CATION–π INTERACTIONS BETWEEN ALKALI METAL CATIONS AND NEUTRAL DOUBLE BONDS

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Dedicated to Professor Ivan Stibor on the occasion of his 60th birthday.

Two-armed lariat ethers having double bonds present in their side arms form stable complexes with sodium and potassium cations. When the double bonds are positioned appropriately, cation–π interactions are observed between the neutral double bonds and the macroring-bound cation as demonstrated by X-ray crystallography.

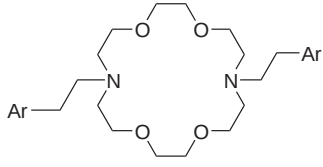
Keywords: Alkali metals; Crown compounds; Azacrown compounds; Alkene complexes; Podands; Macrocycles; Supramolecular chemistry; X-ray diffraction.

Cation–π interactions are electrostatic attractions that may occur between any Lewis base containing a π bond and a positively charged Lewis acid[1]. Those that are of the greatest potential relevance to biology involve ammonium, guanidinium, sodium, or potassium cations as the Lewis acid. Three amino acid side chains possess aromatic π donors. The arenes are benzene (in phenylalanine), phenol (tyrosine), and indole (tryptophan). Two amino acid side chains possess amino groups: ammonium ion in lysine and guanidinium ion in arginine. Many metallic cations are present in the biological milieu, but Na^+ and K^+ are typically present in concentrations of >100 mmol/l. The side-chain arenes of phenylalanine, tyrosine, and tryptophan occur once in every 11 amino acids in all known protein sequences, so the likelihood that a cation–π interaction will occur is high.

Early crystallographic studies revealed clear evidence for alkali metal cation–π interactions with arene anions. Stucky and coworkers showed, as early as 1972, that lithium cation was π-bonded to naphthalenide anion.

The earliest indication of a favorable interaction between K^+ and benzene was reported by Kebarle and coworkers[2]. They demonstrated by mass spectrometric methods that the interaction between K^+ and benzene was about as strong as between K^+ and CH_3OH. Shortly thereafter, Meot-Ner and Deakyne demonstrated a cation–π interaction between benzene and ammonium cation[3]. Burley and Petsko surveyed the Protein Data Bank (PDB) and reported evidence for ammonium–π interactions in the limited structural database available at the time[4]. Extensive effort has been made during recent years to more fully characterize the interactions of alkali metals with arenes in the gas phase by use of mass spectrometric[5–8] and computational methods[9–11]. Several solid-state structures, in which cation–π interactions were found, have also been reported recently[12–14].

Our first efforts used lariat ethers and a combination of solution and solid-state methods but these proved equivocal at best[15]. Our first successful efforts focused on demonstrating by unambiguous solid-state structural data that Na^+ and K^+ are complexed by benzene[16], phenol[17], and indole[18]. In this, we used lariat ether receptors[19] in which the side arms were terminated by the same arenes that occur in essential amino acids. The receptor system is illustrated generically as **A**. When the arene was indole, the structural results obtained[20] did not comport with calculations, which predicted that benzene, rather than pyrrole, would be the subunit of indole that was in contact with the cation[21]. This issue was resolved by tethering indole at its position 5, rather than at position 3[22]. When so bonded, benzene was the primary donor for the ring-bound cation. These studies demonstrated the remarkable versatility of indole as a potential π donor within a protein environment.

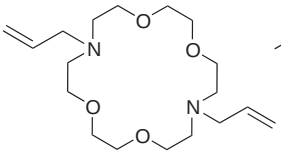


A

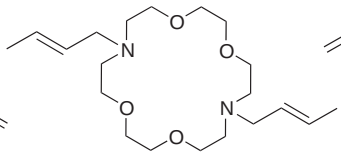
We then turned our attention to the question of double and triple bonds as potential donors for alkali metal cations. Cation–π interactions were demonstrated using a receptor system similar to **A** in which double[23] or triple[24] bonds replaced the arenes. In this report, we present additional data conclusively demonstrating that double bonds can interact with alkali metal cations and that the double-bond position on the side chain is of critical importance.

