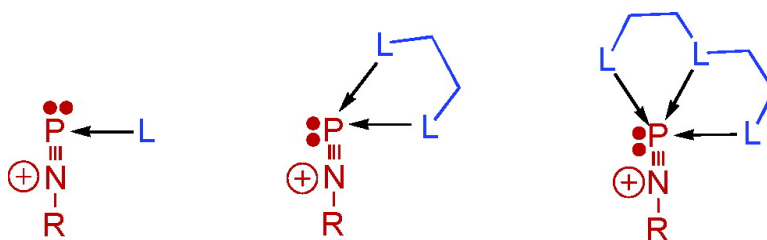


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## Hypervalent, Low-Coordinate Phosphorus(III) Centers in Complexes of the Phosphadiazonium Cation with Chelate Ligands

Neil Burford,<sup>\*†</sup> Andrew D. Phillips,<sup>†</sup> Heather A. Spinney,<sup>†</sup> Michael Lumsden,<sup>†‡</sup> Ulrike Werner-Zwanziger,<sup>†‡</sup> Michael J. Ferguson,<sup>§</sup> and Robert McDonald<sup>§</sup>

Contribution from the Department of Chemistry and Atlantic Region Magnetic Resonance Centre, Dalhousie University, Halifax, Nova Scotia B3H 4J3, Canada, and X-ray Crystallography Laboratory, Department of Chemistry, University of Alberta, Edmonton, Alberta T6G 2G2, Canada

Received October 17, 2004; E-mail: neil.burford@dal.ca

**Abstract:** Trifluoromethylsulfonyloxy-(2,4,6-tri-*tert*-butylphenylimino)phosphine, Mes\*NPOTf (Mes\* = 2,4,6-tri-*tert*-butylphenyl, OTf = trifluoromethanesulfonate, triflate) reacts quantitatively with the multifunctional ligands 2,2'-bipyridine (2,2'-BIPY), *N,N,N',N'*-tetramethylethylenediamine (TMEDA), 1,2-bis(diethylphosphino)ethane (DEPE), 1,2-bis(diphenylphosphino)ethane (DIPHOS), and *N,N,N',N'*-pentamethyldiethylenetriamine (PMDETA) to give the Lewis acid–base complexes [Mes\*NP(2,2'-BIPY)][OTf], [Mes\*NP(TMEDA)][OTf], [Mes\*NP(DIPHOS)][OTf], [Mes\*NP(DEPE)][OTf], and [Mes\*NP(PMDETA)][OTf], respectively. Single-crystal X-ray diffraction studies indicate that the closest contact of the ligand donor atoms occurs at phosphorus in all cases, affecting significant displacement of the OTf anion. The resulting cations [Mes\*NP(L)]<sup>+</sup> are best described as complexes of a neutral chelating ligand on a phosphadiazonium Lewis acceptor, and highlight the potential for electron-rich centers to behave as Lewis acids despite the presence of a lone pair of electrons at the acceptor site. More importantly, the new complexes represent rare examples of systems containing hypervalent, low-coordinate phosphorus(III) centers.

### Introduction

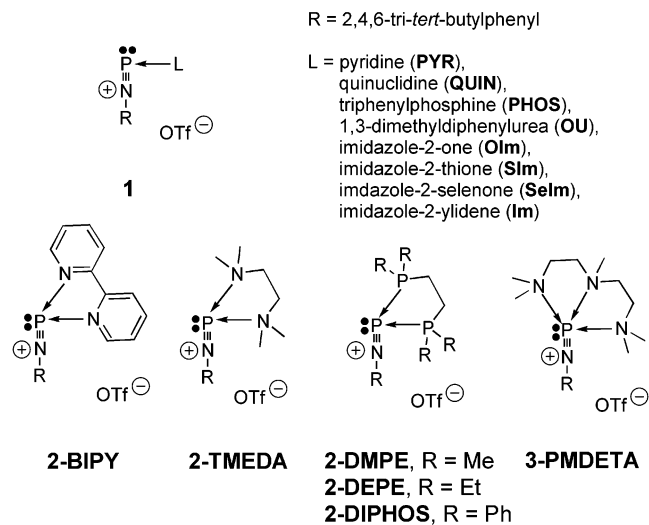
Compounds containing electron-rich (lone pair bearing) phosphorus(III) centers typically behave as ligands or Lewis bases in coordination chemistry. Nevertheless, a variety of complexes involving Lewis acceptor phosphorus(III) centers are known,<sup>1</sup> and the formation of an E → P(III) coordinate bond (E = C,<sup>2–4</sup> N,<sup>5–11</sup> O, S, Se,<sup>12</sup> P,<sup>13–32</sup> Ga<sup>33</sup>) represents a new

