Supplementary Material (ESI) for Chemical Communications

Supporting Information

Bifunctional Diphosphorus Lewis Acids from *cyclo*-Diphosphadiazanes

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1. Experimental section

General Remarks. All reactions were carried out in a glove box under an N_2 atmosphere. Solvents were dried on an MBraun solvent purification system and stored under nitrogen and over molecular sieves prior to use. Deuterated solvents were dried over CaH_2. 4-(Dimethylamino)pyridine (DMAP), silver trifluoromethanesulfonate (AgOTf), trimethylsilyl trifluoromethanesulfonate (Me_3SiOTf), PMe_3 (1M in toluene) and all other chemicals and reagents were purchased from Sigma-Aldrich and if not other stated, used as received. PCl_3 and $DmpNH_2$ were distilled prior to use. **5b** was prepared according to literature methods.[1] NMR: Bruker AVANCE 500 and Bruker AC 250 (^{1}H (500.13 MHz), ^{13}C (125.76 MHz) chemical shift referenced to δ_{TMS} = 0.00; ^{31}P (202.46 MHz, 101.26 MHz) to $\delta_{H3PO4(85\%)}$ = 0.00) and are reported in ppm; *J* values are reported in Hz. ^{31}P NMR parameters for higher ordered Spin systems were derived by fitting the observed experimental spectra with a computer simulation using the software program gNMR, version 5.0, by Cherwell Scientific.[2] The line shapes of the isotropic shift resonances in the solid state NMR spectrum of sample **6b**$[OTf]_2$ were simulated by using fixed J-coupling values from the solution state ^{31}P NMR spectra and varying the isotropic shift values and the line width. The solid state NMR experiments were carried out on a Bruker Avance DSX NMR spectrometer with a 9.4T magnet (400.24 MHz proton Larmor frequency, 162.06MHz ^{31}P Larmor frequency) using ^{31}P cross-polarization (CP)/Magic Angle Spinning (MAS) experiments with TPPM proton decoupling. Powdered crystalline samples were carefully packed in 4 mm rotors under an inert atmosphere. The MAS speed was varied between 8.0 kHz and 12.5 kHz to identify isotropic shift resonances and spinning sidebands. Spin-Lattice relaxation times for the protons in the sample were estimated by an inversion recovery sequence. From these experiments recycle delays between 14 and 60 seconds for the ^{31}P CP/MAS experiments were determined. Other parameters for the ^{31}P CP/MAS experiments were optimized on

ammonium dihydrogen phosphate, whose resonance also served as external, secondary chemical shift standard at 0.81 ppm. Between 16 and 128 scans were accumulated for the ^{31}P CP/MAS NMR spectra, using 500 micro seconds CP contact times. Infrared spectra were recorded as Nujol mulls in NaCl plates on a Bruker Vektor 22 FT-IR. The intensities are reported in order of most to least intense peak and are given in brackets. Raman spectra were obtained for powdered and crystalline samples on a Bruker RFS 100 instrument equipped with a Nd:YAG laser (1064 nm). The intensities are reported in % relative to the most intense peak and given in brackets. Melting points were recorded on an Electrothermal melting point apparatus in sealed capillaries tubes under N_2. Chemical analyses were determined by Canadian Microanalytical Service LTD., Delta, BC, Canada.

