131.74(15).

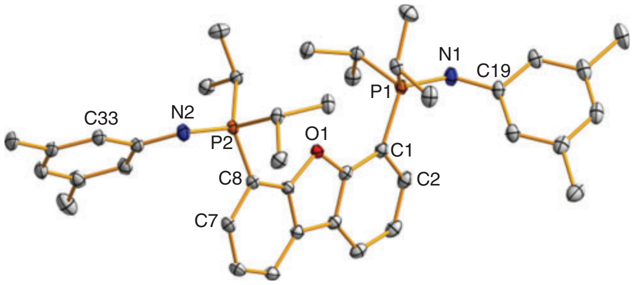


Fig. 4. Thermal ellipsoid plot (30 % probability) for the molecular structure of **3c**, with H-atoms omitted for clarity. Selected bond distances (Å) and angles (deg.): P1–N1 = 1.5635(13), P2–N2 = 1.5673(13), C19–N1 = 1.391(2), C33–N2 = 1.393(2); C19–N1–P1 = 133.83(12), C33–N2–P2 = 132.71(12), N1–P1–C1 = 115.00(8), N2–P2–C8 = 114.64(7).

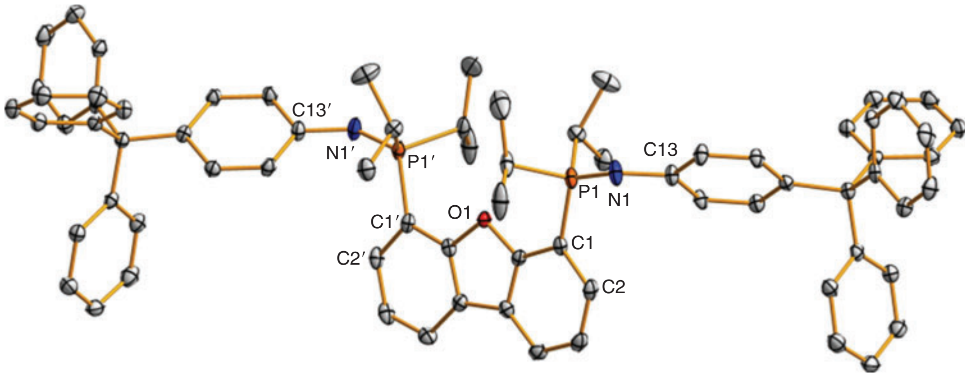


Fig. 5. Thermal ellipsoid plot (30 % probability) for the molecular structure of **3d**, with H-atoms and CH_2Cl_2 solvent molecules omitted for clarity. Selected bond distances (Å) and angles (deg.): P1–N1 = 1.566(3), C13–N1 = 1.394(4); C13–N1–P1 = 132.0(3).

bromobenzene, respectively, while single crystals of **3c** (Fig. 4) and **3d** (Fig. 5) were obtained from dichloromethane layered with pentane at −35°C. In the case of **3a**, the structure contained two independent molecules of the ligand in addition to a toluene solvent molecule in the asymmetric unit. Due to this, a truncated structure is represented in Fig. 2. A summary of X-ray crystallography data collection and structure refinement is listed in Table 1.

All four structures unambiguously confirm the molecular connectivity of the ligands, previously established by spectroscopic evidence. As expected, the phosphorus atoms exhibit tetrahedral geometry, with P=N bond lengths similar to those of related bis(phosphinimine) ligands (P–N = ~1.56 Å).[14–16,18] The angle about the phosphinimine nitrogens (C–N–P = ~131.3°) confirms the presence of an octet-required lone pair and bestows a donor site for coordination to Zn via both

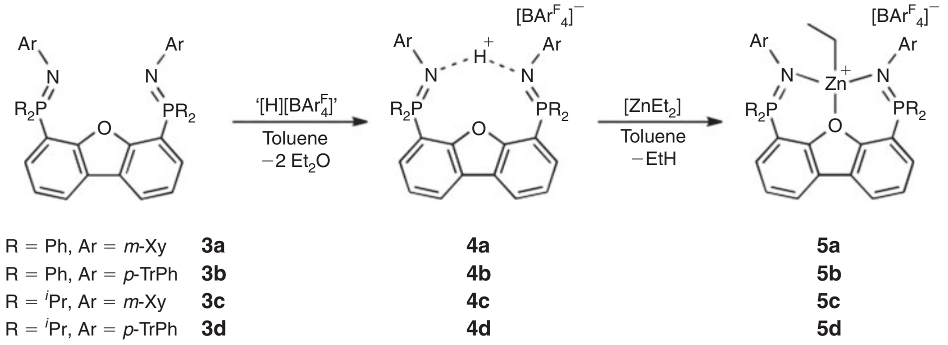
Table 1. Summary of X-ray crystallography data collection and structure refinement for compounds 3a–d, 4c, and 5c′

A Bruker D8/APEX II CCD Diffractometer was used with a Mo Kα (0.71073 Å) fine focussed sealed tube source. Programs for diffractometer operation, data collection, data reduction, and absorption correction were those supplied by Bruker

Parameter	**3a · 0.5 $C_6H_5CH_3$**	**3b**	**3c**	**3d · 3CH_2Cl_2**	**4c · 2C_6H_6**	**5c′**
Formula	$C_{104}H_{88}N_4O_2P_4{\cdot}C_6H_5CH_3$	$C_{86}H_{64}N_2OP_2$	$C_{40}H_{52}N_2OP_2$	$C_{74}H_{72}N_2OP_2{\cdot}3CH_2Cl_2$	$C_{72}H_{65}BF_{24}N_2OP_2{\cdot}2\ C_6H_6$	$C_{72}H_{64}BClF_{24}N_2OP_2Zn$
Formula weight [g mol^{-1}]	1641.80	1203.33	638.78	1322.05	1659.22	1602.82
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	*P*–1	*P*–1	$P2_1/c$	*C*2/*c*	*P*–1	*P*2/*c*
Unit cell parameters						
a [Å]	11.783(2)	14.858(2)	10.4353(8)	28.237(4)	12.6388(10)	15.6897(12)
b [Å]	17.376(3)	17.413(2)	15.1715(12)	18.019(3)	16.6365(13)	12.8393(10)
c [Å]	23.695(6)	17.730(3)	22.9993(18)	13.512(2)	20.6531(16)	36.156(3)
α [deg.]	102.178(3)	104.046(2)	90	90	103.1217(10)	90
β [deg.]	92.176(3)	110.095(2)	101.3860(10)	99.785(2)	96.8990(10)	94.2180(10)
γ [deg.]	109.759(2)	108.641(2)	90	90	102.7035(10)	90
V [Å^3]	4431.5(15)	3747.7(9)	3569.6(5)	6775.0(17)	4059.1(6)	7263.8(10)
Z	2	2	4	4	2	4
ρ_{calcd} [mg m^{-3}]	1.230	1.066	1.189	1.296	1.358	1.466
μ [mm^{-1}]	0.141	0.102	0.155	0.348	0.155	0.525
Crystal dimensions [mm]	0.22 × 0.22 × 0.06	0.34 × 0.11 × 0.07	0.32 × 0.15 × 0.27	0.35 × 0.11 × 0.07	0.51 × 0.42 × 0.19	0.30 × 0.17 × 0.14
Crystal colour	Yellow	Yellow	Yellow	Colourless	Colourless	Colourless
Crystal habit	Plate	Prism	Block	Needle	Block	Prism
θ range [deg.]	2.40 to 26.63	2.18 to 25.36	1.62 to 27.10	2.26 to 25.06	2.41 to 27.42	2.30 to 27.16
Temperature [K]	173	173	173	173	173	173
Total data collected	50550	42798	39977	31861	60409	81108
Independ reflns [R_{int}]	19 400 (0.0476)	16 407 (0.0370)	6407 (0.0303)	5981 (0.0493)	18 635 (0.0362)	16 027 (0.0318)
Obsd reflns [$F_o^2 \geq 2\sigma(F_o^2)$]	12 564	10 333	7880	4331	12 474	13 604
Restraints/params	39/1164	0/820	0/418	0/402	91/1099	0/949
Goodness-of-fit $(S)^A$ [all data]	1.019	1.005	1.035	1.061	1.028	1.118
Final *R* indices^B						
R_1 [$F_o^2 \geq 2\sigma(F_o^2)$]	0.0528	0.0572	0.0390	0.0629	0.0568	0.0759
wR_2 [$F_o^2 \geq 2\sigma(F_o^2)$]	0.1243	0.1453	0.0992	0.1756	0.1316	0.1975
R_1 [all data]	0.0922	0.0880	0.0520	0.0911	0.0926	0.0862
wR_2 [all data]	0.1449	0.1559	0.1072	0.1931	0.1498	0.2033
Largest diff peak, hole [e Å^{-3}]	0.430 and −0.403	0.425 and −0.322	0.330 and −0.330	0.750 and −0.827	0.613 and −0.413	1.695 and −1.331

[A] $S = [w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0540P)^2 + 22.8160P]^{-1}$ where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$).

[B] $R_1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.



Scheme 2. Synthesis of **4** and complexes **5**. '[H][BAr$^F_4$]' = [H(OEt$_2$)$_2$][BAr$^F_4$].

phosphinimine nitrogen atoms in addition to the dibenzofuran oxygen atom.