synthetic approach in phosphorus chemistry. The iminophosphine Mes\*NPOTf (Mes\* = 2,4,6-tri-*tert*-butylphenyl, OTf = trifluoromethanesulfonate, triflate)<sup>34</sup> is a particularly versatile

- <sup>†</sup> Department of Chemistry, Dalhousie University.  
<sup>‡</sup> Atlantic Region Magnetic Resonance Centre, Dalhousie University.  
<sup>§</sup> University of Alberta.
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reagent that engages ligands with consequential dissociation of the triflate anion. Nevertheless, coordination complexes of the phosphadiazonium cation acceptor all involve a single ligand **1**,<sup>3,10,12,21</sup> consistent with 1:1 adducts that are typical for Lewis acids of the lighter p-Block elements (e.g., H<sub>3</sub>B-NR<sub>3</sub>). This contrast with transition metal coordination chemistry that typically involves multiple donors (ML<sub>n</sub>, n = 1–6) is circumvented with the use of bifunctional and trifunctional ligands enabling the isolation and characterization of chelate complexes **2** and **3**, respectively. Retention of N–P multiple bonding in these complexes, together with a lone pair of electrons and ligand interactions, imposes new hypervalent bonding environments for phosphorus.



## Experimental Procedures

Preparation of Mes<sup>\*</sup>NPOTf and **2-BIPY** was performed in evacuated (10<sup>−3</sup> Torr) reactors,<sup>35</sup> and all glassware was flame-dried under a dynamic vacuum prior to use. The remaining reactions were performed in 20-mL glass vials (sealed with Teflon caps) in a glovebox with a nitrogen atmosphere (O<sub>2</sub>, H<sub>2</sub>O < 0.1 ppm). Solvents and liquid reagents were transferred by reduced pressure distillation or using a syringe.

Solvents were dried and degassed using three freeze–pump–thaw cycles prior to use. Benzene, toluene, *n*-hexane, and *n*-pentane were dried at reflux over potassium. Dichloromethane was first set to reflux over calcium hydride, then over phosphorus pentoxide, and again over calcium hydride. *d*<sub>2</sub>-Dichloromethane was dried over calcium hydride. 2,2′-Bipyridine (2,2′-BIPY), *N,N,N′,N′*-tetramethylethylenediamine (TMEDA), and *N,N,N′,N′,N′*-pentamethyldiethylenetriamine (PMDETA) were obtained from Aldrich Chemical Co., and used as received unless otherwise stated. 1,2-Bis(diphenylphosphino)ethane (DIPHOS), 1,2-bis(diethylphosphino)ethane (DEPE), and 1,2-bis(dimethylphosphino)ethane (DMPE) were obtained from Strem Chemical Co. and used as received. Phosphorus trichloride was distilled prior to use. Triethylamine was purified by fractional distillation from potassium hydroxide and then calcium hydride. TMEDA was stirred over potassium hydroxide and then distilled prior to use. Mes<sup>\*</sup>NPOTf was synthesized according to a previously reported procedure.<sup>34</sup>

NMR data were collected at 298 K on Bruker AC-250 and Bruker Avance 500 NMR spectrometers. Chemical shifts are reported in ppm

relative to external references, SiMe<sub>4</sub> for <sup>1</sup>H and <sup>13</sup>C, 10% CCl<sub>3</sub>F for <sup>19</sup>F, and 85% H<sub>3</sub>PO<sub>4</sub> for <sup>31</sup>P. For <sup>1</sup>H and <sup>13</sup>C spectra, the solvent signal was used as a secondary reference (<sup>1</sup>H: CHDCl<sub>2</sub>, 5.32 ppm; <sup>13</sup>C: CD<sub>2</sub>-Cl<sub>2</sub>, 54.00 ppm). NMR spectra were obtained within 1 day of sample preparation.