RESULTS AND DISCUSSION

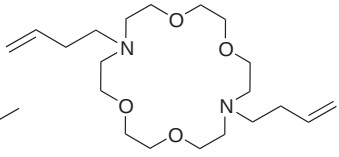
Compounds **1**, **2**, and **3** were prepared for our study of alkali metal cation–π interactions. Each is a 1,10-diaza-18-crown-6 derivative in which the two macroring nitrogen atoms are alkylated by an unsaturated chain. The side chains are $CH_2CH{=}CH_2$ (allyl, **1**)[25], $CH_2CH{=}CHCH_3$ (but-2-enyl, **2**), and $CH_2CH_2CH{=}CH_2$ (but-3-enyl, **3**). The double bonds in the allyl and but-2-enyl side chains are in the same relative position with respect to the macrocyclic ring. The 3-double bond of **3** is one carbon more remote from the ring. The structures of compounds **1**–**3** are shown.



1



2



3

The synthetic approach involved the single-step cyclization of aliphatic amines such as $CH_2{=}CH{-}CH_2{-}NH_2$ with $I(CH_2CH_2O)_2CH_2CH_2I$ in CH_3CN in the presence of Na_2CO_3. By this method, diallyl macrocycle **1** was obtained in 26% yield as a white solid, m.p. 45–46 °C [25]. Compounds **2** and **3** were prepared by treating 1,10-diaza-18-crown-6 with Na_2CO_3 and the appropriate alkenyl bromide in CH_3CN [23]. By this method, **2** was obtained as a white powder in 45% yield and **3** was obtained in 67% yield as a colorless oil[23].

*Previous Attempts to Observe π Complexation with **1** and **4***

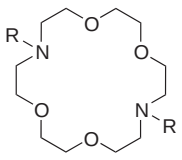
In a previous study, we found that diallyldiaza-18-crown-6 (**1**) formed typical crown complexes but the side arms did not interact with the cation[15]. This was also true of a single-armed *N*-allyldiaza-18-crown-6 (**4**) crown complex[26]. Indeed, in contrast to the success noted above in π-donor complexation involving benzene rings terminating ethyl chains, no π participation was noted in *N*,*N*′-dibenzyl-1,10-diaza-18-crown-6 [15].

Literature Examples of Diaza-18-crown-6 Compounds Having Aromatic Side Arms

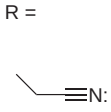
One possible explanation for these failures was that the side-arm chain length was simply too short to permit appropriate positioning of the arene over a ring-bound cation. A search of the Cambridge Structural Database

(CSD) revealed the structures of several diaza-18-crown-6 compounds that have potential π-donor side arms. In some cases, these compounds are complexed and in others the structures are of the free receptor. The compounds are shown as **5**–**12** along with their CSD locator codes.

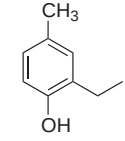
Compound **5** (CSD: CAYXOP)[27] is the structurally most closely related to the compounds studied for this report. It has a π bond rather than an arene as a part of its side arm. Terminal nitriles form complexes in which the cyano nitrogen serves as an axial donor for adjacent, ring-bound cations[28].



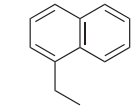
5–12



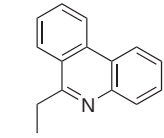
5, CAYXOP



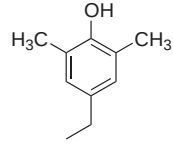
6, NAGQOB



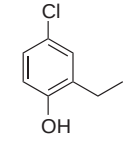
7, NUDRAF



8, TEJTOR
8, WEKBET

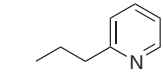


9, TOZNUR
9, TOZPAZ



10, TUKDAE
10, ZUGDOU10

11, VOZCAO



12, YETXIE

Compounds **6**–**10** are particularly relevant to a study of cation–π interactions. Their side-arm arenes are electron rich and therefore capable, in principle, of serving as π donors. The heterocyclic side chains of **8**, **11**, and **12** are all electron poor and any interaction with a ring-bound cation is expected to involve σ donation by a heteroatom. We have demonstrated that when a phenol terminates a side-arm ethylene chain in diaza-18-crown-6, a cation–π complex forms. Phenols **6**[29] and **10**[30,31] form complexes in which the hydroxy group serves as a σ donor to the ring-bound cation. The hydroxy group of **9** is remote from the ring-bound cation and could give a π complex if benzyl derivatives did so[32]. As in our own studies of dibenzyldiaza-18-crown-6, no cation–π complex is apparent. Naphthalene side armed **7** could, in principle, form a π complex with a ring-bound cation but the structure only of the free receptor is reported[33]. Cation complexes of the *ortho*-phenolic receptors all show σ interactions between the ring-bound cation and oxygen. The phenolic oxygen of **9** is positioned improperly for σ interactions and the side arms are not involved in intramolecular complexation.