Protonation and Zinc Complexation

As demonstrated in our previous work,[15] and in that of Bochmann and co-workers,[13] the synthesis of cationic zinc complexes can be accomplished by first protonating a nitrogenous ligand with an appropriate Brønsted acid. Accordingly, protonation of **3a**–**d** using Brookhart's acid [H(OEt$_2$)$_2$][BAr$^F_4$] ([BAr$^F_4$] = tetrakis[(3,5-trifluoromethyl)phenyl]borate) yielded the protonated salts **4** under ambient conditions in near-quantitative yields, as outlined in Scheme 2. During the course of protonation, elimination of diethyl ether was observed by ^{1}H NMR spectroscopy, and a substantial downfield shift of the ^{31}P{^{1}H} NMR resonance, relative to **3**, was observed (**4a**, δ 18.8; **4b**, δ 19.6; **4c**, δ 25.7; **4d**, δ 40.9). Furthermore, ^{31}P{^{1}H} NMR signals were unusually broad, with widths at half height (whh) ranging from 180–240 Hz, implying some degree of fluxionality. This phenomenon is most likely due to exchange of the proton between both nitrogen atoms, as represented by the dotted lines in Scheme 2. Finally, the diagnostic NH protons appeared upfield in the ^{1}H{^{31}P} NMR spectrum, resonating at ~δ 5.30. The NMR spectra for other nuclei (^{13}C{^{1}H}, ^{11}B{^{1}H}, ^{19}F{^{1}H}) also exhibited characteristic chemical shifts and multiplicities representative of the structure proposed.

Single crystals of **4c** were grown from benzene layered with pentane at ambient temperature. As shown in Fig. 6, H2 was located at one position in the Fourier difference map and isotropically refined with a fixed N–H bond length despite the fluxionality of this proton in solution. Protonation notwithstanding, this variant exhibits similar structural parameters to that of its predecessor. Specifically, the phosphinimine angle (C19–N1–P1 = 131.72(18)°) and bond distances (P1–N1 = 1.566(2) Å, N1–C19 = 1.381(3) Å) of one P=N group are comparable to those observed in **3c**. However, notable differences include the aforementioned H2, a BAr$^F_4$ anion (not pictured), a slightly more acute angle (C33–N2–P2 = 125.90(17)°), and elongated bond distances (P2–N2 = 1.635(2) Å, N2–C33 = 1.443(3) Å) associated with the protonated phosphinimine. This asymmetry of the P=N lengths also appears to support the localization of H2. A summary of X-ray crystallography data collection and structure refinement is also listed in Table 1.

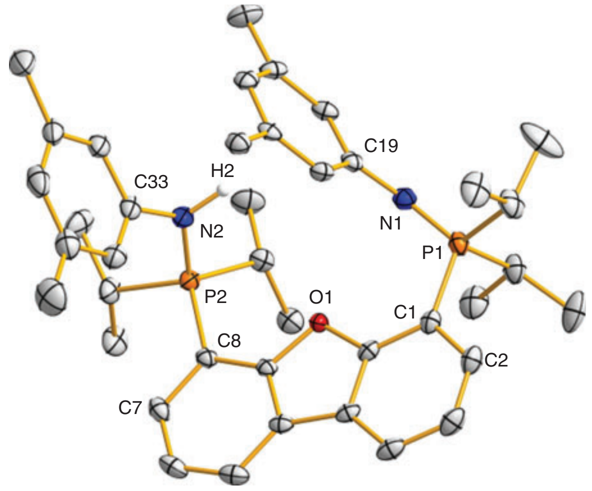


Fig. 6. Thermal ellipsoid plot (30 % probability) for the molecular structure of **4c**, with the BAr$^F_4$ anion and H-atoms, except for H2, omitted for clarity. Selected bond distances (Å) and angles (deg.): P1–N1 = 1.566(2), P2–N2 = 1.635(2), N1–C19 = 1.381(3), N2–C33 = 1.443(3); C19–N1–P1 = 131.72(18), C33–N2–P2 = 125.90(17), N1–P1–C1 = 117.81(11), N2–P2–C8 = 112.52(11).

Although the focus of our previous cationic zinc studies had an emphasis on alkoxide complexes, [LZnOR][BAr$_4$], the mild conditions involved in using [ZnEt$_2$] for complexation made the preparation of alkyl analogues, [LZnEt][BAr$^F_4$], a far more attractive endeavour. Specifically, injection of [ZnEt$_2$] to a solution of **4** at ambient temperature, as opposed to heating a bromobenzene solution of **4** and ethyl(phenoxy)zinc at 110°C in a sealed glass bomb to induce complexation,[15,16,19] appeared ideal for initial studies involving these new ligands. Furthermore, these proposed alkyl zinc targets could serve as an interesting comparison to similar [LZnR][X] complexes previously published by our group.[9d,14–16,18b,19]

Accordingly, the synthesis of zinc-ethyl complexes of the general formula [LZnEt][BAr$^F_4$] (**5**) was performed by reaction of **4** with diethylzinc in toluene solvent. Analysis by ^{1}H NMR spectroscopy indicated complete conversion into **5** via an alkane elimination reaction after a mere 5 min at ambient temperature.[20] More specifically, extrusion of ethane was apparent from the emergence of a singlet at δ 0.80 in the ^{1}H NMR spectrum, as well as effervescence detected in the NMR tube upon injection of [ZnEt$_2$]. Furthermore, the disappearance of the NH resonance, appearance of upfield quartet (~δ −0.14) and triplet (~δ 0.59) resonances displaying mutual coupling, along with a slight change in the aromatic region of the spectrum further supported the structures proposed in Scheme 2. In addition to changes observed in the ^{1}H NMR spectrum, a significant downfield shift was observed in the ^{31}P{^{1}H} spectrum, with a new sharp singlet emerging at ~δ 28.5 (**5a**–**b**) or ~δ 50.0 (**5c**–**d**).

Despite exhaustive efforts, single crystals suitable for an X-ray diffraction experiment of any of the complexes **5a**–**d** remained elusive. In one case however, we reacted [EtZn(lac)] (lac = methyl-L-lactate) and **4c** to attempt the preparation of an ester-coordinated analogue of **5c** with an aim of improved crystallinity. The obtained material was initially believed to be the targeted complex, namely [LZn(lac)][$\mathrm{BAr^F}_4$] involving the R = ^{i}Pr and Ar = *m*-Xy combination. However, an X-ray diffraction study on crystals procured from a dichloromethane solution of this reaction mixture indicated that either the lactate group of [LZn(lac)][$\mathrm{BAr^F}_4$] or the ethyl group of [LZnEt][$\mathrm{BAr^F}_4$], which could also be present in solution if alcohol elimination routes are operative, had reacted with the solvent, resulting in the corresponding cationic chlorido complex [LZnCl][$\mathrm{BAr^F}_4$] (**5c′**, Fig. 7).

Despite the serendipitous formation of this complex, this intriguing species serves as a potential starting material for alternative cationic Zn complexes that remain elusive through conventional alkane elimination strategies, or for targets in which requisite Zn starting materials are not readily available. More conventional methods for the independent synthesis of **5c′** are currently underway. For the purposes of this study, the following structural analysis establishes the ligands' coordinative ability despite the unique chlorido ancillary, and therefore the structural parameters are presented below.

Structure of **5c′**

As expected, the ancillary ligand coordinates to the metal centre in a tridentate fashion, along with a coordinated chlorido ligand to form a 4-coordinate structure wherein the geometry is best described as a trigonal planar Zn centre that is capped by the oxygen of the dibenzofuran ring. The phosphinimine nitrogens (Zn1–N1 = 1.977(3) Å, Zn1–N2 = 1.978(3) Å) and the chlorido group (Zn1–Cl1 = 2.1726(12) Å) occupy the equatorial positions, and the oxygen (Zn1–O1 = 2.176(2) Å) is in the apical site. The equatorial groups do not deviate significantly from planarity despite the interaction between Zn1 and O1, as indicated by the sum of angles about the equatorial positions (357.8°). This may be due to the chlorido group demanding significant *s*-character,[21] which is more prominent in a true equatorial arrangement as opposed to one that is more pyramidalized.

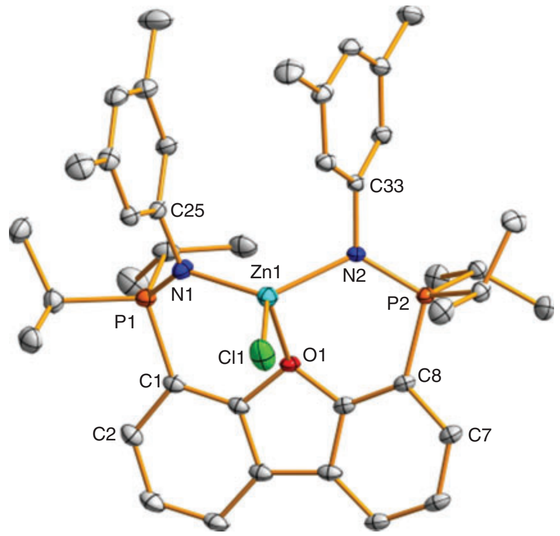


Fig. 7. Thermal ellipsoid plot (30 % probability) for the cationic component of **5c′**, with H-atoms omitted for clarity. Selected bond distances (Å) and angles (deg.): P1–N1 = 1.609(3), P2–N2 = 1.611(3), C25–N1 = 1.442(5), C33–N2 = 1.436(4), Zn1–O1 = 2.176(2), Zn1–N1 = 1.977(3), Zn1–N2 = 1.978(3), Zn1–Cl1 = 2.1726(12); C25–N1–P1 = 120.9(3), C33–N1–P1 = 121.4(2); N1–P1–C1 = 107.50(17), N2–P2–C8 = 107.64(16), N1–Zn–N2 = 123.61(13), Cl1–Zn1–O1 = 109.28(8).