Solid-state <sup>31</sup>P NMR spectra were obtained for ground crystalline solids. The samples were packed in zirconium oxide rotors fitted with Kel-F caps (4 mm o.d.). Chemical shifts are reported in ppm and are referenced to external 85% aqueous H<sub>3</sub>PO<sub>4</sub> by setting the isotropic peak of external solid [NH<sub>4</sub>][H<sub>2</sub>PO<sub>4</sub>] to 0.81 ppm. Solid-state <sup>31</sup>P NMR spectra were obtained with a 4-mm Bruker double-resonance MAS probe using a combination of cross-polarization, magic-angle spinning, and high-power <sup>1</sup>H decoupling (**2-BIPY**, **2-DIPHOS**) on a Bruker AMX 400 MHz spectrometer. All other solid-state <sup>31</sup>P NMR spectra were obtained with a similar probe using direct excitation with proton decoupling under magic-angle spinning on a Bruker Avance 400 MHz spectrometer. Data were typically collected over a period of 128 scans, with a contact time of 5 ms and spinning speeds of 10–12 kHz. Spectra were acquired at different spinning speeds to distinguish the spinning sidebands from the centerband and determine the isotropic chemical shift.

Infrared spectra were collected on samples prepared as Nujol mulls on CsI plates using Nicolet 510P FT-IR or Bruker Vector FT-IR spectrometers. Raman spectra were collected on powdered samples, sealed in glass capillaries under dry nitrogen, using a Bruker RFS 100 FT-Raman spectrometer. Vibrational spectra are reported in wavenumbers (cm<sup>−1</sup>) followed by ranked intensities in parentheses, where a value of one corresponds to the most intense peak in the spectrum. Melting points were obtained on samples sealed in glass capillaries under dry nitrogen using an electrothermal apparatus. Chemical analyses were performed by Beller Laboratories, Göttingen, Germany, or by Desert Analytics, Tucson, Arizona.

Single-crystal X-ray diffraction data were collected using Siemens/Bruker PLATFORM diffractometers fitted with Bruker SMART CCD detectors. All measurements were made with graphite monochromated Mo–Kα radiation at 193(2) K. The data were corrected for Lorentz and polarization effects. Absorption corrections were also applied to each structure. Decay corrections were not necessary. The structures were solved by direct methods and expanded using Fourier techniques. Full matrix least squares refinement was carried out on F<sup>2</sup> data using the program *SHELXL97*.<sup>36</sup> Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in geometrically calculated positions but were not refined. In the case of **3-PMDETA**, the data were corrected for electron density due to disordered solvent molecules through the use of the *SQUEEZE*<sup>37</sup> procedure as implemented in *PLATON*.<sup>38</sup> A total solvent-accessible void volume of 230.3 Å<sup>3</sup> with a total electron count of 62 (consistent with one molecule of solvent Et<sub>2</sub>O) was found in the unit cell. Refinement details are summarized in Table 1, and important geometrical parameters are listed in Table 2.

**Isolation Procedures and Characterization Data. 2-BIPY.** A solution of 2,2′-bipyridine (0.084 g, 0.54 mmol) in benzene (15 mL) was added to a stirred solution of Mes<sup>\*</sup>NPOTf (0.25 g, 0.57 mmol) in benzene (25 mL) over a period of 5 min to give a red-orange solution and a dark orange solid. The reaction mixture was stirred for 1 h, the solution was decanted, and the solid was washed 3 times with 5-mL portions of *n*-hexane, yield 0.29 g, 0.48 mmol, 84%; mp 201°C; irreproducible elemental analysis determinations are likely due to incomplete release or removal of CH<sub>2</sub>Cl<sub>2</sub> solvate from the solid; IR: 1602(14), 1491(8), 1446(5), 1392(18), 1364(15), 1314(16), 1280(2), 1275(3), 1256(4), 1226(11), 1200(22), 1160(7), 1151(9), 1055(23),