As noted above, the heterocycles contained in receptors **8**, **11**, and **12** are all electron poor and are therefore more likely to serve as σ donors to a ring-bound cation. Receptor **8** is reported to form complexes both with sodium[34] and potassium[35] cations. It is interesting that both Na^+·**8** and K^+·**8** form complexes in which both side arms interact with the ring-bound cation from the same side of the macrocycle. Compound **11** forms a complex with two silver cations in which two macroring nitrogens and two side-arm nitrogen atoms serve as donors[36]. The structure reported for **12** is particularly interesting. Two molecules of **12** are present in the asymmetric unit[37]. One receptor is uncomplexed and in a conformation in which the side arms are *anti* to each other. The second molecule is a dicalcium complex in which the two side arms serve as donors from the same (*syn*) side. A water molecule in the center of the complex bridges the two calcium cations.

The recent work by Cragg, Steed and coworkers should be noted[38]. They have examined (primarily) complexation of silver and lead cations by allyl- and butenyl-substituted macrocycles. Of special relevance here is a KPF_6 complex of *N*-allylaza-15-crown-5. It forms a dimer assembly in which two ring-perched K^+ ions are bridged by two PF_6^- anions. In this complex, four fluorine atoms in each anion serve as donors to K^+, three to one and the fourth to the other halide. No interaction is apparent between either side-arm double bond or cation. In contrast, when $AgBF_4$ replaces KPF_6, an infinite coordination network forms in which ring-perched silver complexes are bridged by the allyl side arms.

Diallyl- and Bis(but-3-enyl)-1,10-diaza-18-crown-6 Receptors

We have previously reported that *N*,*N*′-diallyl-1,10-diaza-18-crown-6 (**1**) forms alkali metal complexes that do not use the side arms as π donors to solvate the ring-bound cation[15]. When the side arms were extended by a single carbon atom from prop-2-enyl to but-3-enyl, a complex formed in

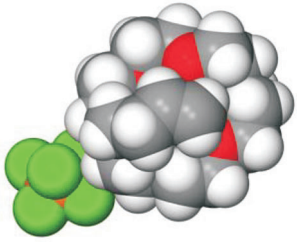


FIG. 1
Structure of **3**·$NaPF_6$ shown in the CPK space-filling representation

which ring-bound sodium cation was coordinated by both double bonds. Figure 1 shows the structure of **3**·$NaPF_6$, which was previously reported[23].

The space-filling representation is useful to demonstrate two important points about these cation–π complexes. First, the ring-bound cation is completely enveloped by the macrocycle and the two side arms; the latter are positioned above and below the cation. Second, the counterion is close to the complex but excluded completely from the cation. Three of the macroring oxygen atoms are visible below the side arm and its double bond. The expected *anti* conformation of the side-arm ethylene unit is apparent, as is the obvious isolation of PF_6^- from the complex.

It is useful to consider the key features of this complex in order to put into perspective the other structures shown here. The four Na^+–O contacts average 2.53 Å. This is a typical distance, as discussed further below. The two Na^+–N contacts are both 2.89 Å. The interaction of the double bond with Na^+ in the axial positions forms, in each case, a triangle. The C=C bond distance is 1.32 Å. The Na^+–C distances are 3.103 and 3.150 Å. A line from sodium dropped to the midpoint of the double bond is 3.13 Å long and intersects the C=C bond at an angle of 87.9°, i.e., nearly perpendicular.