The Zn1–O1 bond distance is particularly noteworthy as it is significantly shorter than other Zn–dibenzofuran bond distances observed in previous cationic [κ^3-LZnR] complexes involving *N*-Pipp-[16,19] or bulkier *N*-Mes-substituted ligands.[18b] However, the shorter Zn–O bond length observed in this case is most likely a consequence of the highly electron-withdrawing chlorido group, as opposed to steric implications.

Finally, the phosphinimine bite angle is dramatically reduced from ideality (N1–P1–C1 = 107.50(17)°, N2–P2–C8 = 107.64(16)°) compared with the angles observed in the free ligand **3c** (N1–P1–C1 = 115.00(8)°, N2–P2–C8 = 114.64(7)°) or in similar *P*-phenyl-substituted [LZnR]$^+$ complexes (*N*–Pipp: 108.88(13)°, 108.41(13)°;[16] *N*–Ph: 114.52(11)°, 113.92(11)°;[19] *N*–Mes: 117.46(18)°, 115.94(18)°[18b]). This significant reduction in bite angle in **5c′** suggests that the ^{i}Pr substituents are interacting with the nitrogen-bound *m*-Xy moieties, pushing these aromatic groups closer together, sterically shielding the metal centre. This effect could also be another cause for a lack of pyramidalization at Zn.

Conclusion

A variety of dibenzofuran-based bis(phosphinimine) pincer ligands were prepared by combining 4,6-bis(phosphino) dibenzofuran compounds with aryl azides under Staudinger reaction conditions. The new P=N ligands are crystalline and provide unique steric environments suitable for metal coordination. In order to effect metal attachment, cationic protonated analogues were generated by reaction of the neutral phosphinimine framework with Brookhart's acid, and subsequently bound to zinc via an alkane elimination reaction with diethylzinc instead of more exotic starting materials such as ethyl(lactate) zinc or the highly electron-withdrawing ethyl(pentafluorophenoxy)zinc precursors, which are often required to effect these kinds of ligand attachments. Furthermore, reaction of these protonated analogues with diethylzinc proceeded at ambient temperature in under 5 min, instead of the harsh experimental conditions and long reaction times previously required to generate alkoxide/ester analogues.

These sterically bulky systems, especially the P^{i}Pr$_2$ variants, are expected to promote transesterification resistance in lactide polymerization, owing to their ability to force the *N*-substituted groups closer together, protecting the naked side of the metal's trigonal pyramid. These species will be tested for their ability to facilitate lactide polymerization in due course.

Finally, the discovery of the unique [LZnCl][$\mathrm{BAr^F}_4$] complex **5c′** serves as a valuable synthetic tipping point since chlorido complexes of this nature may serve as useful starting materials for the synthesis of cationic complexes bearing other functionalities.

Experimental

General Procedures

Manipulations of air- and moisture-sensitive materials and reagents were carried out under an argon atmosphere using double manifold vacuum techniques or in a glove box. Solvents used for air-sensitive manipulations were purified using an

MBraun solvent purification system (SPS), stored in polytetraflouroethylene (PTFE)-sealed glass vessels over sodium benzophenone ketyl (THF and ether), CaH_2 (CH_2Cl_2 and bromobenzene), or 'titanocene' (pentane, benzene, and toluene), and freshly distilled at the time of use. Deuterated solvents were dried over sodium benzophenone ketyl (benzene-d_6 and toluene-d_8) or CaH_2 (chloroform-d, dichloromethane-d_2, and bromobenzene-d_5), degassed via three freeze–pump–thaw cycles, distilled under vacuum and stored over 4 Å molecular sieves in glass bombs under argon. All NMR spectra were recorded at ambient temperature with a Bruker Avance II NMR spectrometer (300.13 MHz for ^{1}H, 75.47 MHz for ^{13}C, 121.49 MHz for ^{31}P, 96.29 MHz for ^{11}B, and 282.40 MHz for ^{19}F). Chemical shifts are reported in parts per million relative to the external standards $SiMe_4$ (^{1}H, ^{13}C), 85 % H_3PO_4 (^{31}P), $BF_3 \cdot OEt_2$ (^{11}B), and $CFCl_3$ (^{19}F); residual H- and C-containing species in benzene-d_6 (δ 7.16, 128.1), toluene-d_8 (δ 2.08, 20.4), chloroform-d (δ 7.26, 77.2), (dichloromethane-d_2) (δ 5.32, 53.8), and bromobenzene-d_5 (δ 7.30, 130.9), were used as internal references (^{1}H and ^{13}C, respectively). Assignments were aided by the use of ^{1}H–^{1}H COSY, ^{13}C{^{1}H} APT, and ^{1}H–^{13}C{^{1}H} HSQC/HMBC experiments (s = singlet, d = doublet, t = triplet, q = quartet, sp. = septet, m = multiplet, br = broad, ov = overlapping signals). Elemental analyses were performed using an Elementar Vario Microcube instrument.[20] The complex [EtZn(*S*-$MeO_2CC(H)(Me)O$)] ([LZn(lac)][$BAr^F{}_4$])[9l] and the protonating agent $[H(OEt_2)_2][B(m\text{-}(CF_3)_2\text{-}C_6H_3)_4]$[22] were prepared according to literature methods. Although reported previously by other methods, **2-Ph**,[17b] **2-^{i}Pr**,[17a] *m*-XyN_3,[23] and *p*-$TrPhN_3$,[24] were prepared in our laboratory from modified procedures as described below. Samples of 3.0 and 5.0 M HCl were prepared by dilution of a concentrated solution. All other reagents, including dibenzofuran (**1**), were purchased from commercial sources and used as received.

1-Azido-3,5-dimethylbenzene (m-XyN_3)

This compound was prepared using a modification of a related literature method.[25] A mixture of 3,5-dimethylaniline (6.817 g, 112.9 mmol) and $NaNO_2$ (4.3 g, 62 mmol) were added to a cooled (−30°C) combination of concentrated HCl (40 mL), distilled H_2O (40 mL), and $NaBF_4$ (12.4 g, 113 mmol). The solution was stirred for 30 min at −30°C, wherein a bright orange precipitate formed. The resulting intermediate diazonium BF_4 salt was quickly filtered through a Büchner funnel and washed with cold distilled H_2O (5 × 4 mL). This sticky orange powder was carefully added to a cooled (0°C) aqueous solution (100 mL) of NaN_3 (11.0 g, 169 mmol). After vigorous gas evolution, the orange mixture was stirred overnight at 25°C. The product was extracted from the aqueous layer with diethyl ether (3 × 30 mL) and dried with $MgSO_4$. The solution was decanted, and the solvent was removed under vacuum, resulting in a dark red oil (5.232 g, 67 %). δ_H (benzene-d_6) 6.52 (s, 1H), 6.47 (s, 2H, Ar H), 1.96 (s, 6H, CH_3).

((4-Azidophenyl)methanetriyl)tribenzene (p-$TrPhN_3$)

This compound was prepared using a modification of a related literature method.[26] A sample of 4-tritylaniline (5.396 g, 16.09 mmol) was added to a 250 mL round-bottomed flask, dissolved in 3.0 M HCl (80 mL), and cooled to 0°C, affording a foamy, white suspension. A solution of $NaNO_2$ (1.304 g, 18.90 mmol) in H_2O (30 mL) was added dropwise to the acidic solution over 25 min at 0°C to afford a foamy, yellow suspension, at which point urea (0.15 g, 2.5 mmol) was added and the solution was stirred for 5 min. A solution of NaN_3 (1.274 g, 19.60 mmol) in H_2O (40 mL) was added dropwise over 60 min at 0°C, generating a foamy suspension. The solution was stirred and warmed to ambient temperature over the course of 2.0 h, at which point Et_2O (100 mL) was added to precipitate an off-white residue. The mixture was filtered and the residue dried under vacuum, resulting in an off-white powder (5.674 g, 98 %). δ_H (chloroform-d) 7.34–7.24 (ov m, 17H), 6.97 (d, 2H, $^{3}J_{HH}$ 8.4), 6.78 (s, 1H), 6.65 (s, 2H, Ar H).