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**Table 1.** Crystal Data for 2-BIPY, 2-TMEDA, 2-DIPHOS, and 3-PMDETA

compound label	2-BIPY·CH <sub>2</sub> Cl <sub>2</sub> <sup>a</sup>	2-TMEDA	2-DIPHOS·C <sub>6</sub> H <sub>6</sub>	3-PMDETA·C <sub>7</sub> H <sub>8</sub> (C <sub>4</sub> H <sub>10</sub> O) <sub>0.5</sub>
formula	C <sub>30</sub> H <sub>39</sub> N <sub>3</sub> O <sub>3</sub> F <sub>3</sub> PSCl <sub>2</sub>	C <sub>25</sub> H <sub>45</sub> N <sub>3</sub> O <sub>3</sub> F <sub>3</sub> PS	C <sub>51</sub> H <sub>59</sub> NO <sub>3</sub> F <sub>3</sub> P <sub>3</sub> S	C <sub>37</sub> H <sub>65</sub> N <sub>4</sub> O <sub>3.5</sub> F <sub>3</sub> P <sub>5</sub>
molecular weight (g/mol)	680.57	555.67	915.96	741.96
crystal system	monoclinic	monoclinic	monoclinic	triclinic
space group	<i>P</i> 2 <sub>1</sub> / <i>a</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> $\bar{1}$
color	red	colorless	orange	colorless
<i>a</i> /Å	18.4174(9)	19.2943(16)	17.4920(8)	10.0330(5)
<i>b</i> /Å	10.9488(6)	10.5163(9)	14.7170(7)	12.5898(6)
<i>c</i> /Å	19.2129(10)	15.1501(13)	19.1407(9)	18.1171(9)
$\alpha$ /deg	90	90	90	106.4874(8)
$\beta$ /deg	116.924(1)	104.1370(16)	101.3930(10)	100.8079(8)
$\gamma$ /deg	90	90	90	98.1714(8)
<i>V</i> /Å <sup>3</sup>	3454.3(3)	2980.9(4)	4830.3(4)	2108.54(18)
<i>Z</i>	4	4	4	2
<i>R</i> <sup>a</sup> ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	0.1000	0.0725	0.0548	0.0667
<i>wR</i> <sub>2</sub> <sup>b</sup> (all data)	0.2621	0.1929	0.1369	0.2003
GOF <sup>c</sup> (all data)	1.173	1.044	1.038	1.091
$\Delta\rho$ max and min /e Å <sup>-3</sup>	+0.93, -0.72	+1.10, -0.83	+0.63, -0.38	+0.84, -0.54

<sup>a</sup>  $R = (\sum |F_o| - |F_c|) / (\sum |F_o|)$ . <sup>b</sup>  $wR_2 = [(\sum w(F_o^2 - F_c^2)^2) / (\sum w(F_o^2)^2)]^{1/2}$ . <sup>c</sup> GOF =  $[(\sum w(F_o^2 - F_c^2)) / (n - p)]^{1/2}$ , where *n* = number of reflections, and *p* = number of parameters.

**Table 2.** Selected Bond Lengths (Å), Angles (deg), and <sup>31</sup>P NMR Chemical Shifts (ppm) for Mes\*NPOTf and Derivatives of 1, 2, and 3, Involving the Ligands Listed<sup>a</sup>