Sodium Complexes of N,N′-Dibut-2-enyl-1,10-diaza-18-crown-6

When the side arms on diaza-18-crown-6 are but-2-enyl (**2**), the double-bond position is analogous to that in allyl (**1**) but the chain length is identical to that in **3**. Previous studies with aromatic side chains suggested that the π donor required being positioned two carbons from the macroring rather than one. If so, the double bonds in the side arms of **2** would not afford a π complex analogous to that shown in Fig. 2, panel B.

Figure 2 shows four complexes of *N*,*N*′-dibutenyl-1,10-diaza-18-crown-6. Panel A shows a structure of **2**·$(NaPF_6)_2$, which has the side-arm double bonds in the 2,3- or allylic position relative to the ring. Panels B–D show complexes of **3**, *N*,*N*′-dibut-3-enyl-1,10-diaza-18-crown-6, one of which (B) is illustrated in Fig. 1 in the space-filling metaphor.

The assembly shown in Fig. 2, panel A, **2**·$(NaPF_6)_2$, is a relatively rare example of a two-cation crown complex. One of the earliest examples was the complex formed between dibenzo-24-crown-8 and two molecules of sodium 2-nitrophenolate[39]. The macroring is too small to accommodate both cations in the ring plane, so one is situated above and the other below the plane. As in the dibenzo-24-crown-8 case, the macroring provides three donors and the counterion provides additional solvation in each case.

It is interesting to compare the Na^+–O bond distances in this unusual arrangement with those typically observed in crown ether complexes. When Na^+ is bound within a 15-crown-5 macrocycle, the typical Na^+–O distance is ≈2.5 Å. When bound within an 18-crown-6, the distances are usually closer to 2.7 Å, although there is obviously a range of bond lengths typically observed. The longer bond lengths reflect the larger number of donors, each of which is required to contribute less to ion stabilization. In **2**·$(NaPF_6)_2$, the Na^+–O distances are 2.99 and 2.86 Å. The Na^+–N distance is 2.83 Å. The sodium ion is also in contact with one of the fluorine atoms of hexafluorophosphate (Na^+–F distance is 2.97 Å). Each Na^+ cation is formally four-coordinate. The two side-arm double bonds are turned away from the complex and no interaction is apparent between the double bonds and the ring-bound cation.

When **3** was crystallized in the presence of KPF_6, a complex was isolated in which K^+ was in the center of the macroring. In the complex **3**·KPF_6, shown in panel C of Fig. 2, the side arms are once again turned outward and the terminal double bonds are disordered. The average K^+–O bond distance in this complex is 2.78 Å and the K^+–N distances are both 2.94 Å. The ring-bound potassium cation is also coordinated to two fluorine atoms from a PF_6^- ion above and two more from below. The K^+–F distances are 3.04 and 3.20 Å. Considering the four ring oxygens, the two nitrogens, and the four fluorines, the potassium cation is formally ten-coordinate.

Evidence for a potassium–double-bond π complex was obtained when **3** was crystallized with potassium tetra(4-chlorophenyl)borate. Two separate

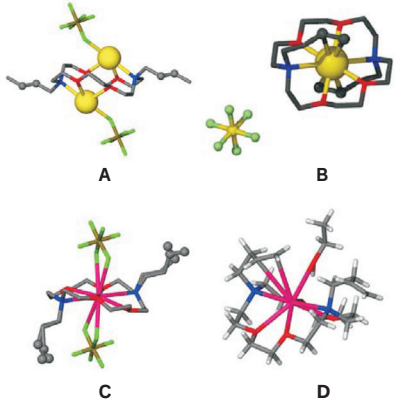


FIG. 2
Solid-state structures of **2**·$(NaPF_6)_2$ (A), **3**·$NaPF_6$ (B), **3**·KPF_6 (C) (note side-chain disorder), and **3**·$KB(4\text{-}ClC_6H_4)_4\cdot CH_3CH_2OH$ (D) (anion omitted)

complexes are present in the asymmetric unit. In each complex, only one of the two side arms interacts with the ring-bound cation. The other is turned away from the complex. An additional feature of **3**·KB(4-$ClC_6H_4)_4$ is that an ethanol molecule also coordinates the ring-bound potassium ion. The K^+–O distances for the ring oxygens in the first complex are, on average, 2.82 Å. The ethanol oxygen-to-K^+ distance is 2.93 Å. The K^+–N distances are 3.04 and 3.20 Å and the N–K^+–N angle is 178.6°. The corresponding values for the second complex are as follows. The K^+–O distances for the ring oxygens are, on average, 2.79 Å. The ethanol oxygen-to-K^+ distance is 2.96 Å. The K^+–N distances are 2.91 and 2.96 Å and the N–K^+–N angle is 174.9°.

