

Nitrogen ligands on a phosphinic Lewis acceptor including a 2,2'-dipyridyl chelate complex

Neil Burford,^{*a} T. Stanley Cameron,^a Katherine N. Robertson,^a Andrew D. Phillips^a and Hilary A. Jenkins^b

^a Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, B3H 4J3, Canada.
E-mail: burford@is.dal.ca

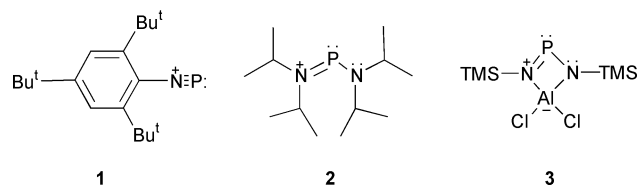
^b Department of Chemistry, Saint Mary's University, Halifax, Nova Scotia, B3H 3C3, Canada

Received (in Irvine, CA, USA) 28th June 2000, Accepted 12th September 2000

First published as an Advance Article on the web 9th October 2000

In the context of the developing coordination chemistry of lone pair bearing phosphinic centers as acceptors, synthesis and characterisation for new complexes of the phosphadiazonium cation with nitrogen donors are described, including the first dipyridyl chelate.

The coordination chemistry of phosphorus(v) as an acceptor is well established^{1,2} and is highlighted by hexacoordinated centers such as PF₆⁻ and the pyridine complex of PF₅.³ The Lewis acidity of phosphines represents a more recent and developing area and demonstrates interesting bonding properties by virtue of the non-bonding electron pair at the acceptor site. Systems **1**, **2** and **3**, containing coordinatively unsaturated

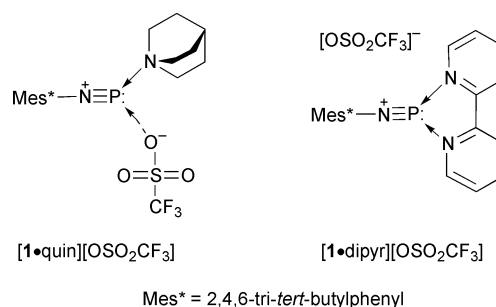


phosphinic centers form complexes with amines,⁴⁻⁷ phosphines,⁸ carbenes⁹ and arenes,¹⁰ and an example of a bis-ligand complex has been mentioned.¹¹ We have now developed the coordination chemistry of the phosphadiazonium cation **1** with nitrogen donors, and have isolated the first chelate complex.

Reactions of [**1**][OSO₂CF₃]¹² with equimolar amounts of quinuclidine (1-azabicyclo[2.2.2]octane, quin) or 2,2'-dipyridyl (dipyr) proceed almost instantaneously and quantitatively at RT as shown by ³¹P NMR spectra of reaction mixtures, which are consistent with those for solutions of isolated crystalline products.^{†‡} Comprehensive characterisation, including X-ray crystallographic analysis, confirm 1:1 association of the reagents and the compounds are best represented as coordination complexes [**1**-quin][OSO₂CF₃] and [**1**-dipyr][OSO₂CF₃] involving phosphorus as an acceptor. Selected structural features for **1**-quin and **1**-dipyr are presented in Table 1 in comparison with analogous parameters for related complexes.

Table 1 Selected structural parameters for complexes of **1**, **2** and **3** with nitrogen donors (pyr = pyridine, DBN = 1,5-diazabicyclo[4.3.0]non-5-ene, tmeda = tetramethylethylenediamine)

Compound	N–P (Å)	N→P/Å	P–O/Å	Mes*–N–P–N°	(Mes*)C–N–P°	Ref.
1	1.467(4)	—	1.923(3)	—	176.4(3)	12
[1 -quin][OSO ₂ CF ₃]	1.519(2)	1.933(2)	2.697(3)	103.7(1)	143.9(2)	This work
[1 -pyr][OSO ₂ CF ₃]	1.472(8)	1.958(8)	2.712(7)	107.8(4)	161.7(7)	9
[1 -dipyr][OSO ₂ CF ₃]	1.497(4)	2.065(4), 2.066(4)	3.490(6)	106.3(2), 113.0(2)	169.4(4)	This work
[2 -DBN][Cl]	1.661(4), 1.666(4)	1.796(3)	—	101.6(2), 99.1(2)	—	5,6
3 -quin	1.686(9), 1.660(9)	2.038(9)	—	—	—	7
(3) ₂ -tmeda	1.658(5), 1.661(5)	2.110(6)	—	—	—	7