compound	$\delta^{31}\text{P}$ (solution)	$\delta^{31}\text{P}_{\text{so}}$ (solid state)	(Mes*)N–P	(L) L–P	P–O	(Mes*)C–N–P	(L) L–P–L	ref
Mes*NPOTf	52	49	1.467(4)	–	1.923(3)	176.4(3)	–	34
1-PYR	71	65	1.472(8)	(N) 1.958(8)	2.712(7)	161.7(7)	–	10
1-QUIN	144	<i>b</i>	1.519(2)	(N) 1.933(2)	2.697(3)	143.9(2)	–	10
1-PHOS	–5, 52 <sup>c</sup>	–1, 71	1.486(4)	(P) 2.625(2)	2.298(4)	169.5(4)	–	21
1-OU	62	73	1.486(2)	(O) 1.790(2)	2.942(2)	166.2(2)	–	12
1-OIm	77	<i>b</i>	1.494(3)	(O) 1.773(3)	2.774(4)	159.7(3)	–	12
1-SIm	156	165	1.498(2)	(S) 2.266(1)	> 3.4	174.4(2)	–	12
1-SeIm	182	195	1.500(2)	(Se) 2.4068(9)	> 3.4	175.5(2)	–	12
1-Im	339	366	1.574(4)	(C) 1.852(5)	2.951(5)	116.2(3)	–	3
2-BIPY	54	67	1.497(4)	(N2) 2.066(4) (N3) 2.065(4)	> 3.4	169.4(4)	(N) 75.10(17)	this work <sup>9</sup>
2-TMEDA	110	146	1.510(2)	(N2) 2.090(2) (N3) 2.154(3)	> 3.4	154.4(2)	(N) 81.99(11)	this work
2-DIPHOS	10, 48 <sup>d</sup> 10, 10, 36 <sup>e</sup>	–17, 12, 35	1.489(2)	(P2) 2.5392(9) (P3) 2.5708(9)	3.299(2)	179.3(2)	(P) 75.62(3)	this work
2-DMPE	16, 16, 62	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	this work
2-DEPE	27, 27, 53	32, 32, 49	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	this work
3-PMDETA	89	93, 103	1.495(2)	(N2) 2.263(2) (N3) 2.436(2) (N4) 2.524(2)	> 3.4	164.4(2)	N2–P–N3, 77.71(8) N3–P–N4, 78.00(9) N2–P–N4, 151.82(8)	this work

<sup>a</sup> Pyridine (PYR), quinuclidine (QUIN), triphenylphosphine (PHOS), 1,3-dimethyldiphenylurea (OU), 1,3-diisopropyl-4,5-dimethylimidazol-2-one (OIm), 1,3-diisopropyl-4,5-dimethylimidazol-2-thione (SIm), 1,3-diisopropyl-4,5-dimethylimidazol-2-selenone (SeIm), 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (Im), 2,2'-bipyridine (BIPY), *N,N,N',N'*-tetramethylethylenediamine (TMEDA), 1,2-bis(diphenylphosphino)ethane (DIPHOS), and *N,N,N',N',N''*-penta-methyldiethylenetriamine (PMDETA). <sup>b</sup> Not determined. <sup>c</sup> Dissociated in solution. <sup>d</sup> 298 K, temperature dependence. <sup>e</sup> 193 K.

1032(1), 1014(10), 880(21), 778(12), 768(17), 755(20), 651(13), 639-(6), 518(19); NMR (C<sub>6</sub>D<sub>6</sub>): <sup>1</sup>H 1.3 (s, 9H), 1.31 (s, 18H), 7.3 (d, 2H, <sup>5</sup>*J*<sub>PH</sub> = 2 Hz), 8.0 (m, 2H), 8.5 (m, 2H), 8.8 (br d, 2H, <sup>3</sup>*J*<sub>HH</sub> = 8 Hz) 9.0 (m, 2H); <sup>13</sup>C{<sup>1</sup>H} 30 (s), 31 (s), 35 (s), 36 (s), 121 (q, <sup>1</sup>*J*<sub>FC</sub> = 320 Hz), 122 (s), 123 (s), 124 (s), 129 (s), 134 (d, <sup>2</sup>*J*<sub>FC</sub> = 47 Hz), 144.6 (s), 145.2 (s) 146 (d, <sup>3</sup>*J*<sub>FC</sub> = 14 Hz), 149 (d, <sup>3</sup>*J*<sub>FC</sub> = 4 Hz); <sup>19</sup>F{<sup>1</sup>H} –79 (s); <sup>31</sup>P{<sup>1</sup>H} 54 (s); CP-MAS <sup>31</sup>P{<sup>1</sup>H} 67 (s); crystals suitable for X-ray diffraction were obtained by liquid–liquid diffusion<sup>12</sup> using dichloromethane and *n*-hexane and were spectroscopically identical to the powder.

