Donor-substituted phosphanes – surprisingly weak Lewis donors for phosphenium cation stabilisation†

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Paradoxically, N- and O-donor substituted tri-arylphosphanes are shown to be weaker donors than PPh3 when binding the soft Lewis acid moiety [PPh2]+. This arises from internal solvation and rehybridisation at phosphorus, precluding chelation and increasing steric demand, in direct contrast to coordination modes observed for metal complexes.

Phosphacations in the form of highly electron poor, four coordinate P(V) cations have been shown to exhibit high Lewis acidity enabling C–F bond activation1 and their use as catalysts for hydrogenation via frustrated Lewis pair (FLP) chemistry has been demonstrated.2,3 In contrast, two coordinate, cationic P(III) (phosphenium) species are less well studied.4 These highly reactive species rapidly insert into C–X bonds,5,6 and in general require significant steric bulk and strongly π-donating substituents to render them sufficiently stable for isolation.4 Stability may also be imparted by quenching the Lewis acidity with a σ donor (Lewis basic) species,7 regenerating the three coordinate phosphorus centre, which for chelating ligands may permit higher coordination modes (Fig. 1).8–10 Phosphanes themselves are good donors for this and the stability of phosphane–phosphenium complexes is attributed to the thermodynamic favourability of the P–P bond.11 Interestingly, whilst tetracoordinate P(III) monocations are known with internal chelating ligands,12,13 there are very few examples for phosphorus donors or intramolecular chelates (Fig. 1). Burford’s attempted syntheses using symmetrical diphosphane ligands instead gave either phosphane–phosphenium complexes with three coordinate phosphacation centres and a free, unbound donor centre or symmetrical bis-phosphenium species for alkyl bridged ligands,14 or rearrangement in the case of aryl bridged species.15

We hypothesised that combination of a phosphane donor moiety with rigidly linked first row main-group donors would favour the formation of the elusive binding mode II by pre-organisation towards binding and the increased stability of hypervalent bonding involving more electronegative elements. In this report, we describe the synthesis of a family of simple donor functionalised phosphane-derived phosphane–phosphenium salts; the effect of donor substitution on the overall donor strength and resultant cation stability is discussed.

Fig. 1. Previously reported and proposed phosphane–phosphenium coordination modes with chelating and multidentate ligands.

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Results and discussion

Initial synthesis and structure

No reaction is observed on combination of phosphanes 1a to 1e with Ph3PCl in DCM; addition of one equivalent of NaBARF lead in all cases to complete loss of 31P NMR signals for both starting materials and signals indicative of phosphane–phosphonium formation – see Table 1. In contrast to the broad, unresolved signals often seen for 2e salts, 1a P–P coupling could be resolved in solution for 2b[BArF] and 2d[BArF] (Table 1).

The reaction with Me3SiOTf or GaCl3 likewise resulted in clean chloride abstraction and the quantitative formation of the desired triflate or [GaCl4]− salts except for 1c which gave complex mixtures for both reagents. Significant variation is seen for the 1a P–P coupling constants, especially for 2a salts indicating varying degree of anion association. Attempted synthesis of the cheaper [AlCl4]− salts by halide abstraction with AlCl3 lead to complex behaviour with multiple species present in solution by 31P NMR, likely due to the more coordinating nature of the anion coupled with competition from the harder nitrogen donor centres. Both the 31P chemical shifts and coupling constants are comparable to those seen for 2e, implying that binding mode II is not adopted. This was confirmed upon successful isolation and characterisation of single crystals of [2c][BARF], revealing that it exhibits the unexpected mode III with short N(1)–P(1) contacts (Fig. 2).

Compound [2c][BARF] crystallises with a single ion pair in the asymmetric unit, with disordered CF3 units in the unit cell (Fig. 2). The P(1)–P(2) bond length is unexceptional but slightly long at 2.2477(9) Å (cf. 2.2302(13) Å for [2e][OTf]), and there is a close contact between the donor group and the adjacent phosphorus centre (dN(1)–P(1) = 3.014(3) Å, less than the sum of the van der Waals radii (3.35 Å) with the nitrogen lone-pair clearly orientated towards the phosphorus centre. The donor phosphorus may therefore be described as either a monocapped tetrahedron or a highly distorted trigonal bipyramid – the sum of equatorial angles = 334.37° (cf. 328.4° for a tetrahedron) but the axial X–P(1) contact, for modelled and also the hypothetical adducts 3b,c,e for comparison of donor strength in a neutral complex (Table 2). The optimised structures of 1b, and 2c were in agreement with experimental data,22 giving confidence in the model. The computed structures for 2b also exhibited a short N(1)–P(1) contact, again in contrast to the behaviour of the ligand 1b with transition metal Lewis acids, but similar to the more substitutedalogues.18,19 Examination of the computed molecular orbitals show that the HOMOs of 1b, 1c and 1e all correspond to phosphorus centred lone pairs, with energies of −7.18 eV, −7.16 eV and −7.46 eV respectively; internal coordination therefore significantly raises the energies of the lone pairs (expected to increase donor strength) whilst also increasing positive charge at phosphorus. Furthermore, the HOMO−1 for

