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Donor-rich and acceptor-rich pyridine-phosphadiazonium adducts: Diversifying the Lewis acceptor chemistry of phosphorus(III)†

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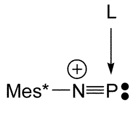
Received (in Cambridge, UK) 9th August 2004, Accepted 27th August 2004
First published as an Advance Article on the web 11th October 2004

[Mes*NP(DMAP)$_2$][OTf] represents the first ligand-rich coordination complex of a phosphorus(III) Lewis acceptor, and a three coordinate hypervalent electron-rich (lone pair bearing) center; further diversification is demonstrated by, [(Mes*NP)$_2$(4,4′-BIPY)][OTf]$_2$, representing an acceptor-rich dication.

The transition metals and the heavy p-block elements (*e.g.* Sn, Pb, Bi) commonly adopt high coordination numbers (ML$_n$, *n* 4–10), defining hypervalent bonding environments. In contrast, most p-block elements access relatively low coordination numbers and complexes of Lewis acidic p-block centers usually involve a single ligand (*e.g.* H$_3$B-NR$_3$).[1] Complexes of boranes are limited by the availability of only one acceptor orbital, while the presence of a lone pair at Lewis acceptor phosphine sites[2] apparently restricts the number of ligands. However, coordinative unsaturation and positive molecular charge in the phosphadiazonium cation (Mes*NP$^+$, Mes* = 2,4,6-tri-*tert*-butylphenyl)[3] impose a relatively high Lewis acidity at phosphorus, and interaction with the strongly basic 4-dimethylaminopyridine (DMAP) gives the first donor-rich complex of phosphorus(III) **2**. The versatile coordination chemistry of the phosphadiazonium cation is further demonstrated by the characterization of an acceptor-rich complex **3** with the 4,4′-bipyridine (4,4′-BIPY) bridging ligand.



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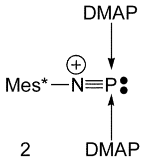

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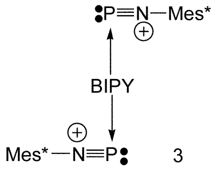

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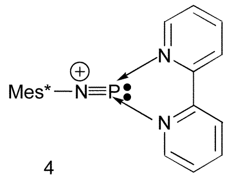

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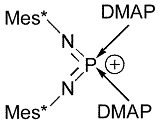

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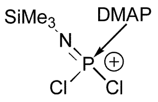

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Trifluoromethylsulfonyloxy-(2,4,6-tri-*tert*-butylphenylimino)-phosphine[4] (Mes*NPOTf) reacts with a variety of ligands (L = ylidene,[5] pyridine,[6] amine,[6] phosphine,[7] urea,[8] thiourea,[8] selenourea[8]), which effect nucleophilic displacement of the triflate anion (OTf$^-$ = OSO$_2$CF$_3$$^-$). The resulting cations are best described as 1:1 adducts of a neutral ligand on a phosphadiazonium Lewis acceptor **1**. Solution ^{31}P NMR spectra of equimolar reaction mixtures of Mes*NPOTf and 4-dimethylaminopyridine (DMAP) show quantitative formation of **1** (OTf, L = DMAP, δ ^{31}P = 132 ppm), but the donor-rich complex [Mes*NP(DMAP)$_2$][OTf] (**2**[OTf], Fig. 1, δ ^{31}P = 123 ppm) is formed quantitatively when an excess of DMAP is present. The antithetic coordination complex is observed when two equivalents of Mes*NPOTf react with one equivalent of 4,4′-bipyridine (4,4′-BIPY) to form the ligand bridged-adduct [(Mes*NP)$_2$(4,4′-BIPY)][OTf]$_2$ (**3**[OTf]$_2$, Fig. 2).