*4,6-Bis(diphenylphosphino)dibenzofuran (**2-Ph**)*

This compound was prepared using a modification of a related literature method.[17b] A sample of dibenzofuran (2.444 g, 14.53 mmol) was added to a 250 mL round-bottomed flask equipped with a reflux condenser attached to a double manifold vacuum line and dissolved in heptane (100 mL) to afford a clear, beige solution. A sample of tetramethylethylenediamine (TMEDA) (3.41 g, 29.3 mmol) was quickly injected into the flask via syringe, and the resulting solution was cooled to 0°C. A solution of ^{t}BuLi (1.7 M in pentane, 18.8 mL, 32 mmol) was added dropwise over 0.5 h, generating a creamy, orange suspension. The solution was stirred and warmed to ambient temperature over the course of 2.0 h, at which point the solution was heated to 98°C for 1.0 h. The resulting creamy, tan-coloured suspension was cooled to 0°C and a solution of chlorodiphenylphosphine (5.90 mL, 32.0 mmol) in heptane (8 mL) was added to the mixture dropwise via syringe over 30 min. The solution was allowed to warm to ambient temperature while stirring over 17.5 h, producing a pale, brown suspension, which was concentrated to 70 mL and transferred to a fine-porosity glass swivel frit apparatus via a cannula. The dark, amber solution was collected, the remaining beige residue was washed with heptane (2 × 30 mL), and the filtrates were combined. Solvents were evaporated to afford a brown solid, which was washed with cold pentane (2 × 10 mL), and dried under vacuum, giving a fine brown powder (3.419 g, 44 %). δ_H (benzene-d_6) 7.55 (dd, 2H, $^{3}J_{HH}$ 7.5, $^{4}J_{HH}$ 1.2), 7.40–7.37 (ov m, 8H), 7.21 (dd, 2H, $^{3}J_{HH}$ 7.5, $^{4}J_{HH}$ 1.2), 7.01–6.95 (ov m, 14H, Ar H). δ_P (benzene-d_6) −14.3 (s, 2P, P=N).

*4,6-Bis(diisopropylphosphino)dibenzofuran (**2-^{i}Pr**)*

This compound was prepared using a modification of a related literature method.[17a] A sample of dibenzofuran (1.993 g, 11.85 mmol) was added to a 250 mL round-bottomed flask equipped with a reflux condenser attached to a double manifold vacuum line and dissolved in heptane (100 mL) to afford a clear, beige solution. A sample of TMEDA (3.03 g, 26.7 mmol) was quickly injected into the flask via syringe, and the resulting solution was cooled to 0°C. A solution of ^{t}BuLi (1.7 M in pentane, 15.4 mL, 26 mmol) was added dropwise over 40 min, generating a creamy, orange suspension. The solution was stirred and warmed to ambient temperature over the course of 2.0 h, at which point the solution was heated to 110°C for 1.0 h. The corresponding creamy, tan-coloured suspension was cooled to 0°C and a solution of chlorodiisopropylphosphine (4.20 mL, 26.2 mmol) in heptane (5 mL) was added to the mixture dropwise via syringe over 20 min. The solution was allowed to warm to ambient temperature while stirring over 63.5 h, producing a pale, brown suspension, which was transferred to a fine-porosity glass swivel frit apparatus via cannula. The clear, amber solution was collected, and the remaining yellow residue was washed with heptane (1 × 20 mL), and the filtrates were combined. Solvents were evaporated to afford an off-white residue, which was reconstituted in toluene (6 mL), layered with pentane (3 mL), and cooled to −35°C for 16 h, resulting in pale, amber crystals. The mother liquor was decanted and the crystals washed with cold pentane (4 mL), recrystallized from toluene and pentane (2 : 1 ratio) at −35°C, and dried under vacuum, resulting in a tan, crystalline powder (2.050 g, 43 %). δ_H (benzene-d_6) 7.66 (d, 2H, $^3J_{HH}$ 7.5), 7.65 (d, 2H, $^3J_{HH}$ 7.5), 7.13 (t, 2H, $^3J_{HH}$ 7.5, Ar H), 2.66 (sp, 4H, $^3J_{HH}$ 6.9, ^{i}Pr CH(CH$_3$)$_2$), 1.20 (d, 12H, $^3J_{HH}$ 7.2), 0.98 (d, 12H, $^3J_{HH}$ 7.2, ^{i}Pr (CH(CH_3)$_2$). δ_P (benzene-d_6) 11.1 (s, 2P, P=N).

N,N′-*(Dibenzofuran-4,6-diylbis(diphenylphosphoranylylidene))bis(3,5-dimethylaniline) (**3a**)*

A sample of **2-Ph** (1.997 g, 3.722 mmol) was added to a 50 mL round-bottomed flask attached to a double manifold vacuum line and dissolved in toluene (20 mL) to afford a clear, dark orange solution. A solution of *m*-XyN$_3$ (1.095 g, 7.440 mmol) in toluene (4 mL) was added dropwise over 3 min at ambient temperature, resulting in a clear, dark brown solution, wherein vigorous foaming was observed during stirring. After 10 min, the reaction mixture was stirred at 55°C for 17 h to generate a clear, brown solution. The solvent was removed under vacuum to afford a dark, amber powder which was washed with pentane (3 × 20 mL) and dried under vacuum, resulting in a yellow powder (2.576 g, 89 %). δ_H (benzene-d_6) 8.34 (dd, 2H, $^3J_{HH}$ 7.6, $^4J_{HH}$ 1.5), 7.72 (dd, 8H, $^3J_{HH}$ 8.2, $^4J_{HH}$ 1.4), 7.47 (dd, 2H, $^3J_{HH}$ 7.6, $^4J_{HH}$ 1.5), 6.99–6.82 (ov m, 14H), 6.78 (s, 4H), 6.46 (s, 2H, Ar H), 2.15 (s, 12H, CH$_3$). δ_C (benzene-d_6) 156.8 (d, J_{CP} 2.3), 151.8 (d, J_{CP} 1.5), 138.2 (s, Ar C), 135.0 (d, 2C, $^2J_{CP}$ 6.8, 3,7-dbf), 132.9 (d, 8C, $^2J_{CP}$ 10.6, PPh$_2$ CH), 132.0 (d, J_{CP} 104.9, 4,6-dbf), 131.8 (d, 4C, $^4J_{CP}$ 3.0, PPh$_2$ CH), 129.0 (d, J_{CP} 12.8), 125.1 (d, J_{CP} 6.8), 124.9 (d, J_{CP} 2.3), 124.1 (d, J_{CP} 10.6), 122.4 (d, J_{CP} 17.4), 120.6 (s), 117.2 (d, J_{CP} 90.6, Ar C), 22.1 (s, CH$_3$). δ_P (benzene-d_6) −4.9 (s, 2P, P=N). Anal. Calc. for $C_{52}H_{44}N_2OP_2$: C 80.60, H 5.72, N 3.62. Found: C 80.28, H 5.87, N 4.46 %.

N,N′-*(Dibenzofuran-4,6-diylbis(diphenylphosphoranylylidene))bis(4-tritylaniline) (**3b**)*

A mixture of **2-Ph** (1.997 g, 3.722 mmol) and *p*-TrPhN$_3$ (1.746 g, 4.831 mmol) was added to a 50 mL round-bottomed flask attached to a double manifold vacuum line and dissolved in toluene (20 mL) to afford an opaque, dark orange suspension, which was then stirred at 55°C for 17.5 h. Solvent was removed under vacuum to afford a bright yellow solid, which was reconstituted in minimal toluene (15 mL) and left to sit at ambient temperature for 24 h, resulting in a pale yellow solid. The solution was filtered through a fine-porosity glass frit and the collected solid was dried under vacuum, resulting in a bright yellow powder (2.107 g, 73 %). δ_H (benzene-d_6) 8.23 (d, 2H, $^3J_{HH}$ 7.5), 7.99 (d, 2H, $^3J_{HH}$ 7.5), 7.52 (d, 8H, $^3J_{HH}$ 7.5), 7.49 (t, 2H, $^3J_{HH}$ 7.5), 7.35 (m, 4H, $^3J_{HH}$ 7.5), 7.1–7.3 (ov m, 38H), 6.73 (d, 4H, $^3J_{HH}$ 8.6), 6.46 (d, 4H, $^3J_{HH}$ 8.6, Ar H). δ_C (dichloromethane-d_2) 156.2 (d, J_{CP} 2.2), 149.1 (d, J_{CP} 2.0), 148.0 (s), 135.7 (s, Ar C), 134.4 (d, 2C, $^2J_{CP}$ 7.1, 3,7-dbf), 132.5 (d, 8C, $^2J_{CP}$ 10.3, PPh$_2$ CH), 132.0 (d, 4C, $^4J_{CP}$ 2.7, PPh$_2$ CH), 131.6 (s, 4C, *m*-Xy CH), 131.4 (s), 130.1 (s), 128.9 (d, J_{CP} 12.4), 127.6 (s), 125.9 (s, Ar C), 125.2 (d, 2C, $^4J_{CP}$ 2.3, 1,9-dbf), 125.0 (d, 2C, J_{CP} 6.5, 2,8-dbf), 124.1 (d, 4C, $^4J_{CP}$ 10.5, *m*-Xy C), 122.5 (d, J_{CP} 17.1, Ar C), 116.0 (d, 2C, $^1J_{CP}$ 94.9, 4,6-dbf), 64.6 (s, 2C, *C*(Ph)$_3$). δ_P (dichloromethane-d_2) −0.3 (s, 2P, P=N). Anal. Calc. for $C_{86}H_{64}N_2OP_2$: C 85.83, H 5.36, N 2.33. Found: C 85.64, H 5.33, N 2.42 %.