Synthesis of *cis*-5c: AgOTf (10.28 g, 40 mmol) was suspended in a hexane solution (100 mL) of **5b** (7.42 g, 20 mmol). The solution was stirred for 24 hours, filtered, and the residue was extracted with CH_2Cl_2. The filtrates were combined and the solvents removed *in vacuo*. Recrystallization from CH_2Cl_2 gave pure *cis*-**5c** as colorless block containing small amounts of the *trans*-**5c** isomer: 10.90 g (83 %); mp 130 – 133 °C; IR (cm^{-1}): 1417(3), 1262(9), 1245(5), 1223(6), 1204(1), 1170(12), 1140(2), 1098(8), 943(14), 928(10), 862(11), 827(4), 670(13), 610(7); Raman (300 mW, 25 °C, cm^{-1}): 3071(34), 3048(34), 2979(25), 2922(81), 2871(21), 2751(7), 2734(7), 2557(4), 1593(68), 1495(5), 1476(14), 1447(13), 1422(14), 1411(13), 1387(24), 1375(13), 1297(100), 1245(29), 1175(15), 1147(12), 1105(18), 1029(4), 991(14), 861(12), 833(6), 769(62), 755(15), 677(19), 647(19), 613(8), 572(36), 562(17), 545(17), 491(9), 383(10), 350(13), 328(16), 308(20), 229(18), 207(15), 190(23), 140(40), 85(100); ^{1}H{^{31}P} NMR ($CDCl_3$, 300 K, [ppm]): δ = 2.64 (12H, s, ***Me***$_2$C$_6$H$_3$), 7.20–7.25 (4H, m, *m*-Me$_2$C$_6$***H***$_3$), 7.25–7.31 (2H, m, *o*-Me$_2$C$_6$***H***$_3$); ^{13}C NMR ($CDCl_3$, 300 K, [ppm]): 18.6 (s, ***Me***$_2$C$_6$H$_3$), 118.2 (q, $^{1}J_{CF}$ = 318.6 Hz, OTf), 129.3 (s), 129.4 (s), 131.9 (t, $^{3}J_{P–C}$ = 6.7 Hz), 137.4 (s); ^{31}P NMR ($CDCl_3$, 300 K, [ppm]): δ = 182.8 (m); ^{31}P MAS NMR (25 C°): δ_{iso}

= 180.3 (s), 178.3 (s); ^{19}F NMR ($CDCl_3$, 300 K, [ppm]): δ = -77.0 (-CF_3, broad "t", $^5J_{PF}$ = 8.7 Hz); elemental analysis for $C_{18}H_{18}F_6N_2O_6P_2S_2$ (598.42): calcd. C 36.13, H 3.03, N 4.68; found: C 35.52, H 3.27, N 4.67.

Synthesis of *cis*-**6a**[OTf]**:** A solution of DMAP (37 mg, 0.30 mmol) in CH_2Cl_2 (2 mL) was added to a solution of **5c** (180 mg, 0.30 mmol) in an equivalent amount of the same solvent and stirred for 10 minutes. The solution was layered with hexane and left at -32 °C for 48 hours leading to the deposition of big rods of *cis*-**6a**[OTf] suitable for crystal structure analysis: 166 mg (77 %); mp 218 – 220 °C; IR (cm^{-1}): 1645(2), 1265(1), 1246(10), 1223(9), 1210(5), 1191(6), 1145(8), 1040(4), 1033(7), 914(12), 852(3), 639(11); Raman (300 mW, 25 °C, cm^{-1}): 3105(17), 3074(18), 3042(23), 2984(24), 2928(43), 2873(15), 2741(8), 1640(29), 1592(61), 1535(7), 1479(16), 1411(11), 1388(10), 1324(6), 1282(60), 1244(11), 1225(10), 1191(9), 1172(11), 1143(6), 1107(16), 1031(30), 1022(15), 992(6), 974(6), 941(9), 848(7), 828(6), 766(31), 754(16), 719(4), 661(26), 619(11), 561(13), 546(9), 515(6), 500(5), 347(13), 312(13), 294(9), 247(10), 231(12), 197(11), 160(17), 102(48), 85(100); ^{1}H{^{31}P} NMR ($CDCl_3$, 300 K, [ppm]): δ = 2.50 (12H, s, ***Me***$_2$C$_6$H$_3$), 3.43 (6H, N***Me***$_2$), 7.14–7.16 (4H, m, *m*-Me$_2$C$_6$***H***$_3$), 7.19–7.22 (4H, m, *o*-Me$_2$C$_6$***H***$_3$ and *m*-ArH (DMAP)) 8.61–8.33 (2H, m, *o*-ArH (DMAP)); ^{13}C NMR ($CDCl_3$, 300 K, [ppm]): 19.6 (s, ***Me***$_2$C$_6$H$_3$), 41.2 (s, NMe$_2$), 108.4 (d, $^2J_{CP}$ = 3.5 Hz, *o*-C (DMAP)), 119.2 (q, $^1J_{CF}$ = 320.6 Hz, OTf), 129.4 (s), 129.9 (s), 132.8 (t, $^3J_{P–C}$ = 4.3 Hz), 136.9 (s), 141.0 (d, $^3J_{CP}$ = 20.7 Hz, *m*-C (DMAP)), 158.3 (s, *p*-C (DMAP)); ^{31}P NMR ($CDCl_3$, 300 K, [ppm], 101.26 MHz): δ = 191.0 (d, A part of the AX spin system), 150.5 (d, X part of the AX spin system, $^2J_{PP}$ = 48.7 Hz) ; ^{31}P MAS NMR (25 C°): δ_{iso} = 193.6 (s), 147.4 (s); ^{19}F NMR ($CDCl_3$, 300 K, [ppm]): δ = -78.9 (-CF_3, s, *br*); elemental analysis for $C_{25}H_{28}F_6N_4O_6P_2S_2$ (720.58): calcd. C 41.67, H 3.92, N 7.78; found: C 41.34, H 4.06, N 7.83.