The N→P interactions are weak and variable in distance (*cf.* N–P single bond distance 1.800(4) Å),¹³ but effect extension of the P–O(triflate) cation–anion interaction, which is most pronounced for the ionic material [**1**-dipyr][OSO₂CF₃]. The chelate complexation of **1** by dipyr, illustrated in Fig. 1, is

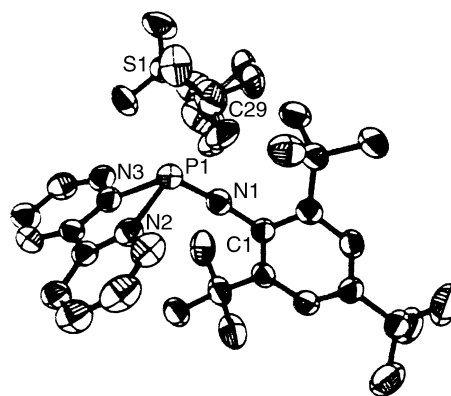
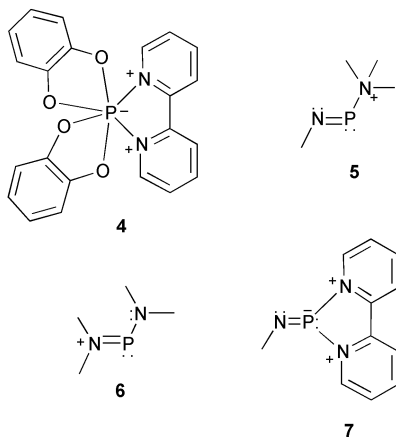


Fig. 1 Crystallographic view of [**1**-dipyr][OSO₂CF₃] with 50% probability displacement ellipsoids. The hydrogen atoms and dichloromethane solvate have been omitted. The CF₃ group of the triflate anion is disordered.



defined by two indistinguishable N→P interactions, contrasting the asymmetric chelate-like cation–anion contact reported for the diselenophosphate salt of **1**,¹⁴ and complementing the established series of 2,2′-dipyridyl complexes of AsCl₃,¹⁵ SbCl₃,¹⁶ and BiCl₃¹⁷ that could not be extended to PCl₃.¹⁸

A pyramidal geometry for phosphorus in **1**-dipyr accommodates the non-bonding electron pair and offers interesting comparisons with the hexafluorophosphate salt of phosphonium **4**,² which involves a distorted octahedral site. The ‘bite’ (N–P–N) angle in **1**-dipyr (75.1(2)°) is substantially less than in **4** (81.7(2)°), due to significantly longer N→P bond distances (*cf.* **4**, 1.896(4) and 1.898(4) Å). Coordinate interactions are demonstrated in both complexes by the small N–C–C(bridge) angles (**1**-dipyr, 111.9(4), 113.6(4)°; **4**, 112.0(4), 112.2(4)°).

Complexes of nitrogen ligands on phosphinic centers provide access to new bonding environments for phosphorus in that [1-quin]⁺ represents a novel structural isomer **5** of a diamino-phosphonium cation **6** and **1**-dipyr represents a cationic iminophosphide⁹ bonding environment **7**, both of which are synthetically accessible only *via* the coordination chemistry of phosphorus as an acceptor.

We thank the Natural Sciences and Engineering Research Council of Canada (N. B. T. S. C.) and the Killam Foundation (N. B.) for funding, the Walter Sumner Foundation for a scholarship (A. D. P.), the Atlantic Regional Magnetic Resonance Centre for the use of instrumentation and Dr D.J. LeBlanc for helpful discussion.