N,N′-*(Dibenzofuran-4,6-diylbis(diisopropylphosphoranylylidene))bis(3,5-dimethylaniline) (**3c**)*

In an argon atmosphere glove box, a sample of **2-^{i}Pr** (459 mg, 1.15 mmol) was added to a 20 mL scintillation vial and dissolved in toluene (5 mL). A solution of *m*-XyN$_3$ (337 mg, 2.29 mmol) in toluene (5 mL) was added dropwise over 5 min at ambient temperature, resulting in an effervescent, orange solution, which was stirred for an additional 17.5 h at ambient temperature. The resulting cloudy brown solution was evaporated to dryness, generating a brown residue which was further dried under vacuum, yielding a brown powder (553 mg, 76 %). δ_H (benzene-d_6) 8.15 (dd, 2H, $^3J_{HH}$ 7.5, $^4J_{HH}$ 1.2), 7.54 (dd, 2H, $^3J_{HH}$ 7.5, $^4J_{HH}$ 1.2), 7.08 (t, 2H, $^3J_{HH}$ 7.5), 6.93 (s, 4H), 6.52 (s, 2H, Ar H), 2.60 (sp, 4H, $^3J_{HH}$ 7.2, ^{i}Pr CH(CH$_3$)$_2$), 2.26 (s, 12H, *m*-Xy CH$_3$), 1.26 (d, 12H, $^3J_{HH}$ 7.2, ^{i}Pr CH(CH_3)$_2$), 0.98 (d, 12H, $^3J_{HH}$ 7.2, ^{i}Pr CH(CH_3)$_2$). δ_C (benzene-d_6) 155.5 (d, J_{CP} 2.8), 152.5 (d, J_{CP} 2.9), 137.8 (d, J_{CP} 0.7, Ar C), 134.9 (d, 2C, $^2J_{CP}$ 5.1, 3,7-dbf), 124.2 (d, J_{CP} 5.7, Ar C), 124.1 (d, 2C, $^4J_{CP}$ 2.3, 1,9-dbf), 123.7 (d, 2C, $^3J_{CP}$ 8.6, 2,8-dbf), 122.5 (d, 4C, $^4J_{CP}$ 14.9, *m*-Xy CH), 119.7 (s, 2C, *m*-Xy CH), 115.6 (d, J_{CP} 64.5, Ar C), 28.6 (d, 4C, $^1J_{CP}$ 70.8, ^{i}Pr *C*H(CH$_3$)$_2$), 21.8 (s, 4C, *m*-Xy CH$_3$), 18.1 (d, 4C, $^2J_{CP}$ 2.2, ^{i}Pr CH(*C*H$_3$)$_2$), 16.2 (d, 4C, $^2J_{CP}$ 3.5, ^{i}Pr CH(*C*H$_3$)$_2$). δ_P (benzene-d_6) 18.5 (s, 2P, P=N). Anal. Calc. for $C_{40}H_{52}N_2OP_2$: C 75.21, H 8.20, N 4.39. Found: C 75.61, H 8.11, N 4.74 %.

N,N′-*(Dibenzofuran-4,6-diylbis(diisopropylphosphoranylylidene))bis(4-tritylaniline) (**3d**)*

A mixture of **2-^{i}Pr** (1.301 g, 3.25 mmol) and *p*-TrPhN$_3$ (2.349 g, 6.50 mmol) was added to a 250 mL round-bottomed flask attached to a double manifold vacuum line and dissolved in toluene (80 mL) to afford a clear yellow solution, which was then stirred at 60°C for 43 h. Solvent was removed and the solid dried under vacuum, resulting in a pale yellow powder (3.303 g, 95 %.). δ_H (benzene-d_6) 8.12 (dd, 2H, $^3J_{HH}$ 7.5, $^4J_{HH}$ 1.2), 7.54–7.51 (ov m, 12H), 7.28 (d, 4H, $^3J_{HH}$ 8.7), 7.11–6.97 (ov m, 26H, Ar H), 2.59 (sp, 4H, $^3J_{HH}$ 6.9, ^{i}Pr CH(CH$_3$)$_2$), 1.15 (d, 12H, $^3J_{HH}$ 6.9, ^{i}Pr CH(CH_3)$_2$), 0.88 (d, 12H, $^3J_{HH}$ 6.9, ^{i}Pr CH(CH_3)$_2$). δ_C (benzene-d_6) 155.2 (d, J_{CP} 2.5), 150.6 (d, J_{CP} 2.6), 148.3 (s), 135.6 (s, Ar C), 135.3 (d, 2C, $^4J_{CP}$ 5.1, 1,9-dbf), 132.1 (s), 131.9 (s), 131.8 (s), 126.0 (s), 124.2 (s), 124.1 (s, Ar C), 123.8 (d, 2C, $^2J_{CP}$ 8.3, 3,7-dbf), 123.2 (d, 2C, $^3J_{CP}$ 15.0, 2,8-dbf), 114.9 (d, 2C, $^1J_{CP}$ 66.0, 4,6-dbf), 65.0 (s, 2C, *C*(Ph)$_3$), 28.4 (d, 4C, $^1J_{CP}$ 70.2, ^{i}Pr *C*H(CH$_3$)$_2$), 17.9 (d, 4C, $^2J_{CP}$ 1.7, ^{i}Pr CH(*C*H$_3$)$_2$), 15.9 (d, 4C, $^2J_{CP}$ 3.4, ^{i}Pr CH(*C*H$_3$)$_2$). δ_P (benzene-d_6) 20.2 (s, 2P, P=N). Anal. Calc. for $C_{74}H_{72}N_2OP_2$: C 83.27, H 6.80, N 2.62. Found: C 83.24, H 6.86, N 2.70 %.

N-*((6-(*N-*(3,5-Dimethylphenyl)*-P,P-*diphenylphosphorimidoyl)-dibenzofuran-4-yl)diphenylphosphoranylidene)-3,5-dimethylbenzenaminium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (**4a**)*

A mixture of **3a** (510 mg, 0.658 mmol) and [H(OEt$_2$)$_2$][B(*m*-(CF$_3$)$_2$-C$_6$H$_3$)$_4$] (666 mg, 0.658 mmol) was added to a 50 mL round-bottomed flask attached to a double manifold vacuum line and dissolved in dichloromethane (25 mL), which was then stirred at ambient temperature for 4 h, affording a cloudy brown suspension. Solvent was removed under vacuum to afford a brown residue, which was washed with cold pentane (3 × 20 mL) and dried under vacuum, resulting in an off-white powder (760 mg, 70 %). δ_H (benzene-d_6) 8.39 (br s, 8H, BAr$^F{}_4$), 7.58 (br s, 4H, BAr$^F{}_4$), 7.52 (d, 2H, J_{HH} 7.43), 7.26 (d, 8H, J_{HH} 7.43), 6.98 (q, 6H, J_{HH} 7.43), 6.86 (q, 12H, J_{HH} 7.87), 6.42 (s, 3H), 6.40 (s, 2H, Ar CH), 1.91 (s, 12H, *m*-Xy CH$_3$). δ_C (benzene-d_6) 162.4 (q, 4C, $^1J_{CB}$ 50.1, BArF4 C), 157.5 (s, 2C, Ar C), 143.5 (br m, 2C), 139.3 (s, 4C, *m*-Xy C), 135.7 (br s, 8C, BAr$^F{}_4$ CH), 134.3 (d, 4C, $^4J_{CP}$ 2.7), 133.3 (d, 8C, $^2J_{CP}$ 10.7, PPh$_2$ CH), 132.2 (d, 2C, $^2J_{CP}$ 7.9, 3,7-dbf CH), 130.2 (qq, 8C, $^2J_{CF}$ 31.4, $^3J_{CB}$ 2.0, BAr$^F{}_4$ C), 129.8 (d, 8C, $^3J_{CP}$ 12.9, PPh$_2$ CH), 128.3 (s, 2C, *m*-Xy CH), 127.4 (d, 4C, $^3J_{CP}$ 1.6, *m*-Xy CH), 125.5 (q, 8C, $^1J_{CF}$ 272.1, BAr$^F{}_4$ CF$_3$), 125.4 (s, 2C, 1,9-dbf CH), 124.6 (d, 2C, J_{CP} 6.6, Ar C), 123.0 (d, 2C, $^3J_{CP}$ 10.8, 2,8-dbf), 118.4 (br sp, 4C, $^3J_{CF}$ 4.3, BAr$^F{}_4$ CH), 113.2 (d, 2C, $^1J_{CP}$ 91.1, 4,6-dbf), 21.4 (s, 4C, *m*-Xy CH$_3$). Signal for PPh$_2$ *ipso*-C was not observed. δ_P (benzene-d_6) 18.8 (br s, 2P, P=N). δ_B (benzene-d_6) −5.8 (s, 1B, BAr$^F{}_4$). δ_F (benzene-d_6) −61.2 (s, 24F, BAr$^F{}_4$). Anal. Calc. for $\mathrm{C_{84}H_{57}BF_{24}N_2OP_2}$: C 61.55, H 3.51, N 1.71. Found: C 61.46, H 3.43, N 1.61 %.