Table 1 31P NMR parameters for phosphane–phosphonium salts in DCM, 1Jp-p/Hz in parenthesis

|       | OTf   | BARF   | GaCl4   |
|-------|-------|--------|---------|
| 1a    | 16.4, −6.4 | 17.1, −6.4 | 18.9, −5.8 |
| 2b    | 13.7, −8.4 | 13.8, −8.9 | 13.8, −8.8 |
|       | (335) | (344) | (344) |
| 2c    | 17.0, −6.1 | −, a   | 17.0, −6.5 a |
|       | (335) |       | (332) |
| 2d    | 12.8, −6.3 | 12.8, −6.8 | 12.8, −6.6 |
|       | (335) | (331) | (335) |
| 2e    | 13.7, −10.1 | 15.3, −10.6 | 13, −1315 |
|       | (≈340) |       | (340) |

* Not cleanly formed.
1b and 1c are in both cases P–N σ bonding interactions. For the cations, the donor-functionalised species are enthalpically stabilised relative to 2e, (Table 4) though only to a small degree. In terms of free energy, 2c is in fact slightly destabilised with respect to 2e, presumably reflecting the entropic cost of binding the otherwise freely rotating benzyl moiety.

The calculated Mayer’s Fuzzy bond indices show a significant degree of covalent bonding between the nitrogen and phosphorus centres for both 1b and 1c, which decreases in 2b and 2c compared to the free phosphanes. A slight increase in negative charge at the donor nitrogen and apical carbon centre is seen in the cationic complexes, coupled with an increased positive charge at P(1) (Table 3) relative to 2e. This suggests a decrease in P–N bonding, supported by P–N bond elongation on complex formation and attributed to steric repulsion. With this in mind, the increased exothermicity of P–P bonding with respect to phosphane exchange (Table 4) cannot arise from the naïve argument of electron donors increasing the electron density available at phosphorus as calculated charges show increased positive charge at phosphorus for 1b and 1c relative to 1e. Instead, the P–N bonding results in a rehydridisation at phosphorus and a change in the nature of the donor orbital. Ultimately, the calculated P–P bond order is (albeit slightly) lower for the internally coordinated salts than for 2e, and the P–P bonds longer. The increased stability likely therefore arises from the change in degree of P–N electrostatic interaction, whilst the decrease in covalency argues for weaker, more reactive P–P bonds.

Phosphane–phosphenium systems are highly susceptible to nucleophilic attack by stronger donor species, resulting in...
immediately upon addition of Ph3P, the experiment using the softer Ph2PI gave dramatically different results. On warming the signals continue to move and at −30 °C, JP–P coupling becomes resolved. By −50 °C, the 31P spectrum is essentially identical to that of [2b]BARF and is ascribed to the formation of [2b]I; on warming the spectra revert to those seen at room temperature. Similar results are observed for the reaction of 1c and 1e with Ph3PI, which converge upon the spectra for [2c]I and [2e]I. In no case were any signals which could be attributed to neutral adducts observed. From this we conclude that the barriers to interconversion (not calculated) are in all cases small such that the intermediate is too short lived to be observed on the NMR timescale. This would also explain the anomalous calculated structure of 3c, indicating narrow, shallow potential wells in the energy surface. The resonances observed are therefore simple weighted averages of the signals of 1, Ph3PI and 2 in fast exchange down to −60 °C.

**Conclusions**

Herein we report simultaneous inter- and intra-molecular phosphorus Lewis donor–acceptor complex formation when internally solvated triarylphosphanes react with the soft main group Lewis acid [Ph3P]+, wherein the donor centre also acts as a Lewis acid. This internal solvation results in higher energy lone pairs at phosphorus, arising from rehybridisation of the phosphorus centre due to hypervalent bonding. This does not translate directly to stronger donor–acceptor bonding in phosphine-phosphonium salts, however, due to competing unfavourable steric interactions and increased positive charge at phosphorus. The existence of this binding mode has implications for the utility of such (conventionally) chelating phosphines in main group cation chemistry.

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