The most interesting feature of this structure is the π bond, however. The C=C distance is the expected 1.30 Å in either case. Since there are two complexes, there are two different values for the potassium-to-double bond distance. In the first complex, a line dropped from K^+ to the double bond is 3.36 Å long and intersects the double bond at an angle of 88.2°. In the second complex, the distance is 3.23 Å and the angle is 85.3°. On average, for the two complexes, the K^+–double bond distance is 3.30 Å and the angle is 86.7°. These values compare with a Na^+–C=$C_{centroid}$ distance of 3.06 Å and an angle of 87.9° in **3**·$NaPF_6$.

It is interesting to note that there is a small change in the apparent C=C bond length upon complexation. Thus, the C=C bond distance in **3**·KB(4-$ClC_6H_4)_4$ is 1.298 Å for the free double bond. It is essentially unchanged (1.303 Å) in the K^+ complex, but it is altered to 1.316 Å in the Na^+ complex.

Theoretical/Computational Studies

There are fewer studies of double and triple π-bond interactions that are focused on arenes. This may well be attributed to the occurrence of arenes, and the absence of double bonds, among the 20 essential amino acids. Notwithstanding, isolated double bonds occur widely in lipids[40], sterols, and many other common biological structures[41].

Several recent studies in this area have appeared, however. The experimentally found binding energy for the NH_4–C_2H_4 π complex is 10.0 kcal/mol [3] and the corresponding calculated value is 10.9 kcal/mol [42]. Theoretical calculations performed by Caldwell and Kollman found that the binding energy for the $Li^+\cdots C_2H_4$ complex is 24.3 kcal/mol and for $Li^+\cdots C_6H_6$, the binding energy is 43.8 kcal/mol. Duncan's group used photo-dissociation spectroscopy to examine the interaction of monovalent

calcium cation with acetylene (Ca^+–C_2H_2) and dideuterioacetylene (Ca^+–C_2D_2). They reported that the metal–acetylene bond distance is 2.80 Å and the dissociation energy is 18.6 ± 5.0 kcal/mol [43]. Another report from this group places the Mg^+–C_2H_2 dissociation energy at 17.4 kcal/mol [44].

Cation–π interactions have also been reported to occur between the complex metal cation $[Co(NH_3)_6]^{3+}$ and double or triple bonds[45]. The same method was applied to benzene[46]. To our knowledge, there is only one paper concerning the binding of alkali metal cations to a triple bond. The values calculated for the binding energies of Li^+, Na^+, and K^+ are 39.31, 15.87, and 14.43 kcal/mol [47], respectively. Amicangelo and Armentrout reported that the binding energies for ethene and benzene to Na^+ are 10.7 and 21.5 kcal/mol, respectively[48]. Kim et al. calculated the binding energies for ethene–Na^+ and for benzene–Na^+. The values obtained are 12.36 kcal/mol (ethene) and 20.79 kcal/mol (benzene)[49]. Taken together, these results show that binding strengths are higher for more charge dense cations with the same π donor and higher for more electron-rich donors with the same cation.

CONCLUSIONS

We have shown by several solid-state examples that an isolated double bond can function in the π sense as an effective donor for alkali metal cations. In the receptor systems that have been studied, a critical steric effect is apparent, as previously observed in arene–cation complexes. Although the 20 essential amino acids do not possess isolated double bonds, many less common natural amino acids do. Moreover, unsaturation is common in phospholipid bilayer membranes where the low polarity of the membrane interior would not compete effectively for such contacts. Studies such as these in which distance and angle information is obtained should help others to discover these interactions in a natural context or permit them to be designed into synthetic supramolecular assemblies.