Notes and references

† Procedures described in ref. 19, equimolar combinations in benzene, crystals obtained by liquid/liquid (CH₂Cl₂ and n-hexane) diffusion; [1-quin][OSO₂CF₃]: yield 0.07 g, 21%; mp 176–178 °C; Anal. Calcd.: C, 56.71; H, 7.69; N, 5.09. Found: C, 57.10; H, 8.38; N, 5.12%. IR (cm⁻¹, ranked intensities): 516(16), 637(2), 752(10), 763(13), 877(17), 891(20), 923(19), 966(15), 1005(14), 1026(1), 1147(9), 1163(8), 1226(7), 1241(3), 1257(5), 1278(6), 1339(11), 1365(4), 1417(12), 1600(18). NMR (ppm, in CD₂Cl₂): ¹H 1.31 (s, 9H, *p*-(CH₃)₃C), 1.47 (s, 18H, *o*-(CH₃)₃C), 1.98, (m, 6H, HC(CH₂)₃), 2.16 (sept, ³J(¹H,¹H) = 3.35 Hz, 1H, HC(CH₂)₃), 3.43 (m, 6H, (CH₂)₃N), 7.40 (d, ⁵J(³¹P,¹H) = 1.53 Hz, 2H, *m*-CH); ¹³C{¹H} 20.8 (s, HC(CH₂)₃), 24.6 (s, HC(CH₂)₃), 31.4 (s, *o*-(CH₃)₃C), 31.5 (s, *p*-(CH₃)₃C), 35.5 (s, *p*-(CH₃)₃C), 36.5 (s, *o*-(CH₃)₃C), 48.1 (s, N(CH₂)₃), 121.3 (q, ¹J(¹⁹F,¹³C) = 319 Hz, CF₃), 123.2 (s, *m*-CH), 136.9 (d, ²J(³¹P,¹³C) = 26.2 Hz, *i*-CNP), 140.4 (d, ³J(³¹P,¹³C) = 8.11 Hz, *o*-(CH₃)₃CC), 150.0 (s, *p*-(CH₃)₃CC); ¹⁹F{¹H} –78.8 (s, ¹J(¹⁹F,¹³C) = 319 Hz); ³¹P{¹H} 144 (s). [1-dipyr][OSO₂CF₃]: yield 0.29 g, 84%; mp 201 °C. CH₂Cl₂ of crystallisation has precluded determination of elemental analysis. IR (cm⁻¹, ranked intensity): 1602(14), 1491(8), 1446(5), 1392(18), 1364(15), 1314(16), 1280(2), 1275(3), 1256(4), 1226(11), 1160(7), 1151(9), 1032(1), 1014(10), 778(12), 768(17), 755(20), 651(13), 639(6), 518(19); NMR (ppm, in CD₂Cl₂): ¹H 1.27 (s, 9H, *p*-(CH₃)₃C), 1.31 (s, 18H, *o*-(CH₃)₃C), 7.31 (d,

⁵J(³¹P,¹H) = 1.83 Hz, 2H, *m*-CH) 7.99 (m, ³J(¹H,¹H) = 6.95 Hz, ³J(¹H,¹H) = 7.55 Hz, 2H, 5,5′-CH), 8.54 (m, ³J(¹H,¹H) = 6.95 Hz, ³J(¹H,¹H) = 5.43, 2H, 4,4′-CH), 8.88 (mm, ³J(¹H,¹H) = 7.55 Hz, 2H, 3,3′-CH), 8.99 (m, ³J(¹H,¹H) = 5.43 Hz, 2H, 6,6′-CH); ¹³C{¹H} 30.1 (s, *o*-(CH₃)₃C), 31.4 (s, *p*-(CH₃)₃C), 35.3 (s, *p*-(CH₃)₃C), 35.8 (s, *o*-(CH₃)₃C), 121.2 (q, ¹J(¹⁹F,¹³C) = 320 Hz, CF₃), 122.3 (s, 3,3′-CH), 122.6 (s, *m*-CH), 123.9 (s, 5,5′-CH), 128.5 (s, 4,4′-CH), 133.9 (d, ³J(³¹P,¹³C) = 46.7 Hz, *i*-CNP), 144.6 (s, 6,6′-CH), 145.2 (s, 2,2′-NCCN), 145.5 (d, ³J(³¹P,¹³C) = 14.3 Hz, *o*-(CH₃)₃CC), 148.6 (d, ⁵J(³¹P,¹³C) = 4.29 Hz, *p*-(CH₃)₃CC); ¹⁹F{¹H} –78.8 (s, ¹J(¹⁹F,¹³C) = 320 Hz); ³¹P{¹H} 54 (s).

‡ Crystal data: for C₂₆H₄₂F₃N₂O₃PS. *M* = 550.65 g mol⁻¹, orthorhombic, *P*2₁2₁1, *a* = 29.469(2), *b* = 10.0650(6), *c* = 9.7745(6), Å, *V* = 2899.2(3) Å³, *T* = 193 K, *Z* = 4, μ(Mo-Kα) = 0.215 mm⁻¹, 18488 measured reflections, 6851 unique, 326 refined parameters, *R*[*I* > 2σ(*I*)] = 0.0530, *wR*2(*F*²) = 0.1294, *S* = 1.037. For C₃₀H₃₉Cl₂F₃N₃O₃PS. *M* = 680.57 g mol⁻¹, monoclinic, *P*2₁/*a*, *a* = 18.4174(9), *b* = 10.9488(6), *c* = 19.213(1) Å, β = 116.924(1)°, *V* = 3454.3(3) Å³, *T* = 193 K, *Z* = 4, μ(Mo-Kα) = 0.345 mm⁻¹, 20945 measured reflections, 8094 unique, 404 refined parameters with 29 restraints, *R*[*I* > 2σ(*I*)] = 0.1000, *wR*2(*F*²) = 0.2381, *S* = 1.173. CCDC 182/1780.