N-*((6-(*P,P*-Diphenyl-*N*-(4-tritylphenyl)phosphorimidoyl)-dibenzofuran-4-yl)diphenylphosphoranylidene)-4-tritylbenzenaminium tetrakis(3,5-bis(trifluoromethyl)-phenyl)borate (**4b**)*

In an argon atmosphere glove box, a mixture of **3b** (300.2 mg, 0.2495 mmol) and [H(OEt$_2$)$_2$][B(*m*-(CF$_3$)$_2$-C$_6$H$_3$)$_4$] (252.9 mg, 0.2498 mmol) was added to a 20 mL scintillation vial and dissolved in toluene (15 mL), which was then stirred at ambient temperature for 1.5 h, affording a clear yellow solution. Solvent was removed under vacuum and the yellow crystalline powder washed with cold pentane (3 × 6 mL), recrystallized from toluene and pentane (1 : 5 ratio) at −35°C, and dried under vacuum, resulting in a yellow, crystalline powder (424.4 mg, 82 %). δ_H (benzene-d_6) 8.39 (br s, 8H, BAr$^F{}_4$), 7.57 (br s, 4H, BAr$^F{}_4$), 7.52 (d, 2H, J_{HH} 7.65), 7.21 (m, 14H), 6.97 (m, 31H), 6.86 (q, 12H, J_{HH} 7.78), 6.58 (d, 5H, J_{HH} 8.55, Ar CH). Signal for NH was not observed. δ_C (benzene-d_6) 163.1 (q, 4C, $^1J_{CB}$ 49.8, BAr$^F{}_4$ C), 157.3 (s, 2C, Ar C), 147.5 (s, 6C, *p-Tr*Ph C), 142.4 (d, 2C, J_{CP} 1.6), 141.5 (d, 2C, J_{CP} 3.1, Ar C), 135.7 (br s, 8C, BAr$^F{}_4$ CH), 134.4 (d, 4C, $^4J_{CP}$ 2.1), 133.2 (d, 8C, $^2J_{CP}$ 10.6, PPh$_2$ CH), 132.7 (br s, 2C, 1,9-dbf CH), 132.4 (d, 2C, $^2J_{CP}$ 8.1, 3,7-dbf), 131.7 (s, 12C, *p*-Tr*Ph*), 130.2 (qq, 8C, $^2J_{CF}$ 31.6, $^3J_{CB}$ 3.0, BAr$^F{}_4$ C), 129.8 (d, 8C, $^3J_{CP}$ 12.8, PPh$_2$ CH), 128.9 (s, 12C, *p*-Tr*Ph*), 127.5 (br s, 4C, *p-Tr*Ph CH), 126.7 (s, 6C, *p*-Tr*Ph* CH), 125.5 (q, 8C, $^1J_{CF}$ 272.5, BAr$^F{}_4$ CF$_3$), 125.2 (d, 2C, $^3J_{CP}$ 11.0, 2,8-dbf), 124.7 (d, 4C, $^1J_{CP}$ 105.5, PPh$_2$ C), 124.6 (d, 2C, J_{CP} 6.4, Ar C), 124.3 (d, 4C, $^3J_{CP}$ 10.7, *p-Tr*Ph CH), 118.4 (br sp, 4C, $^3J_{CF}$ 4.0, BAr$^F{}_4$ CH), 111.4 (d, 2C, $^1J_{CP}$ 96.1, 4,6-dbf), 65.2 (s, 2C, *p-Tr*Ph). δ_P (benzene-d_6) 19.6 (s, 2P, P=N). δ_B (benzene-d_6) −5.8 (s, 1B, BAr$^F{}_4$). δ_F (benzene-d_6) −61.2 (s, 24F, BAr$^F{}_4$). Anal. Calc. for $\mathrm{C_{118}H_{77}BF_{24}N_2OP_2}$: C 68.55, H 3.75, N 1.35. Found: C 68.73, H 3.85, N 1.57 %.

N-*((6-(*N*-(3,5-Dimethylphenyl)-*P,P*-diisopropylphosphorimidoyl)dibenzofuran-4-yl)diisopropylphosphoranylidene)-3,5-dimethylbenzenaminium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (**4c**)*

In an argon atmosphere glove box, a mixture of **3c** (437 mg, 0.684 mmol) and [H(OEt$_2$)$_2$][B(*m*-(CF$_3$)$_2$-C$_6$H$_3$)$_4$] (695 mg, 0.686 mmol) was added to a 20 mL scintillation vial and dissolved in toluene (8 mL) to afford a clear, dark brown solution, which was then stirred at ambient temperature for 72.5 h. Solvent was removed under vacuum and the off-white powder washed with cold pentane (3 × 6 mL), recrystallized from toluene and pentane (1 : 5 ratio) at −35°C, and dried under vacuum, resulting in a pale peach, crystalline powder (834 mg, 81 %). δ_H (benzene-d_6) 8.39 (br s, 8H, BAr$^F{}_4$), 7.76 (d, 2H, $^3J_{HH}$ 7.15, 3,7-dbf), 7.62 (br s, 4H, BAr$^F{}_4$), 7.57 (d, 2H, $^3J_{HH}$ 7.68, 1,9-dbf), 7.07 (dd, 2H, $^3J_{HH}$ 7.42, $^3J_{HH}$ 7.68), 6.71 (s, 4H), 6.50 (s, 2H, Ar CH), 3.90 (br s, 1H, NH), 2.53 (sp, 4H, $^3J_{HH}$ 7.15, ^{i}Pr C*H*(CH$_3$)$_2$), 2.15 (s, 12H, Ar CH$_3$), 1.07 (d, 12H, $^3J_{HH}$ 7.02), 0.92 (d, 12H, $^3J_{HH}$ 7.11, ^{i}Pr CH(C*H*$_3$)$_2$). δ_C (benzene-d_6) 163.1 (q, 4C, $^1J_{CB}$ 50.2, BAr$^F{}_4$ C), 156.5 (d, 2C, J_{CP} 2.2, Ar C), 150.3 (br m, 2C), 138.6 (s, 4C, *m*-Xy C), 135.8 (br s, 8C, BAr$^F{}_4$ CH), 133.8 (d, 2C, $^2J_{CP}$ 5.1, 3,7-dbf CH), 130.2 (qq, 8C, $^2J_{CF}$ 31.3, $^3J_{CB}$ 3.1, BAr$^F{}_4$ C), 125.5 (q, 8C, $^1J_{CF}$ 272.2, BAr$^F{}_4$ CF$_3$), 125.3 (d, 2C, $^4J_{CP}$ 2.1, 1,9-dbf), 124.7 (d, 2C, J_{CP} 8.8, Ar C), 124.2 (d, 2C, $^3J_{CP}$ 8.8, 2,8-dbf), 122.4 (d, 4C, $^3J_{CP}$ 13.3), 121.6 (s, 2C, *m*-Xy CH), (br sp, 4C, $^3J_{CF}$ 3.7, BAr$^F{}_4$ CH), 113.9 (d, 2C, $^1J_{CP}$ 68.8, 4,6-dbf), 28.0 (d, 4C, $^1J_{CP}$ 68.2, ^{i}Pr *C*H(CH$_3$)$_2$), 21.9 (s, 4C, *m*-Xy CH$_3$), 18.0 (d, 4C, $^2J_{CP}$ 2.2), 16.3 (d, 4C, $^2J_{CP}$ 2.9, ^{i}Pr CH (*C*H$_3$)$_2$). δ_P (benzene-d_6) 25.7 (br s, 2P, P=N). δ_B (benzene-d_6) −5.8 (s, 1B, BAr$^F{}_4$). δ_F (benzene-d_6) −61.2 (s, 24F, BAr$^F{}_4$). Anal. Calc. for $\mathrm{C_{72}H_{65}BF_{24}N_2OP_2}$: C 57.54, H 4.36, N 1.86. Found: C 57.17, H 4.03, N 1.55 %.

N-*((6-(*P,P*-Diisopropyl-*N*-(4-tritylphenyl)phosphorimidoyl)-dibenzofuran-4-yl)diisopropylphosphoranylidene)-4-tritylbenzenaminium tetrakis(3,5-bis(trifluoromethyl)-phenyl)borate (**4d**)*

