Tris-2-(3-methylindolyl)phosphine as an anion receptor†

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A C_3-symmetric phosphine with indolyl substituents has been synthesized that demonstrates the capability to bind anions through the indole NH sites and coordinate metal centres through the phosphorus centre.

Receptors of anions have been gaining considerable interest in areas that include sensors, probes, ion transport studies, and catalysis.[1] Anion receptors require the appropriate functionalities to accommodate the anionic guest, usually through hydrogen bonding or electrostatic interactions. Electroneutral anion recognition hosts are commonly small molecules with organic scaffolds employing NH donors such as amide,[2] pyrrole,[3] or urea[4] functional groups.

Indole-based hosts have been reported only recently and they have demonstrated high selectivity in their anion binding capability.[5] In previous studies, we have reported mono- and di-indolylphosphines that have demonstrated the propensity to form intramolecular (Fig. 1a) as well as intermolecular hydrogen bonds (Fig. 1b) in their solid-state structures.[6] The C_3-symmetric tris-2-(3-methylindolyl)phosphine, **1**, was synthesized to investigate whether the three indolyl NH sites are suitably positioned to act collectively to form strong hydrogen bonding interactions with anions (Scheme 1). Its phosphorus centre serves as an additional site of reactivity through which the receptor may, in principle, simultaneously coordinate to transition metals or other Lewis acids. The close spatial proximity of the phosphorus centre to the NH moieties in **1** lies in contrast to phosphines which have previously been reported to act as anion receptors in which the phosphorus centres are well-displaced from the sites of hydrogen-bonding.[7] Herein we report the synthesis of tris-2-(3-methylindolyl)phosphine and its anion binding properties.

Following previously established methods,[6] the synthesis of receptor **1** was carried out by lithiation of 1-[(*N*,*N*-dimethylamino)methyl]-3-methylindole, followed by the addition of trichlorophosphine and subsequent reaction with $NaBH_4$. After trituration from methanol, air-stable phosphine **1** was obtained in 32% yield.

The anion binding properties of receptor **1** were examined using ^{1}H NMR titration techniques in anhydrous CD_2Cl_2. The interaction of **1** with anions, as their tetrabutylammonium salts,‡ was monitored by the downfield shift of the indolyl NH resonances (δ = 7.87 ppm for uncomplexed **1**) with increasing anion concentration until no further significant change in the chemical shift of the indolyl NH resonance was observed. The single NH resonance implies that all three of the NH sites are involved in hydrogen bonding to the anion at 298 K on the NMR time scale. Treatment of the data using the EQNMR software[8] optimally obtained a 1 : 1 receptor : anion binding model with stability constants shown in Table 1. The ability of **1** to bind anions in solution is likely due to its three indolyl NH moieties synergistically acting to capture anion guests. The symmetry and position of the NH groups of the receptor

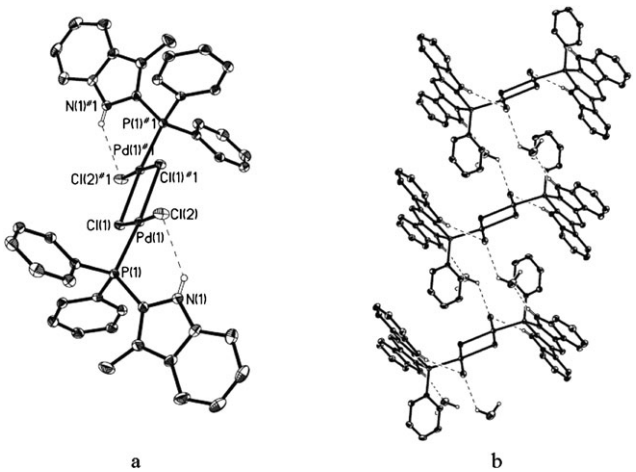
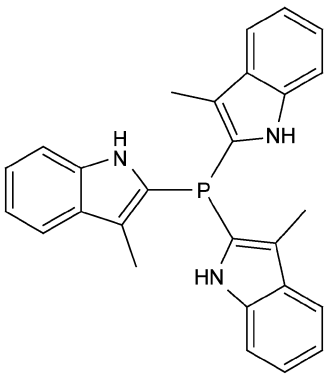


Fig. 1 (a) Intramolecular hydrogen bonding in the Pd[2-(3-methylindolyl)diphenylphosphine]Cl_2 dimer and (b) intermolecular hydrogen bonding in the Pd[di(1H-3-indolyl)methane-(2,12)-phenylphosphine]Cl_2 dimer. Thermal ellipsoids are drawn at 35% probability.



Scheme 1 Receptor **1**.