- R. R. Holmes, *Chem. Rev.*, 1996, **96**, 927; R. R. Holmes, *Acc. Chem. Res.*, 1998, **31**, 535; F. Carre, C. Chuit, R. J. P. Corriu, P. Monforte, N. K. Nayyar and C. Reye, *J. Organomet. Chem.*, 1995, **499**, 147; K. Kamijo, A. Otoguro, K. Toyota and M. Yoshifujii, *Bull. Chem. Soc. Jpn.*, 1999, **72**, 1335; M. Meisel, P. Lonneck, A. R. Grimmer and D. Wulff. *Molder, Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1869.
- W. S. Sheldrick, A. Schimidpeter and T. von Criegern, *Z. Naturforsch., Teil B*, 1978, **33**, 583.
- W. S. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 1974, 1402.
- R. W. Kopp, A. C. Bond and R. W. Parry, *Inorg. Chem.*, 1976, **15**, 3042; C. Payrastra, Y. Madaule, J. G. Wolf, T. C. Kim, M. R. Mazières, R. Wolf and M. Sanchez, *Heteroat. Chem.*, 1992, **3**, 157; T. Kaukorat, I. Neda and R. Schmutzler, *Coord. Chem. Rev.*, 1994, **137**, 53; Y. V. Balitzky, S. E. Pipko, A. D. Sinita, A. N. Chernega and Y. G. Gololobov, *Phosphorus Sulfur, Silicon*, 1993, **75**, 167; F. Carre, C. Chuit, R. J. P. Corriu, A. Mehdi and C. Reye, *J. Organomet. Chem.*, 1997, **529**, 59.
- R. Reed, R. Réau, F. Dahan and G. Bertrand, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 399.
- G. Bouhadir, R. W. Reed, R. Reau and G. Bertrand, *Heteroat. Chem.*, 1995, **6**, 371.
- N. Burford, P. Losier, P. K. Bakshi and T. S. Cameron, *Chem. Commun.*, 1996, 307.
- N. Burford, T. S. Cameron, J. A. C. Clyburne, K. Eichele, K. N. Robertson, S. Sereda, R. E. Wasylishen and W. A. Whittle, *Inorg. Chem.*, 1996, **35**, 5460; R. W. Alder, D. D. Ellis, J. K. Hogg, A. Martin, A. G. Orpen and P. N. Taylor, *Chem. Commun.*, 1996, 537; R. W. Alder, D. D. Ellis, A. G. Orpen and P. N. Taylor, *Chem. Commun.*, 1996, 539; G. David, E. Niecke, M. Nieger, J. Radseck and W. W. Schoeller, *J. Am. Chem. Soc.*, 1994, **116**, 2191; N. Burford, T. S. Cameron, D. J. LeBlanc, P. Losier, S. Sereda and G. Wu, *Organometallics*, 1997, **16**, 4712.
- 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.
- N. Burford, J. A. C. Clyburne, P. K. Bakshi and T. S. Cameron, *Organometallics*, 1995, **14**, 1578.
- M. Blättner, A. Ruban, D. Gudat, M. Nieger and E. Niecke, *Phosphorus Sulfur, Silicon*, 1999, **147**, 31.
- E. Niecke, R. Detsch, M. Nieger, F. Reichert and W. W. Schoeller, *Bull. Soc. Chim. Fr.*, 1993, **130**, 25.
- T. S. Cameron, C. Chan and W. J. Chute, *Acta Crystallogr., Sect. B*, 1980, **36**, 2391.
- E. Niecke, M. Nieger, F. Reichert and W. W. Schoeller, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1713.
- J. U. Cameron and R. C. G. Killeen, *Cryst. Struct. Commun.*, 1972, **1**, 31.
- A. Lipka and H. Wunderlich, *Z. Naturforsch., Teil B*, 1980, **35**, 1548.
- G. A. Bowmaker, F. M. M. Hannaway, P. C. Junk, A. M. Lee, B. W. Skelton and A. H. White, *Aust. J. Chem.*, 1988, **51**, 331.
- W. R. Roper and C. J. Wilkins, *Inorg. Chem.*, 1964, **3**, 500.
- N. Burford, J. Müller and T. M. Parks, *J. Chem. Educ.*, 1994, **71**, 807.