EXPERIMENTAL

^{1}H NMR spectra were recorded at 300 MHz in $CDCl_3$ unless otherwise specified. Chemical shifts (δ-scale) are reported in ppm, coupling constants, *J*, in Hz. Infrared spectra (in cm^{-1}) were recorded on a Perkin–Elmer 1310 infrared spectrophotometer and were calibrated against the 1601 cm^{-1} band of polystyrene. Melting points were determined on a Thomas–Hoover apparatus in open capillaries and are uncorrected. Thin layer chromatographic (TLC) analyses were performed on silica gel HLO F-254 (0.25 mm thickness), Scientific Adsorbents, Inc. Combustion analyses were performed by Atlantic Microlab, Inc., Atlanta (GA). Commer-

cially available solvents and salts were used without further purification. All structures were analyzed and rendered using X-Seed[50].

N,*N*′-Dibut-2-enyl-1,10-diaza-18-crown-6 (**2**)

A solution of but-2-enyl bromide (1.22 g, 9 mmol), 1,10-diaza-18-crown-6 (0.79 g, 3 mmol), and Na_2CO_3 (3.18 g, 30 mmol) was stirred in refluxing CH_3CN (60 ml) for 24 h. The reaction mixture was cooled, filtered, concentrated in vacuo, redissolved in CH_2Cl_2 (100 ml), and washed with water (3 × 15 ml). The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. Column chromatography (0–5% Et_3N, Me_2CO/hexanes (1:1) on silica gel) afforded **2** as a light yellow oil, which solidified when maintained under high vacuum for 2 days. Recrystallization from acetone/hexane afforded **2** (0.50 g, 45%) as a white powder, m.p. 56–57 °C. IR: 2916, 2858, 1451, 1351, 1125. ^{1}H NMR: 1.68 (d, 6 H, *J* = 5.4, -CH_3); 2.75–2.79 (m, 8 H, -NCH_2O-); 3.09 (d, 4 H, *J* = 5.4, -CH_2N-); 3.59–3.64 (m, 16 H, -CH_2OCH_2-); 5.51–5.56 (m, 4 H, -CH=CH-). ^{13}C NMR: 17.79, 53.35, 58.06, 69.87, 69.94, 70.72, 128.30, 128.50. For $C_{20}H_{38}N_2O_4$ (370.54) calculated: 64.83% C, 10.34% H, 7.56% N; found: 65.01% C, 10.22% H, 7.47% N.

N,*N*′-Dibut-3-enyl-1,10-diaza-18-crown-6 (**3**)

A solution of 4-bromobut-1-ene (1.49 g, 11 mmol), 1,10-diaza-18-crown-6 (1.31 g, 5 mmol), and Na_2CO_3 (5.3 g, 50 mmol) was stirred in refluxing CH_3CN (100 ml) for 24 h. The usual workup and column chromatography (Me_2CO on silica gel) afforded **3** (1.24 g, 67%) as a yellow oil. IR: 3074, 2859, 1640, 1457, 1351, 1129, 1069. ^{1}H NMR: 2.18–2.25 (m, 4 H, -CH_2CH=); 2.59–2.62 (m, 4 H, -NCH_2CH_2-); 2.80 (t, 8 H, *J* = 6.0, -NCH_2O-); 3.59–3.64 (m, 16 H, -CH_2OCH_2-); 4.96–5.08 (m, 2 H, =CH_2-); 5.72–5.84 (m, 2 H, -CH=). ^{13}C NMR: 31.56, 53.78, 55.27, 69.97, 70.73, 115.56, 136.88. The NMR spectrum observed for this compound is identical with those reported in[38,51].

Crystallization. Equivalent amounts of receptor and salt were dissolved in boiling polar solvents. Vapor diffusion of this solution with less polar solvents for weeks afforded the crystals suitable for X-ray crystallography. Complex **2**·$(NaPF_6)_2$, m.p. 132–133 °C, colorless needles (ethanol/hexane). Complex **3**·$NaPF_6$, m.p. 116–117 °C, colorless rhombohedroid (acetone/ ether). **3**·$KB(4\text{-}ClC_6H_4)_4$, m.p. 74–75 °C, colorless needles (ethanol/hexane). **3**·KPF_6, m.p. 92– 93 °C, colorless needles (ethanol/hexane).