Synthesis of *cis*-**7a[**OTf]$_2$: A solution of DMAP (73 mg, 0.60 mmol) in CH_2Cl_2 (2 mL) was added to a solution of [DmpNPOTf]$_2$ (180 mg, 0.30 mmol) in an equivalent amount of the same solvent and stirred for 2 hours. The solution was layered with hexane and left at -32 °C for 48 hours leading to the deposition of big coarse crystals of *cis*-**7a[**OTf]$_2$ suitable for crystal structure analysis: 230 mg (89%); mp 240 – 242 °C; IR (cm^{-1}): 1637(2), 1576(12), 1569(10), 1560(11), 1402(13), 1282(5), 1259(4), 1219(6), 1182(14), 1146(7), 1030(1), 1017(3), 872(9), 636(8); Raman (300 mW, 25 °C, cm^{-1}): 3126(22), 3039(38), 2928(66), 2871(23), 2739(7), 1642(69), 1588(100), 1533(17), 1476(27), 1418(18), 1403(19), 1380(14), 1323(14), 1273(67), 1237(23), 1224(23), 1184(15), 1167(12), 1107(24), 1034(46), 969(8), 942(25), 873(23), 812(8), 770(51), 754(23), 717(11), 702(8), 666(28), 636(49), 606(10), 574(13), 559(16), 549(12), 495(9), 463(9), 350(21), 313(18), 253(17), 198(22), 85(100); ^{1}H{^{31}P} NMR ($CDCl_3$, 300 K, [ppm]): δ = 2.44 (12H, s, ***Me***$_2$C$_6$H$_3$), 3.40 (12H, N***Me***$_2$), 7.10–7.11 (4H, m, *m*-Me$_2$C$_6$***H***$_3$), 7.15–7.18 (2H, m, *o*-Me$_2$C$_6$***H***$_3$), 7.51 (4H, d, *m*-ArH (DMAP), $^3J_{HH}$ = 8 Hz), 8.60 (4H, d, *o*-ArH, (DMAP), $^3J_{HH}$ = 8 Hz)); ^{13}C NMR ($CDCl_3$, 300 K, [ppm]): 19.2 (s, ***Me***$_2$C$_6$H$_3$), 41.0 (s, NMe$_2$), 109.7 (s, *o*-C (DMAP)), 121.2 (q, $^1J_{CF}$ = 318.6 Hz, OTf$^-$), 129.3 (s), 130.2 (s), 133.6 (t, $^3J_{P-C}$ = 8.2 Hz), 136.9 (s), 141.1 (t, $^3J_{CP}$ = 11.1 Hz, *m*-C (DMAP)), 158.5 (s, *p*-C (DMAP)); ^{31}P NMR ($CDCl_3$, 300 K, [ppm]): δ = 149.08 (s); ^{19}F NMR ($CDCl_3$, 300 K, [ppm]): δ = -79.5 (-CF$_3$, s); elemental analysis for $C_{32}H_{38}F_6N_6O_6P_2S_2$ (842.75): calcd. C 45.61, H 4.54, N 9.97; found: C 44.48, H 4.14, N 9.65.