**2-TMEDA.** A mixture of Mes\*NPOTf (0.050 g, 0.11 mmol) and TMEDA (17  $\mu$ L, 0.11 mmol) in toluene (1.5 mL) gave a yellow solution. After the sample was stirred for 10 min at RT, the solution was stored at –35 °C for 3 days giving pale yellow, needlelike crystals, which were washed with 1 mL of *n*-hexane and characterized as C<sub>25</sub>H<sub>45</sub>N<sub>3</sub>O<sub>3</sub>F<sub>3</sub>PS, 555.69 g/mol, yield 0.040 g, 0.07 mmol, 64%; d. p. 120–122°C; slow (days) decomposition at RT to a bright orange solid (<sup>31</sup>P{<sup>1</sup>H} 137 ppm) precluded determination of reliable and reproducible

elemental analyses; IR: 1603(18), 1361(7), 1263(1), 1224(6), 1158-(5), 1143(4), 1101(15), 1030(2), 1004(12), 943(9), 929(16), 880(13), 774(8), 752(11), 637(3), 571(17), 517(10), 488(14); Raman: 2962(1), 2926(3), 1604(5), 1456(4), 1428(2), 1392(6), 1377(7), 1292(8), 1193-(10), 1029(9); NMR (CD<sub>2</sub>Cl<sub>2</sub>): <sup>1</sup>H 1.3 (s, 9H), 1.5 (s, 18H), 2.8 (s, 12H), 3.3 (s, 4H), 7.4 (s, 2H); <sup>13</sup>C{<sup>1</sup>H} 31 (s), 32 (s), 35 (s), 37 (s), 46 (d, <sup>2</sup>*J*<sub>FC</sub> = 12 Hz), 58 (s), 121 (q, <sup>1</sup>*J*<sub>FC</sub> = 321 Hz), 123 (s), 135 (d, <sup>2</sup>*J*<sub>FC</sub> = 39 Hz), 144 (d, <sup>3</sup>*J*<sub>FC</sub> = 10 Hz), 148 (s); <sup>19</sup>F{<sup>1</sup>H} –80(s); <sup>31</sup>P{<sup>1</sup>H} 107(s); MAS <sup>31</sup>P{<sup>1</sup>H} 146 (s).

**2-DIPHOS.** Mes\*NPOTf (0.050 g, 0.11 mmol) and DIPHOS (0.045 g, 0.11 mmol) in benzene (3 mL) gave an orange solution. After the sample was stirred for 30 min at RT, a 5-mL vial containing pentane (3 mL) was placed inside the larger vial, which was then capped. After 2 days at RT, large orange, blocklike crystals were isolated by decantation, washed with 0.5 mL of benzene, and characterized as C<sub>45</sub>H<sub>53</sub>NO<sub>3</sub>F<sub>3</sub>P<sub>3</sub>S, 837.91 g/mol, yield 0.046 g, 0.05 mmol, 48%; mp 100–101 °C; anal. calcd. % (found): C 64.5 (64.8), H 6.4 (6.1), N 1.7 (1.7); IR: 3056(14), 1598(24), 1418(13), 1362(9), 1310(18), 1255(1),