In an argon atmosphere glove box, a mixture of **3d** (239.7 mg, 0.2246 mmol) and [H(OEt$_2$)$_2$][B(*m*-(CF$_3$)$_2$-C$_6$H$_3$)$_4$] (225.7 mg, 0.2229 mmol) was added to a 20 mL scintillation vial and dissolved in toluene (7.5 mL), which was then stirred at ambient temperature for 1.5 h, affording a clear yellow solution. Solvent was removed under vacuum and the yellow crystalline powder washed with cold pentane (3 × 6 mL), recrystallized from toluene and pentane (1 : 5 ratio) at −35°C, and dried under vacuum, resulting in a yellow, crystalline powder (340.9 mg, 79 %). δ_H (benzene-d_6, 21°C) 8.39 (br s, 8H, BAr$^F{}_4$), 7.62 (s, 2H, Ar CH), 7.59 (br s, 4H, BAr$^F{}_4$), 7.32 (d, 12H, J_{HH} 7.32), 7.05 (m, 24H), 6.99 (m, 2H), 6.39 (d, 4H, J_{HH} 8.62, Ar CH), 5.10 (br s, 1H, NH), 2.20 (sp, 4H, $^3J_{HH}$ 7.10, ^{i}Pr C*H*(CH$_3$)$_2$), 0.66 (d, 12H, $^3J_{HH}$ 6.59), 0.64 (d, 12H, $^3J_{HH}$ 6.68, ^{i}Pr CH(C*H*$_3$)$_2$). δ_C (benzene-d_6, 22°C) 163.1 (q, 4C, $^1J_{CB}$ 49.0, BAr$^F{}_4$ C), 157.8 (d, 2C, J_{CP} 2.2, Ar C), 147.5 (s, 6C, *p-Tr*Ph C), 135.7 (br s, 8C, BAr$^F{}_4$ CH), 132.9 (br s, 2C, 1,9-dbf CH), 131.6 (s, 12C, *p*-Tr*Ph*), 131.2 (br s, 2C, 3,7-dbf), 130.3 (qq, 8C, $^2J_{CF}$ 31.8, $^3J_{CB}$ 2.9, BAr$^F{}_4$ C), 128.3 (s, 12C, *p*-Tr*Ph*), 127.0 (br s, 4C, *p-Tr*Ph CH), 126.8 (s, 6C, *p*-Tr*Ph* CH), 125.5 (q, 8C, $^1J_{CF}$ 272.8, BAr$^F{}_4$ CF$_3$), 125.0 (d, 2C, J_{CP} 5.8, Ar C), 124.7 (d, 2C, $^3J_{CP}$ 8.1, 2,8-dbf), 124.2 (d, 4C, $^3J_{CP}$ 8.1, *p-Tr*Ph CH), 118.4 (br sp, 4C, $^3J_{CF}$ 2.9, BAr$^F{}_4$ CH), 65.3 (s, 2C, *p-Tr*Ph), 30.7 (br d, 4C, $^1J_{CP}$ 61.3, ^{i}Pr *C*H(CH$_3$)$_2$), 16.4 (br s, 4C), 15.4 (br s, 4C, ^{i}Pr CH(*C*H$_3$)$_2$). Signals for two aromatic quaternary carbon environments (2C each) were not observed. δ_P (benzene-d_6, 21°C) 40.9 (br s, 2P, P=N). δ_F (benzene-d_6, 21°C) −61.1 (s, 24F, CF$_3$). δ_B (benzene-d_6, 21°C) −5.8 (s, 1B, BAr$^F{}_4$). Anal. Calc. for $\mathrm{C_{106}H_{85}BF_{24}N_2OP_2}$: C 65.91, H 4.44, N 1.45. Found: C 65.85, H 4.39, N 1.39 %.

*Ethyl(*N,N′*-(dibenzofuran-4,6-diylbis(diphenylphosphoranylylidene))bis(3,5-dimethylaniline)) Zinc (**5a**)*

In an argon atmosphere glove box, a sample of **4a** (100.3 mg, 0.06119 mmol) was added to a 20 mL scintillation vial and dissolved in toluene (1.5 mL) to afford a clear, colourless solution. An aliquot of [$ZnEt_2$] (6.3 µL, 0.061 mmol) was injected, and the resulting faint yellow solution was then stirred at ambient temperature for 1 h. Solvent was removed under vacuum and the off-white powder washed with cold pentane (3 × 6 mL), recrystallized from toluene and pentane (1 : 5 ratio) at −35°C, and dried under vacuum, resulting in a pale orange, crystalline powder (93.5 mg, 93 %). δ_H (benzene-d_6) 8.41 (br s, 8H, $BAr^F{}_4$), 7.58 (br s, 4H, $BAr^F{}_4$), 7.47 (m, 2H), 7.37 (dd, 8H, J_{HH} 12.42, J_{HH} 7.07), 7.13 (m, 2H), 7.03 (m, 7H), 6.89 (m, 8H), 6.31 (s, 3H), 6.22 (s, 2H, Ar CH), 1.81 (s, 12H, *m*-Xy CH_3), 0.94 (t, 3H, $^3J_{HH}$ 8.14, $ZnCH_2CH_3$), 0.18 (q, 2H, $^3J_{HH}$ 8.14, $ZnCH_2CH_3$). δ_C (benzene-d_6) 163.1 (q, 4C, $^1J_{CB}$ 49.4, $BAr^F{}_4$ C), 156.5 (s, 2C, Ar C), 145.6 (d, 2C, $^2J_{CP}$ 5.1), 139.3 (d, 4C, $^4J_{CP}$ 1.4, *m*-Xy C), 135.7 (br s, 8C, $BAr^F{}_4$ CH), 134.2 (d, 4C, $^4J_{CP}$ 2.6), 133.7 (d, 8C, $^2J_{CP}$ 10.3, PPh_2 CH), 131.8 (d, 2C, $^2J_{CP}$ 9.0, 3,7-dbf CH), 130.2 (qq, 8C, $^2J_{CF}$ 31.6, $^3J_{CB}$ 2.8, $BAr^F{}_4$ C), 129.8 (s, 2C, *m*-Xy CH), 129.7 (d, 8C, $^3J_{CP}$ 12.8, PPh_2 CH), 128.9 (d, 4C, $^3J_{CP}$ 1.7, *m*-Xy CH), 126.0 (s, 2C, 1,9-dbf CH), 125.5 (q, 8C, $^1J_{CF}$ 272.1, $BAr^F{}_4$ CF_3), 124.6 (d, 2C, J_{CP} 6.6, Ar C), 123.8 (d, 2C, $^3J_{CP}$ 10.2, 2,8-dbf), 118.4 (br sp, 4C, $^3J_{CF}$ 4.1, $BAr^F{}_4$ CH), 113.2 (d, 2C, $^1J_{CP}$ 110.9, 4,6-dbf), 21.4 (s, 4C, *m*-Xy CH_3), 13.1 (s, 1C, $ZnCH_2CH_3$), 2.3 (s, 1C, $ZnCH_2CH_3$). Signal for PPh_2 *ipso*-C was not observed. δ_P (benzene-d_6) 27.1 (s, 2P, P=N). δ_B (benzene-d_6) −5.8 (s, 1B, $BAr^F{}_4$). δ_F (benzene-d_6) −61.2 (s, 24F, $BAr^F{}_4$). Anal. Calc. for $C_{86}H_{61}BF_{24}N_2OP_2Zn$: C 59.62, H 3.55, N 1.62. Found: C 59.98, H 3.85, N 1.99 %.

*Ethyl(N,N′-(dibenzofuran-4,6-diylbis(diphenylphosphoranylylidene))bis(4-tritylaniline)) Zinc (**5b**)*

In an argon atmosphere glove box, a sample of **4b** (75.0 mg, 0.03627 mmol) was added to a 20 mL scintillation vial and dissolved in toluene (4 mL) to afford a clear, yellow solution. An aliquot of [$ZnEt_2$] (4.1 µL, 0.040 mmol) was injected, and the resulting faint yellow solution was then stirred at ambient temperature for 1.5 h. Solvent was removed under vacuum and the off-white powder washed with cold pentane (3 × 6 mL), recrystallized from toluene and pentane (1 : 5 ratio) at −35°C, and dried under vacuum, resulting in a yellow, crystalline powder (77.1 mg, 98 %). δ_H (benzene-d_6) 8.39 (br s, 8H, $BAr^F{}_4$), 7.54 (br s, 4H, $BAr^F{}_4$), 7.46 (d, 2H, J_{HH} 7.24), 7.27 (d, 8H, J_{HH} 7.58), 6.99(m, 50H), 6.52 (d, 4H, J_{HH} 8.59, Ar CH), 0.62 (t, 3H, $^3J_{HH}$ 7.97, $ZnCH_2CH_3$), −0.01 (q, 2H, $^3J_{HH}$ 7.97, $ZnCH_2CH_3$). δ_C (benzene-d_6) 163.1 (q, 4C, $^1J_{CB}$ 50.2, $BAr^F{}_4$ C), 156.6 (s, 2C, Ar C), 147.3 (s, 6C, *p-Tr*Ph C), 144.0 (d, 2C, J_{CP} 4.3), 142.6 (d, 2C, J_{CP} 3.1, Ar C), 135.7 (br s, 8C, $BAr^F{}_4$ CH), 134.3 (d, 4C, $^4J_{CP}$ 2.8), 133.7 (d, 8C, $^2J_{CP}$ 10.7, PPh_2 CH), 132.7 (br s, 2C, 1,9-dbf CH), 132.0 (d, 2C, $^2J_{CP}$ 8.1, 3,7-dbf), 131.7 (s, 12C, *p*-Tr*Ph*), 130.2 (qq, 8C, $^2J_{CF}$ 31.3, $^3J_{CB}$ 2.6, $BAr^F{}_4$ C), 129.7 (d, 8C, $^3J_{CP}$ 10.5, PPh_2 CH), 128.2 (s, 12C, *p*-Tr*Ph*), 127.5 (br s, 4C, *p-Tr*Ph CH), 126.7 (s, 6C, *p*-Tr*Ph* CH), 126.0 (d, 2C, $^3J_{CP}$ 11.6, 2,8-dbf), 125.5 (q, 8C, $^1J_{CF}$ 272.8, $BAr^F{}_4$ CF_3), 125.5 (d, 4C, $^3J_{CP}$ 9.7, *p-Tr*Ph CH), 125.1 (d, 4C, $^1J_{CP}$ 92.3, PPh_2 C), 124.8 (d, 2C, J_{CP} 6.4, Ar C), 118.4 (br sp, 4C, $^3J_{CF}$ 3.9, $BAr^F{}_4$ CH), 112.8 (d, 2C, $^1J_{CP}$ 96.1, 4,6-dbf), 65.0 (s, 2C, *p-Tr*Ph), 12.8 (s, 1C, $ZnCH_2CH_3$), 2.5 (s, 1C, $ZnCH_2CH_3$). δ_P (benzene-d_6) 29.9 (s, 2P, P=N). δ_B (benzene-d_6) −5.8 (s, 1B, $BAr^F{}_4$). δ_F (benzene-d_6) −61.2 (s, 24F, $BAr^F{}_4$). Anal. Calc. for $C_{120}H_{81}BF_{24}N_2OP_2Zn$: C 66.69, H 3.78, N 1.30. Found: C 66.21, H 3.44, N 0.99 %.