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Table 1 Stability constants (M^{-1}) of receptor **1** with anion guests (as their tetrabutylammonium salts) at 298 K in CD_2Cl_2[a]

Anion	K_a
Cl^-	3920
Br^-	320
I^-	20
CH_3COO^-	2730
HSO_4^-	35
NO_3^-	100
BF_4^-	150

[a] All titration plots were fitted to a 1 : 1 receptor : anion binding model. Stability constants given are <10% error.

provide a well-defined hydrogen bonding cavity of geometry and size suitable for binding well to spherical anions such as halides. While the absence of a clean fit to a 1 : 1 receptor : anion binding profile precluded an accurate determination of its stability constant, the ^{1}H NMR of **1** in the presence of F^- anion exhibited the largest downfield change in chemical shift of the indolyl NH signals (*ca.* 6.7 ppm). This is consistent with the well-known propensity of F^- to serve as a strong hydrogen bond acceptor. The high charge densities on the oxygen atoms of CH_3COO^- are likely responsible for the strong interaction that it exhibits with **1**. It is currently unclear whether the binding of acetate to the receptor involves hydrogen bonding by one or both of its oxygen atoms. While the NO_3^-, HSO_4^-, and BF_4^- anions provide an improved complement in symmetry to the hydrogen bond cavity of receptor **1**, the reduced ability of **1** to bind these anions may be due to their diffuse singly negative charges being delocalized over several terminal atoms.

In order to confirm the nature of the host–guest interaction, single crystals of the 1 : 1 receptor : anion pair of F^-, as its tetraethylammonium salt, were acquired from a solution of the complex in a MeCN–MeOH mixture layered with Et_2O.§ The $[NEt_4][\mathbf{1}\cdot F]$ ion pair, **2**, crystallizes with two independent complexes, **2a** and **2b**, in the asymmetric unit (Fig. 2). The solid state structure of **2** shows the F^- guest hydrogen bonding to **1** in an adamantoid arrangement involving all three suitably oriented indolyl NH groups. N···F hydrogen bond donor-to-acceptor distances range from 2.632(3) Å to 2.790(2) Å, and are typical N···F^- separations.[9] The F^- guest of complex **2a** hydrogen bonds further to one MeOH solvent molecule and has a distorted tetrahedral coordination geometry. The F^- guest of **2b** binds to **1** in a similar manner to that observed in **2a** and hydrogen bonds to two MeOH solvent molecules.

To study its coordination chemistry, **1** was reacted with 1,10-phenanthroline (phen), and $[Cu(MeCN)_4]BF_4$ in CH_2Cl_2 in a 2 : 1 : 1 stoichiometry. The reaction resulted in the formation of a $[Cu(\mathbf{1})(phen)]BF_4$ complex, **3**, where the ligand stoichiometry was confirmed by single crystal X-ray diffraction.¶ Crystals of **3** were grown from Et_2O vapour diffusion into a CH_2Cl_2 solution of the complex (Fig. 3).‖ The Cu(I) centre adopts a three-coordinate trigonal planar geometry in which P(1) deviates from the plane defined by the chelated phenanthroline ligand and Cu(I) by 0.654(3) Å.

In contrast to the weak BF_4^- binding ability of **1** in solution, the solid state structure of **3** clearly shows the indolylphosphine ligand binding the tetrafluoroborate counteranion. The anion does not interact with **1** through one of its fluoride atoms only, as might be anticipated from the crystal structure of **2**. Rather, the hydrogen bonding between **1** and BF_4^- demonstrates the C_3-symmetric complementarity between the tetrahedral geometry of the anion and the three hydrogen bond donors of **1**. It appears that the BF_4^- anion is too large in size to fit well inside the receptor cavity of **1** as the hydrogen bonding distances are longer than typical N···F^- distances[9] and the NH···F^- bond angles (130 to 152°) are much less than ideally linear hydrogen bonding interactions.

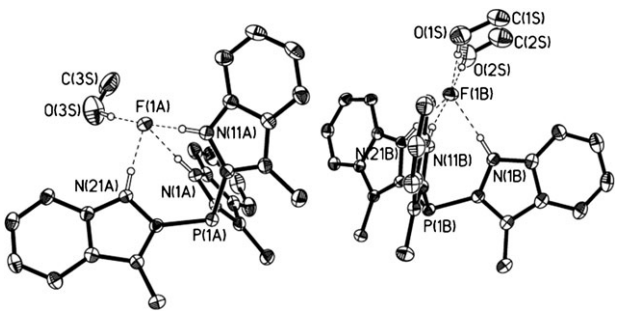

Fig. 2 X-Ray crystal structure of the two independent F^- complexes of receptor **1** in the asymmetric unit. The F^- guests are solvated with MeOH. Non-acidic hydrogen atoms and tetraethylammonium cations were removed for clarity. Thermal ellipsoids are drawn at 35% probability.