1222(6), 1153(3), 1101(10), 1072(16), 1027(2), 998(12), 926(23), 879-(15), 747(7), 695(8), 684(5), 660(22), 636(4), 615(19), 571(20), 518-(11), 509(17), 468(21); Raman: 3061(3), 2948(6), 2907(7), 1599(4), 1584(2), 1496(1), 1096(8), 1027(9), 999(5); NMR (CD<sub>2</sub>Cl<sub>2</sub>): <sup>1</sup>H 1.1 (s, 18H), 1.3 (s, 9H), 3.1 (d, <sup>2</sup>J<sub>PH</sub> = 1 Hz, 4H) 7.2 (s, 2H), 7.3–7.6 (m, 20H); <sup>13</sup>C{<sup>1</sup>H} 24 (s), 31 (s), 32 (s), 35.5 (s), 36.4 (s), 122 (q, <sup>1</sup>J<sub>FC</sub> = 321 Hz), 123 (s), 128 (s), 129 (s), 130 (s), 132.7 (s), 133.1 (s), 136 (d, <sup>1</sup>J<sub>PC</sub> = 197 Hz), 145 (s), 148 (s); <sup>19</sup>F{<sup>1</sup>H} –80(s); <sup>31</sup>P{<sup>1</sup>H}(RT) 10 (broad s), 47 (broad s); <sup>31</sup>P{<sup>1</sup>H}(193 K) 10.2 (d, <sup>1</sup>J<sub>PP</sub> = 492 Hz), 10.3 (d, <sup>1</sup>J<sub>PP</sub> = 419 Hz), 36 (dd, <sup>1</sup>J<sub>PP</sub> = 419 Hz, <sup>1</sup>J<sub>PP</sub> = 492 Hz); <sup>31</sup>P{<sup>1</sup>H} simulation (gNMR version 4.0): 10.77 (d, <sup>1</sup>J<sub>PP</sub> = 410 Hz), 10.84 (d, <sup>1</sup>J<sub>PP</sub> = 474 Hz), 40 (dd, <sup>1</sup>J<sub>PP</sub> = 410 Hz, <sup>1</sup>J<sub>PP</sub> = 474 Hz); CP-MAS <sup>31</sup>P{<sup>1</sup>H} –17 (d, <sup>1</sup>J<sub>PP</sub> = 469 Hz), 12 (d, <sup>1</sup>J<sub>PP</sub> = 360 Hz), 35 (unresolved multiplet); slow (days) reaction with solvent at RT evidenced by the appearance of new signals in the <sup>31</sup>P NMR spectra.

**2-DEPE.** A mixture of Mes\*NPOTf (0.100 g, 0.23 mmol) and DEPE (53 μL, 0.23 mmol) in benzene (3 mL) gave a red-orange solution. After the sample was stirred for 30 min at RT, *n*-hexane (15 mL) was added to the solution, and fine, yellow, needlelike crystals formed over a period of 2 h and were isolated by decantation, washed with 1.5 mL of *n*-hexane, and characterized as C<sub>29</sub>H<sub>53</sub>NO<sub>3</sub>F<sub>3</sub>P<sub>3</sub>S, 645.73 g/mol, yield 0.121 g, 0.19 mmol, 82%; d. p. 97–131 °C; anal. calcd. % (found): C 53.9 (53.8), H 8.3 (7.9), N 2.2 (2.1); IR: 1411(8), 1367(7), 1274(3), 1259(1), 1222(6), 1151(5), 1102(15), 1031(2), 982(16), 878(11), 805-(17), 780(12), 761(10), 735(9), 639(4), 571(14), 517(13); Raman: 2951-(3), 2914(2), 1597(4), 1446(1), 1396(5), 1292(7), 1031(6); NMR (CD<sub>2</sub>Cl<sub>2</sub>): <sup>1</sup>H 1.23 (m, 12H), 1.27 (s, 9H), 1.4 (s, 18H), 2.1 (m, 8H), 2.5 (d, <sup>2</sup>J<sub>PH</sub> = 8 Hz, 4H), 7.3 (d, <sup>5</sup>J<sub>PH</sub> = 2 Hz, 2H); <sup>13</sup>C{<sup>1</sup>H} 8 (s), 16 (s), 19 (t, <sup>1</sup>J<sub>PC</sub> = 9 Hz), 31 (s), 32 (s), 35 (s), 37 (s), 122 (q, <sup>1</sup>J<sub>FC</sub> = 321 Hz), 123 (s), 138 (d, <sup>2</sup>J<sub>PC</sub> = 41 Hz), 142 (d, <sup>3</sup>J<sub>PC</sub> = 15 Hz), 145 (s); <sup>19</sup>F{<sup>1</sup>H} –80 (s); <sup>31</sup>P{<sup>1</sup>H} 27.0 (d, <sup>1</sup>J<sub>PP</sub> = 575 Hz), 27.2 (d, <sup>1</sup>J<sub>PP</sub> = 471 Hz), 53 (dd, <sup>1</sup>J<sub>PP</sub> = 471 Hz, <sup>1</sup>J<sub>PP</sub> = 575 Hz); MAS <sup>31</sup>P{<sup>1</sup>H} 32 (d, <sup>1</sup>J<sub>PP</sub> = 599 Hz), 32 (unresolved multiplet under the doublet), 49 (d, <sup>1</sup>J<sub>PP</sub> = 477 Hz); slow (days) reaction with solvent at RT evidenced by the appearance of new signals in the <sup>31</sup>P NMR spectra.