Selected structural parameters for derivatives of **1**[OTf], **2**[OTf] and **3**[OTf]$_2$‡ are presented in Table 1, together with comparative parameters for Mes*NPOTf, and complexes of phosphorus(V) involving DMAP (**5**[9] and **6**[10]). In both **2**[OTf] and **3**[OTf]$_2$, the nitrogen donor sites are closer to the phosphorus centers than the oxygen centers of the triflate anions. In general, nitrogen donors effect a substantial displacement (>0.8 Å) of the triflate anion with respect to the free Lewis acid Mes*NPOTf. Predictably, the two DMAP ligands in **2**[OTf] impose a greater P–O dissociation than a single ligand in derivatives of **1**[OTf], consistent with the structure of the chelate complex **4**[OTf].[11] Most importantly, the phosphorus center in **2**[OTf] adopts a pyramidal geometry (sum of N–P–N

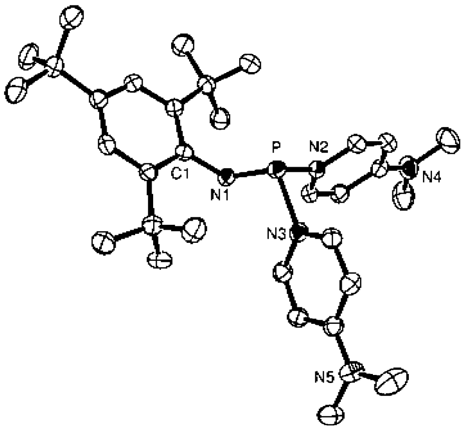

Fig. 1 Structural view of the cation in the solid state structure of **2**[OTf] drawn with 50% probability displacement ellipsoids. Hydrogen atoms and the anion have been omitted.

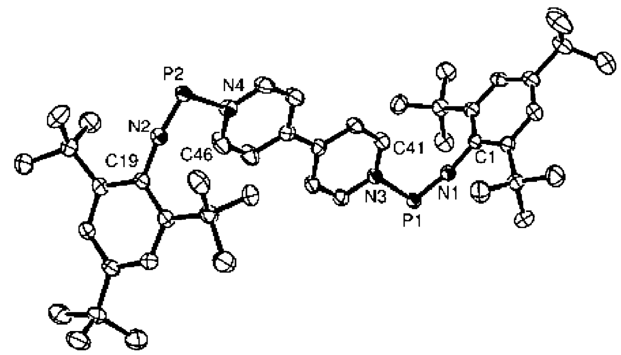

Fig. 2 Structural view of the cation in the solid state structure of [(Mes*NP)$_2$(4,4′-BIPY)][OTf]$_2$ (**3**[OTf]$_2$) drawn with 50% probability displacement ellipsoids. Hydrogen atoms and anions have been omitted.

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† Electronic supplementary information (ESI) available: experimental and spectroscopic data for **1**[OTf], **2**[OTf] and **3**[OTf]$_2$. See http://www.rsc.org/suppdata/cc/b4/b412267d/

DOI: 10.1039/b412267d

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Table 1 Selected bond lengths (Å), angles (°) and ^{31}P NMR (CD_2Cl_2) chemical shifts (ppm) for Mes*NPOTf, [(Mes*N)$_2$P(DMAP)$_2$][Br], [Me_3SiNP(Cl)$_2$(DMAP)][Cl], and complexes of Mes*NPOTf with the nitrogen ligands: quinuclidine (QUIN), pyridine (PYR), 4-dimethylaminopyridine (DMAP), 4,4′-bipyridine (4,4′-BIPY) and 2,2′-bipyridine (2,2′-BIPY)

Compound	Label	δ ^{31}P	P–O	N → P	(R)N–P	R–N–P	Reference
Mes*NPOTf	—	50	1.923(3)	No ligand	1.467(4)	176.4(3)	4
[Mes*NP(QUIN)][OTf]	**1**[OTf]	144	2.697(3)	1.933(2)	1.519(2)	143.9(2)	6
[Mes*NP(PYR)][OTf]	**1**[OTf]	71	2.712(7)	1.958(8)	1.472(8)	161.7(7)	6
[Mes*NP(DMAP)$_2$][OTf]	**2**[OTf]	123	>3.4	1.873(2); 1.879(2)	1.559(2)	125.2(2)	This work
[(Mes*NP)$_2$(4,4′-BIPY)][OTf]$_2$	**3**[OTf]$_2$	61	2.776(2) (P1) 2.879(2) (P2)	1.984(2) (P1) 2.025(2) (P2)	1.488(2) (P1) 1.489(2) (P2)	165.6(2) (P1) 164.4(2) (P2)	This work
[Mes*NP(2,2′-BIPY)][OTf]	**4**[OTf]	54	>3.4	2.065(4); 2.066(4)	1.497(4)	169.4(4)	9
[(Mes*N)$_2$P(DMAP)$_2$][Br]	**5**[Br]	-57	–	1.830(4), 1.812(4)	1.528(4), 1.526(4)	—	9
[Me_3SiNP(Cl)$_2$(DMAP)][OTf]	**6**[OTf]	-54	—	1.713(2)	1.490(3)	144.1(2)	10