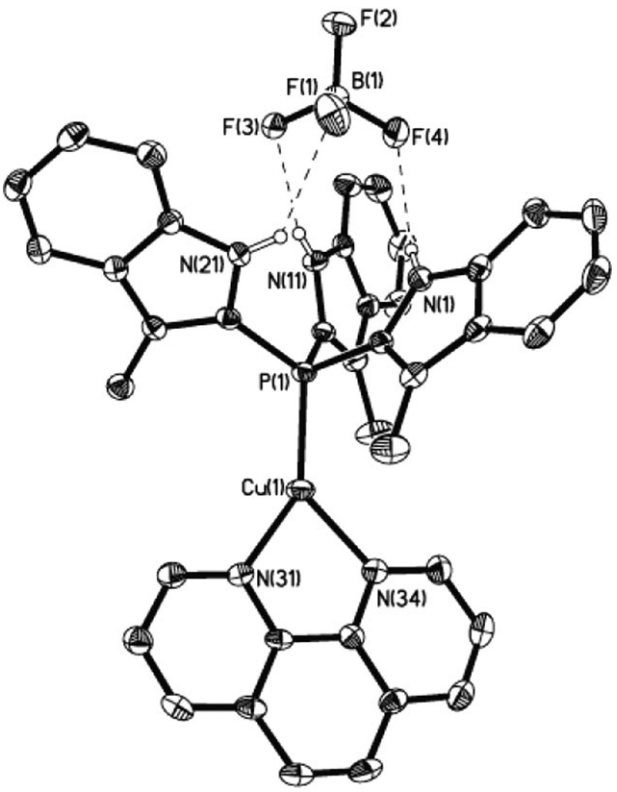

Fig. 3 X-Ray crystal structure of the $[Cu(\mathbf{1})(phen)]BF_4$ complex. The Cu(I) coordinates to the phosphorus donor of receptor **1** while the BF_4^- anion hydrogen bonds to receptor **1**. Non-acidic hydrogen atoms are removed for clarity. Thermal ellipsoids are drawn at 35% probability.

We have synthesized a symmetric tris-2-(3-methylindolyl)-phosphine **1** that demonstrates an anion binding ability that is not as readily exploited in other indolylphosphines.[10] ^{1}H NMR titration techniques in CD_2Cl_2 have shown a 1 : 1 binding of anionic guests with **1**. Although the stability constant for F^- binding could not be ascertained, a high affinity of **1** for F^- was evident in the large downfield shift in the NH resonances of its ^{1}H NMR spectrum. A 1 : 1 binding of F^- with **1** was established in its crystal structure. The solid-state structure of [Cu(**1**)(phen)]BF_4 exhibits the phosphine's ability to hydrogen bond anions while it is coordinated to a transition metal centre. Studies in our laboratory are currently underway examining the utility of these anion-adducts of **1** in catalysis.

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Notes and references

‡ All tetrabutylammonium salts are anhydrous.

§ Crystal data for complex **2**: $C_{73}H_{100}F_2N_8O_3P_2$ M_r = 1237.55, T = 150(1) K, orthorhombic space group $P2_12_12_1$, a = 11.3758(1), b = 24.2008(2), c = 24.9237(2) Å, V = 6861.58(10) Å^3, ρ_{calc} = 1.198 g cm^{-1}, μ = 0.121 mm^{-1}, Z = 4, reflections collected: 46447, independent reflections: 8609 (R_{int} = 0.0807), absolute structure parameter: 0.01(7), final R indices [$I > 2\sigma I$]: $R1$ = 0.0531, w$R2$ = 0.1273, R indices (all data): $R1$ = 0.0706, w$R2$ = 0.1385. CCDC 662466. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b714889e

¶ The ligand stoichiometry of [Cu(**1**)(phen)]$^+$ suggests that **1** is larger than PPh_3 (cone angle 145°)[11] which can readily form four-coordinate tetrahedral [Cu(PPh_3)$_2$(phen)]$^+$ complexes.[12] We have previously suggested that the monoindolylphenylphosphine, $P(C_5H_5)_2(C_9H_8N)$, and the diindolylphenylphosphine, $P(C_6H_5)(C_9H_8N)_2$, are likely to possess cone angles larger than PPh_3, and may be similar in size to P(*o*-tolyl)$_3$.[6] Therefore, it is in agreement that **1** should also be similar in size to P(*o*-tolyl)$_3$, as is suggested by the ligand stoichiometry of [Cu(**1**)(phen)]$^+$.

‖ Crystal data for complex **3**: $C_{39}H_{32}BCuF_4N_5P$ M_r = 752.02, T = 150(1) K, triclinic space group $P\bar{1}$, a = 12.1112(4), b = 12.1741(4), c = 13.4482(6) Å, α = 68.866(2), β = 70.427(2), γ = 72.803(2)°, V = 1707.76(11) Å^3, ρ_{calc} = 1.426 g cm^{-1}, μ = 0.746 mm^{-1}, Z = 2, reflections collected: 18062, independent reflections: 7758 (R_{int} = 0.1151), final R indices [$I > 2\sigma I$]: $R1$ = 0.0549, w$R2$ = 0.1297, R indices (all data): $R1$ = 0.1177, w$R2$ = 0.1534. CCDC 662467. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b714889e

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