Crystal Information

Crystal data for **2**·$(NaPF_6)_2$: $C_{20}H_{38}F_{12}N_2Na_2O_4P_2$, *M* = 706.44, colorless needle, 0.20 × 0.20 × 0.20 mm^3, triclinic, space group *P*-1 (No. 2), *a* = 8.424(4) Å, *b* = 9.839(5) Å, *c* = 11.492(5) Å, α = 115.086(7)°, β = 91.323(9)°, γ = 113.237(7)°, *V* = 771.6(6) Å^3, *Z* = 1, D_c = 1.520 g/cm^3, F_{000} = 364, MoKα radiation, λ = 0.71073 Å, *T* = 173(2) K, $2\theta_{max}$ = 54.4°, 4474 reflections collected, 3266 unique (R_{int} = 0.0260). Final GooF = 1.029, *R*1 = 0.0764, *wR*2 = 0.1920, *R* indices based on 2107 reflections with $I > 2\sigma(I)$ (refinement on F^2), 191 parameters, 0 restraint. Lp and absorption corrections applied, μ = 0.271 mm^{-1}.

Crystal data for **3**·$NaPF_6$: $C_{20}H_{38}F_6N_2NaO_4P$, *M* = 538.48, colorless needle, 0.30 × 0.20 × 0.20 mm^3, monoclinic, space group *C*2/*c* (No. 15), *a* = 18.199(6) Å, *b* = 10.588(3) Å, *c* = 15.485(5) Å, β = 119.440(4)°, *V* = 2598.6(13) Å^3, *Z* = 4, D_c = 1.376 g/cm^3, F_{000} = 1136, MoKα radiation, λ = 0.71073 Å, *T* = 173(2) K, $2\theta_{max}$ = 54.2°, 7817 reflections collected, 2831

unique (R_{int} = 0.0521). Final GooF = 1.042, *R*1 = 0.0553, *wR*2 = 0.1281, *R* indices based on 2151 reflections with $I > 2\sigma(I)$ (refinement on F^2), 157 parameters, 0 restraint. Lp and absorption corrections applied, μ = 0.194 mm^{-1}.

Crystal data for **3**·KPF_6: $C_{20}H_{38}F_6KN_2O_4P$, *M* = 554.59, colorless needle, 0.20 × 0.20 × 0.10 mm^3, monoclinic, space group *C*2/*c* (No. 15), *a* = 12.9975(14) Å, *b* = 25.736(3) Å, *c* = 8.0482(8) Å, β = 98.383(2)°, *V* = 2663.4(5) $Å^3$, *Z* = 4, D_c = 1.383 g/cm^3, F_{000} = 1168, MoKα radiation, λ = 0.71073 Å, *T* = 173(2) K, $2\theta_{max}$ = 54.2°, 8319 reflections collected, 2932 unique (R_{int} = 0.0336). Final GooF = 1.099, *R*1 = 0.0860, *wR*2 = 0.2513, *R* indices based on 1957 reflections with $I > 2\sigma(I)$ (refinement on F^2), 152 parameters, 29 restraints. Lp and absorption corrections applied, μ = 0.329 mm^{-1}.

Crystal data for **3**·KB(4-$ClC_6H_4)_4$: $C_{46}H_{60}BCl_4KN_2O_5$, *M* = 912.67, colorless needle, 0.35 × 0.25 × 0.20 mm^3, triclinic, space group *P*-1 (No. 2), *a* = 9.9524(10) Å, *b* = 15.2220(16) Å, *c* = 31.965(3) Å, α = 92.345(2)°, β = 97.585(2)°, γ = 92.798(2)°, *V* = 4788.9(9) $Å^3$, *Z* = 4, D_c = 1.266 g/cm^3, F_{000} = 1928, MoKα radiation, λ = 0.71073 Å, *T* = 173(2)K, $2\theta_{max}$ = 54.2°, 30 373 reflections collected, 20 647 unique (R_{int} = 0.0399). Final GooF = 0.939, *R*1 = 0.0598, *wR*2 = 0.1097, *R* indices based on 10620 reflections with $I > 2\sigma(I)$ (refinement on F^2), 1071 parameters, 2 restraints. Lp and absorption corrections applied, μ = 0.379 mm^{-1}.

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