angles = 295.8°) consistent with the presence of a stereochemically active lone pair at the acceptor site.

The N → P(III) coordinate bonds listed in Table 1 adopt a narrow range (1.87–2.07 Å), yet are all longer than the benchmark N–P single bond [1.800(4) Å] in [H_3NPO_3]$^-$.[12] Due to the higher basicity of DMAP with respect to the other nitrogen donors, the shortest N → P bonds are observed in **2**[OTf], **5**[Br] and **6**[OTf], despite the potential for competition between the ligands. Correspondingly, the N → P bonds in the dication of **3**[OTf]$_2$ are slightly longer than that in **1**[OTf] (L = PYR), reflecting the reduction in basicity of the ligand on introduction of a greater cationic charge. Pyridine or DMAP complexes of P(V) acceptors exhibit shorter N → P coordinate bonds than their P(III) congeners with a distance range of 1.71–1.88 Å;[9,10,13,14] the longest bond occurring in the pyridine adduct of PF_5(PYR).[15]

In general, ligand interactions have minor influence on the structural features of the acceptor Mes*NP$^+$ unit. The (Mes*)N–P bond lengths are only slightly longer in the adducts than in the Lewis acid Mes*NPOTf, and the (Mes*)C–N–P angles are only slightly more acute, implicating retention of (Mes*C)N–P multiple-bonding in the complexes. Predictably, the imposition of two donors in the ligand-rich complex **2**[OTf] has the largest influence on the N–P distance and the C–N–P angle of the acceptor. In contrast, the two donors in the chelate ligand 2,2′ bipyridine effect minimal structural change on the acceptor in **4**[OTf].[11] This indicates that the basicity of the donor is more influential than the number of donors present. Consistently, one quinuclidine ligand[6] has a larger impact on the phosphadiazonium acceptor than the two donor sites of the less basic chelate ligand 2,2′-bipyridine (Table 1). Retention of an N–P multiple bond order, implicates hypervalency for the phosphorus acceptor sites in **2**[OTf] and **3**[OTf]$_2$.

The two phosphadiazonium units in **3**[OTf]$_2$ are not related by crystallographic symmetry. The 4,4′-BIPY ligand is slightly twisted (4°) about the central C–C bond, and the N → P coordinate bonds are inequivalent. Consequently, a single ^{31}P NMR signal is observed in solution (61 ppm), while two isotropic signals (60 and 63 ppm) are observed in the solid state CP-MAS ^{31}P NMR spectrum. By comparison, complexes of phosphines tethered by TMEDA[6] or 1,4-dimethylpiperazine[16] involve a crystallographic center of symmetry. The *anti*-configuration of the phosphadiazonium units in **3**[OTf]$_2$ is consistent with structures observed for complexes representing phosphenium cations tethered by diphosphine ligands,[17] and the torsional angles N1–P1–N3–C41 [−0.7(2)°] and N2–P2–N4–C46 [21.3(2)°] indicate the possibility of conjugation between the phosphadiazonium and the π-system of the bipyridine donor.

We thank NSERC, the Killam Foundation, the CRC Program, CFI, NSRIT, and the Walter C. Sumner Foundation for funding, the ARMRC for use of instrumentation, and Dr Mike Lumsden and Dr Ulrike Werner-Zwanziger for solid state NMR data.