Synthesis of *trans*-**7b[**OTf]$_2$**:** Trimethylphosphine (1000µL, 1M in toluene, 1.0 mmol) was added to a solution of **5c** (0.33 g, 0.55 mmol) in an equivalent amount of the same solvent and stirred for 10 minutes. The precipitate was washed several times with CH_2Cl_2 (4 x 3 mL) and Et_2O (4 x 3 mL) to remove the slight excess of **5c**. Recrystallization from CH_3CN/Et_2O gave pure *trans*-**7b**[OTf]$_2$ as bright yellow-orange needles within 5 hours. *trans*-**7b**[OTf]$_2$ readily decomposes in solution: 0.368 g (91 %); mp 135 – 136 °C; IR (cm^{-1}):

1292(7), 1271(2), 1254(1), 1221(8), 1194(6), 1166(3), 1106(11), 1025(4), 928(10), 906(12), 850(9), 774(13), 635(5); Raman (300 mW, 25 °C, cm^{-1}): 3067(12), 2987(45), 2915(100), 1592(36), 1469(12), 1406(13), 1266(28), 1228(9), 1171(7), 1111(12), 1032(34), 769(10), 756(16), 666(14), 584(23), 546(7), 527(9), 416(24), 347(17), 320(9), 258(10), 120(19), 84(90); $^{1}H\{^{31}P\}$ NMR (d_3-MeCN, 300 K, [ppm]): δ = 1.79-1.85 (18H, m, P-P***Me***$_3$), 2.65 (12H, s, ***Me***$_2C_6H_3$); 7.22 (6H, m, Me_2C_6***H***$_3$), Due to the high instability of compound **7b[**OTf]$_2$ in solution, ^{13}C NMR data could not be recorded; $^{31}P\{^{1}H\}$ NMR (d_3-MeCN, 300 K, [ppm]): 17.49 (2P, P-***P***$_X$Me$_3$), 279.50 (2P, ***P***$_A$-PMe$_3$, AA'XX' spin system, $^{1}J_{AX} = {}^{1}J_{A'X'}$ = -474.2, $^{2}J_{AA'}$ = 21.4, $^{3}J_{AX'} = {}^{3}J_{XA'}$ = 41.2, $^{4}J_{XX'}$ = 107.0 Hz); ^{19}F NMR (d_3-MeCN, 300 K, [ppm]): δ = -74.9 (-CF_3, s); elemental analysis was not performed due to the high sensitivity of **7b**[OTf]$_2$.

2. Crystallographic Details

Table S1: Crystal and Refinement Data for *cis*-**5c**, *cis*-**6a**[OTf] and *cis*-**7a**$[OTf]_2$ and *trans*-**7b**$[OTf]_2$.

	cis-**5c**	*cis*-**6a**[OTf]	*cis*-**7a**$[OTf]_2$	*trans*-**7b**$[OTf]_2$
formula	$C_{18}H_{18}F_6N_2O_6P_2S_2$	$C_{25}H_{28}F_6N_4O_6P_2S_2$	$C_{35}H_{44}Cl_6F_6N_6O_6P_2S_2$	$C_{24}H_{36}F_6N_2O_6P_4S_2$
molecular weight [g mol^{-1}]	598.40	720.57	1097.52	750.56
color, habit	colorless, irregular	colorless, rod	colorless, irregular	pale-yellow, needle
crystal System	monoclinic	triclinic	triclinic	monoclinic
space group	$P2_1/n$	P-1	P-1	$P2_1/n$
a [Å]	12.985(4)	8.871(3)	10.872(4)	10.3471(6)
b [Å]	10.925(3)	11.269(4)	12.643(5)	14.3075(6)
C [Å]	18.101(6)	16.513(6)	18.914(8)	11.3770(6)
α [°]	90.0	75.406(5)	99.381(5)	90.0
β [°]	93.012(4)	81.369(5)	101.844(6)	103.427(4)
γ [°]	90.0	86.308(5)	97.875(6)	90.0
V [Å^3]	2564.2(14)	1578.9(9)	2471.1(17)	1638.2(2)
Z	4	2	2	2
T [K]	173(1)	173(1)	173(1)	123.1(2)
crystal size [mm]	0.45x0.45x0.25	0.45x0.10x0.05	0.40x0.28x0.05	0.18x0.19x0.60
ρ_c [mg m^{-3}]	1.550	1.516	1.475	1.521
F(000)	1216	740	1124	776
$\lambda_{MoK\alpha}$, Å	0.71073	0.71073	0.71073	0.71073
θ_{min} [°]	1.57	1.29	1.66	2.3
θ_{max} [°]	27.50	27.50	27.49	72.4
index range	$-16 \le h \le 16$	$-11 \le h \le 11$	$-12 \le h \le 13$	$-22 \le h \le 26$
	$-13 \le k \le 12$	$-14 \le k \le 14$	$-16 \le k \le 16$	$-23 \le k \le 38$
	$-22 \le l \le 23$	$-21 \le l \le 21$	$-24 \le l \le 21$	$-30 \le l \le 27$
μ [mm^{-1}]	0.413	0.351	0.567	0.433
absorption correction	SADABS	SADABS	SADABS	multi-scan
reflections collected	17263	10866	16613	83406
reflections unique	5721	6807	10597	29460
R_{int}	0.0393	0.0288	0.0262	0.042
reflection obs. [F > 2σ(F)]	4520	4850	10597	4762
residual density [e Å^{-3}]	0.637, –0.701	0.517, –0.377	0.967, –0.827	0.40, –0.55
parameters	329	421	576	272
GooF	1.043	1.043	1.047	1.088
R_1 [I > 2σ(I)]	0.0452	0.0446	0.0672	0.036
wR_2 (all data)	0.1288	0.1283	0.2139	0.105
CCDC	650721	650722	650720	650811