*Ethyl(N,N′-(dibenzofuran-4,6-diylbis(diisopropylphosphoranylylidene))bis(3,5-dimethylaniline)) Zinc (**5c**)*

In an argon atmosphere glove box, a sample of **4c** (232.9 mg, 0.2348 mmol) was added to a 20 mL scintillation vial and dissolved in toluene (12 mL) to afford a clear, orange solution. An aliquot of [$ZnEt_2$] (24.5 µL, 0.238 mmol) was injected, and the resulting faint yellow solution was then stirred at ambient temperature for 1 h. Solvent was removed under vacuum and the pale beige powder washed with cold pentane (3 × 6 mL), recrystallized from toluene and pentane (1 : 5 ratio) at −35°C, and dried under vacuum, resulting in a yellow, crystalline powder (347.4 mg, 93 %). δ_H (dichloromethane-d_2) 8.40 (d, 2H, $^3J_{HH}$ 6.6), 7.72 (ov m, 12H), 7.55 (s, 4H), 6.48 (s, 2H), 6.32 (s, 4H, Ar H), 4.55 (br s, 1H, NH), 2.94 (br s, 4H, ^{i}Pr C*H*(CH_3)$_2$), 1.20 (ov m, 24H, ^{i}Pr CH(C*H*$_3$)$_2$). Inappreciable solubility in all solvents precluded satisfactory signal-to-noise for $^{13}C\{^1H\}$ analysis. δ_P (benzene-d_6) 50.1 (s, 2P, P=N). δ_B (benzene-d_6) −6.1 (s, 1B, $BAr^F{}_4$). δ_F (benzene-d_6) −61.1 (s, 24F, $BAr^F{}_4$). Anal. Calc. for $C_{74}H_{69}BF_{24}N_2OP_2Zn$: C 55.67, H 4.36, N 1.75. Found: C 54.61, H 4.01, N 1.41 %.

*Ethyl(N,N′-(dibenzofuran-4,6-diylbis(diisopropylphosphoranylylidene))bis(4-tritylaniline)) Zinc (**5d**)*

In an argon atmosphere glove box, a sample of **4d** (290.5 mg, 0.1504 mmol) was added to a 20 mL scintillation vial and dissolved in toluene (12 mL) to afford a clear, orange solution. An aliquot of [$ZnEt_2$] (17.0 µL, 0.165 mmol) was injected, and the resulting faint yellow solution was then stirred at ambient temperature for 0.5 h. Solvent was removed under vacuum and the dark yellow powder washed with cold pentane (3 × 6 mL), redissolved in benzene (0.5 mL), and passed through a Celite filter. Solvent was removed under vacuum and the bright yellow powder was recrystallized from toluene and pentane (1 : 5 ratio) at −35°C, and dried under vacuum, resulting in a yellow, crystalline powder (219.7 mg, 72 %). δ_H (benzene-d_6) 8.39 (br s, 8H, $BAr^F{}_4$), 7.59 (br s, 4H, $BAr^F{}_4$), 7.56 (s, 2H, 2,8-dbf), 7.30 (d, 4H, $^3J_{HH}$ 7.49, *p*-Tr*Ph*), 7.06 (m, 30H, *p-Tr*Ph), 7.06 (d, 4H, $^3J_{HH}$ 7.60, *p*-Tr*Ph*), 6.75 (d, 2H, $^3J_{HH}$ 7.64, 3,7-dbf), 6.48 (d, 2H, $^3J_{HH}$ 7.42, 1,9-dbf), 2.16 (br sept, 4H, ^{i}Pr C*H*(CH_3)$_2$), 0.61 (d, 12H, $^3J_{HH}$ 6.65), 0.56 (d, 12H, $^3J_{HH}$ 6.96, ^{i}Pr CH(C*H*$_3$)$_2$), 0.40 (t, 3H, $^3J_{HH}$ 7.89, $ZnCH_2CH_3$), −0.23 (q, 2H, $^3J_{HH}$ 7.95, $ZnCH_2CH_3$). δ_C (benzene-d_6) 163.1 (q, 4C, $^1J_{CB}$ 49.2, $BAr^F{}_4$ C), 157.0 (s, 2C, Ar C), 147.4 (s, 6C, *p-Tr*Ph C), 144.5 (d, 2C, J_{CP} 4.7), 143.6 (d, 2C, J_{CP} 3.1, Ar C), 135.7 (br s, 8C, $BAr^F{}_4$ CH), 133.1 (br s, 2C, 1,9-dbf CH), 131.7 (s, 12C, *p*-Tr*Ph*), 130.7 (d, 2C, $^2J_{CP}$ 6.6, 3,7-dbf), 130.3 (qq, 8C, $^2J_{CF}$ 31.5, $^3J_{CB}$ 3.0, $BAr^F{}_4$ C), 128.9 (s, 12C, *p*-Tr*Ph*), 127.3 (br s, 4C, *p-Tr*Ph CH), 126.7 (s, 6C, *p*-Tr*Ph* CH), 125.8 (d, 2C, $^3J_{CP}$ 7.2, 2,8-dbf), 125.7 (d, 4C, $^3J_{CP}$ 13.8, *p-Tr*Ph CH), 125.5 (q, 8C, $^1J_{CF}$ 272.5, $BAr^F{}_4$ CF_3), 124.8 (d, 2C, J_{CP} 5.3, Ar C), 118.4 (br sp, 4C, $^3J_{CF}$ 3.9, $BAr^F{}_4$ CH), 65.3 (s, 2C, *p-Tr*Ph), 26.3[27] (br d, 4C, ^{i}Pr *C*H(CH_3)$_2$), 16.1 (d, 4C, $^2J_{CP}$ 2.0), 15.6 (d, 4C, $^2J_{CP}$ 1.9, ^{i}Pr CH(*C*H$_3$)$_2$), 12.4 (s, 1C, $ZnCH_2CH_3$), 1.6 (s, 1C, $ZnCH_2CH_3$). Signal for 4,6-dbf was not observed. δ_P (benzene-d_6) 49.9 (s, 2P, P=N). δ_B (benzene-d_6) −5.8 (s, 1B, $BAr^F{}_4$). δ_F (benzene-d_6) −61.1 (s, 24F, $BAr^F{}_4$). Anal. Calc. for $C_{108}H_{89}BF_{24}N_2OP_2Zn$: C 64.06, H 4.43, N 1.38. Found: C 64.38, H 4.04, N 1.57 %.

X-Ray Crystallography

Single crystals suitable for X-ray diffraction were readily obtained from concentrated toluene (**3a**) or bromobenzene solutions (**3b**) at ambient temperature, by slow diffusion of pentane into a dichloromethane solution (**3c**, **3d**, and **5c′**) at −35°C, or by slow diffusion of pentane into a benzene solution (**4c**) at ambient temperature. Crystals were coated in dry Paratone oil under an argon atmosphere and mounted onto a glass fibre. Data were collected at 173 K using a Bruker SMART APEX II diffractometer (Mo$_{K\alpha}$ radiation, λ 0.71073 Å) outfitted with a CCD area-detector and a KRYO-FLEX liquid nitrogen vapour cooling device. A data collection strategy using ω and φ scans at 0.5° steps yielded full hemispherical data with excellent intensity statistics. Unit cell parameters were determined and refined on all observed reflections using *APEX2* software.[28] Data reduction and correction for Lorentz polarization were performed using *SAINT-Plus* software.[29] Absorption corrections were applied using *SADABS*.[30] The structures were solved by direct methods and refined by the least-squares method on F^2 using the *SHELXTL*[31] or *Olex2*[32] software suites. All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated and isotropically refined as riding models to their parent atoms, except the N–H hydrogen of **4c** which was located from the Fourier difference map and isotropically refined with a fixed N–H bond length. Table 1 provides a summary of selected data collection and refinement parameters. Special considerations were required in the refinement of disordered moieties in the structures of **3a**, **3b**, **4c**, and **5c′**. In the structure of **3a**, one toluene solvent molecule (C1s, 60 %/C1r, 40 %) was disordered and some restraints were applied in order to obtain reasonable bond distances and angles. Similarly, two CF_3 groups in the anion of **4c** were disordered over two positions with occupation factor ratios of 53 : 47 and 60 : 40. Furthermore, the structure of **3b** contained two severely disordered bromobenzene solvent molecules in the asymmetric unit, for which no suitable model could be found. Likewise, the structure of **5c′** contained one severely disordered tetrahydrofuran solvent molecule in the asymmetric unit, for which no suitable model could be found. The electron density associated with the disordered regions in both **3b** and **5c′** was removed from the reflection files using the SQUEEZE subroutine of *PLATON*,[33] leaving voids of ~847.3 and 330.8 Å^3, respectively.

Crystallographic Data

Atomic coordinates, interatomic distances and angles, anisotropic thermal parameters, and hydrogen parameters for **3a**–**d**, **4c**, and **5c′** are available as CIF files from the Cambridge Crystallographic Data Centre (CCDC) using depository numbers 1023936–1023941.

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