Notes and references

‡ *Crystal Data for* **2[OTf]**: $C_{33}H_{49}N_5O_3F_3PS$, MW = 683.80 g mol^{-1}, triclinic, $P\bar{1}$, a = 9.6256(8) Å, b = 10.3665(8) Å, c = 19.7482(19) Å, α = 92.2375(16)°, β = 98.4811(15)°, γ = 113.4698(15)°, V = 1777.3(2) Å^3, T = 193(2) K, Z = 2, μ(Mo Kα) = 0.192 mm^{-1}, 11079 measured reflections (unique 6223), 419 refined parameters, R_1(F) [4268 reflections with $I > 2\sigma(I)$] = 0.0580, wR2(F^2) [all data] = 0.155. *Crystal Data for* **3[OTf]$_2$**: $C_{48}H_{66}N_4O_6F_6P_2S_2 \cdot (CH_2Cl_2)_{1.5}$, MW = 1162.50 g mol^{-1}, triclinic, $P\bar{1}$, a = 10.1616(4) Å, b = 16.9451(6) Å, c = 18.9324(7) Å, α = 110.8114(7)°, β = 91.4223(7)°, γ = 90.1012(7)°, V = 3046.1(2) Å^3, T = 193(2) K, Z = 2, μ(Mo Kα) = 0.336 mm^{-1}, 14079 measured reflections (unique 10613), 635 refined parameters, R_1(F) [9229 reflections with $I > 2\sigma(I)$] = 0.0489, wR2(F^2) [all data] = 0.141. The data were corrected for disordered electron density through use of the SQUEEZE[18] procedure as implemented in PLATON.[19] CCDC 247395 and 247396. See http://www.rsc.org/suppdata/cc/b4/b412267d/ for crystallographic data in .cif or other electronic format.

1 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, John Wiley & Sons, New York, 5th edn., 1988.

2 N. Burford and P. J. Ragogna, *Dalton Trans.*, 2002, 4307–4315.

3 E. Niecke, M. Nieger and F. Reichert, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1715–1716.

4 E. Niecke, R. Detsch, M. Nieger, F. Reichert and W. W. Schoeller, *Bull. Soc. Chim. Fr.*, 1993, **130**, 25–31.

5 N. Burford, T. S. Cameron, D. J. LeBlanc, A. D. Phillips, T. E. Concolino, K. C. Lam and A. L. Rheingold, *J. Am. Chem. Soc.*, 2000, **122**, 5413–5414.

6 N. Burford, P. Losier, A. D. Phillips, P. J. Ragogna and T. S. Cameron, *Inorg. Chem.*, 2003, **42**, 1087–1091.

7 N. Burford, T. S. Cameron, J. A. C. Clyburne, K. Eichele, K. N. Robertson, S. Sereda, R. E. Wasylishen and W. A. Whitla, *Inorg.Chem.*, 1996, **35**, 5460–5467.

8 N. Burford, A. D. Phillips, H. A. Spinney, K. N. Robertson, T. S. Cameron and R. McDonald, *Inorg. Chem.*, 2003, **42**, 4949–4954.

9 M. Blättner, M. Nieger, A. Ruban, W. W. Schoeller and E. Niecke, *Angew. Chem. Int. Ed.*, 2000, **39**, 2768–2771.

10 E. Rivard, K. Huynh, A. J. Lough and I. Manners, *J. Am. Chem. Soc.*, 2004, **126**, 2286–2287.

11 N. Burford, T. S. Cameron, K. N. Robertson, A. D. Phillips and H. A. Jenkins, *Chem. Commun.*, 2000, 2087–2088.

12 T. S. Cameron, C. Chan and W. J. Chute, *Acta Cryst.*, 1980, **B36**, 2391–2393.

13 M. T. Averbuch-Pouchot and M. Meisel, *Acta Cryst.*, 1989, **C45**, 1937–1939.

14 M. Meisel, P. Lönnecke, A. R. Grimmer and D. Wulff-Molder, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1869–1870.

15 W. S. Sheldrick, *Dalton Trans.*, 1974, 1402–1405.

16 G. Muller, J. Brand and S. E. Jetter, *Z. Naturforsch.*, 2001, **56b**, 1163–1171.

17 N. Burford, P. J. Ragogna, R. McDonald and M. J. Ferguson, *Chem. Commun.*, 2003, 2066–2067.

18 P. v. d. Sluis and A. L. Spek, *Acta Crystallogr.*, 1990, **A46**, 194–201.

19 A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7–13.