Crystallography. Single crystals of *cis*-**5c**, *cis*-**6a**[OTf] and *cis*-**7a**$[OTf]_2$ and *trans*-**7b**$[OTf]_2$ were coated with Paratone-N oil, mounted using a 20 micron cryo-loop and frozen in the cold nitrogen stream of the goniometer. In the case of *cis*-**5c**, *cis*-**6a**[OTf] and *cis*-**7a**$[OTf]_2$ a hemisphere of data was collected on a Bruker AXS P4/SMART 1000 diffractometer using ω and θ scans with a scan width of 0.3° and 10 s (*cis*-**5c**), 25 s (*cis*-

6a[OTf]) and 30 s (*cis*-**7a**[OTf]$_2$) exposure times. The detector distance was 5 cm in all cases. For *trans*-**7b**[OTf]$_2$ the data were collected on a Rigaku RAXIS Rapid imaging plate area detector to a maximum of 2Θ value of 144.8°. Three sweep of data were collected using ω oscillation from 20.0 to 200°, 38.8 to 113.8° and 20.0 to 192.0° in 5.0° steps with a exposure rate of 360 [sec./°]. The detector swing angles were in all cases -0.01°. The crystal-to-detector distance was 127.40 mm and readout was performed in the 0.100 mm pixel mode. For *cis*-**5c**, *cis*-**6a**[OTf] and *cis*-**7a**[OTf]$_2$, the data were reduced (SAINT 6.02, 1997-1999, Bruker AXS, Inc., Madison, Wisconsin, USA) and corrected for absorption (SADABS George Sheldrick, 1999, Bruker AXS, Inc., Madison, Wisconsin, USA). The data for *trans*-**6b**[OTf]$_2$ were reduced (CrystalStructure 3.6.0. Single Crystal Structure Analysis Software. Rigaku/MSC, 2004, Japan) and empirical corrected for absorption resulting in transmission factors ranging from 0.83 to 1.00. The data were corrected for Lorentz and polarization effects. The structures were solved by direct methods and refined by full-matrix least squares on F^2 (SHELXTL 6.14, George Sheldrick, 2000, Bruker AXS, Inc., Madison,Wisconsin, USA) and in the case of *trans*-**7b**[OTf]$_2$ on F using only the "observed" data (CrystalStructure 3.6.0 Single Crystal Structure Analysis Software. Rigaku/MSC, 2004, Japan). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms in *cis*-**5c**, *cis*-**6a**[OTf] and *cis*- and **7a**[OTf]$_2$ were included in calculated positions and refined using a riding model; in the case of *trans*-**7b**[OTf]$_2$ they were refined isotropically. Further information on the crystal structure determination (excluding structure factors) has been deposit with the Cambridge Crystallographic Data Centre as supplementary publications nos. 650721, 650722, 650720, and 650811, (*cis*-**5c**, *cis*-**6a**[OTf], *cis*-**7a**[OTf]$_2$ and *trans*-**7b**[OTf]$_2$). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033. e-mail: deposit@ccdc.cam.ac.uk).

Reference List

[1.] N. Burford, T. S. Cameron, K. D. Conroy, B. Ellis, C. L. B. Macdonald, R. Ovans, A. D. Phillips, P. J. Ragogna, D. Walsh, *Can.J.Chem.* **2002,** *80* 1404-1409.

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