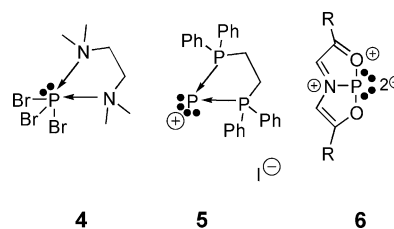
**2-DMPE.** A mixture of Mes\*NPOTf (0.050 g, 0.11 mmol) and DMPE (19 μL, 0.11 mmol) in benzene (3 mL) gave a red solution, which was stirred for 30 min at RT; NMR <sup>31</sup>P{<sup>1</sup>H} 16.2 (d, <sup>1</sup>J<sub>PP</sub> = 545 Hz), 16.3 (d, <sup>1</sup>J<sub>PP</sub> = 490 Hz), 62 (dd, <sup>1</sup>J<sub>PP</sub> = 490 Hz, <sup>1</sup>J<sub>PP</sub> = 545 Hz) assigned to **2-DMPE**, along with several other phosphorus-containing products that have not been identified.

**3-PMDETA.** A mixture of Mes\*NPOTf (0.100 g, 0.23 mmol) and PMDETA (48 μL, 0.23 mmol) in *n*-hexane (5 mL) gave a yellow solution and an off-white solid, which were separated by decantation, and the powder was washed with 2 × 4 mL portions of *n*-hexane and characterized as C<sub>28</sub>H<sub>52</sub>N<sub>4</sub>O<sub>3</sub>F<sub>3</sub>PS, 612.78 g/mol, yield 0.116 g, 0.19 mmol, 82%; d. p. 116 °C; slow (days) decomposition at RT to a bright yellow solid (<sup>31</sup>P{<sup>1</sup>H} 137 ppm) precluded determination of reliable and reproducible elemental analyses; IR: 1602(20), 1488(3), 1422(9), 1363(8), 1273(1), 1265(2), 1226(7), 1156(5), 1099(13), 1076(21), 1031-(4), 968(12), 943(15), 929(14), 891(18), 878(19), 785(11), 764(10), 748(16), 638(6), 573(22), 518(17), 279(23); Raman: 3090(8), 2962-(2), 2926(3), 2892(4), 2875(5), 2796(10), 2773(11), 1602(6), 1485(1), 1361(7), 1291(9), 1031(9), 350(12); NMR: <sup>1</sup>H 1.3 (s, 9H), 1.5 (s, 18H), 2.4 (s, 12H), 2.6–2.8 (m, 4H), 2.8 (d, <sup>3</sup>J<sub>PH</sub> = 2.5 Hz, 3H), 3.0–3.2 (m, 4H), 7.3 (d, <sup>5</sup>J<sub>PH</sub> = 1 Hz, 2H); <sup>13</sup>C{<sup>1</sup>H} 31 (s), 32 (s), 35 (s), 37 (s), 44 (s), 46 (s), 57.0 (s), 57.2 (s), 122 (q, <sup>1</sup>J<sub>FC</sub> = 321 Hz), 123 (s), 135 (d, <sup>2</sup>J<sub>PC</sub> = 46 Hz), 142 (d, <sup>3</sup>J<sub>PC</sub> = 12 Hz), 147 (s); <sup>19</sup>F{<sup>1</sup>H} –80 (s); <sup>31</sup>P{<sup>1</sup>H} 89(s); MAS <sup>31</sup>P{<sup>1</sup>H} 93 (s), 103 (s). Crystals suitable for X-ray diffraction were obtained by dissolving 70 mg in a 50/50 mixture of ether and toluene (4 mL) and placing the solution in a freezer at –35 °C for one week and were spectroscopically identical to the powder.

## Results and Discussion

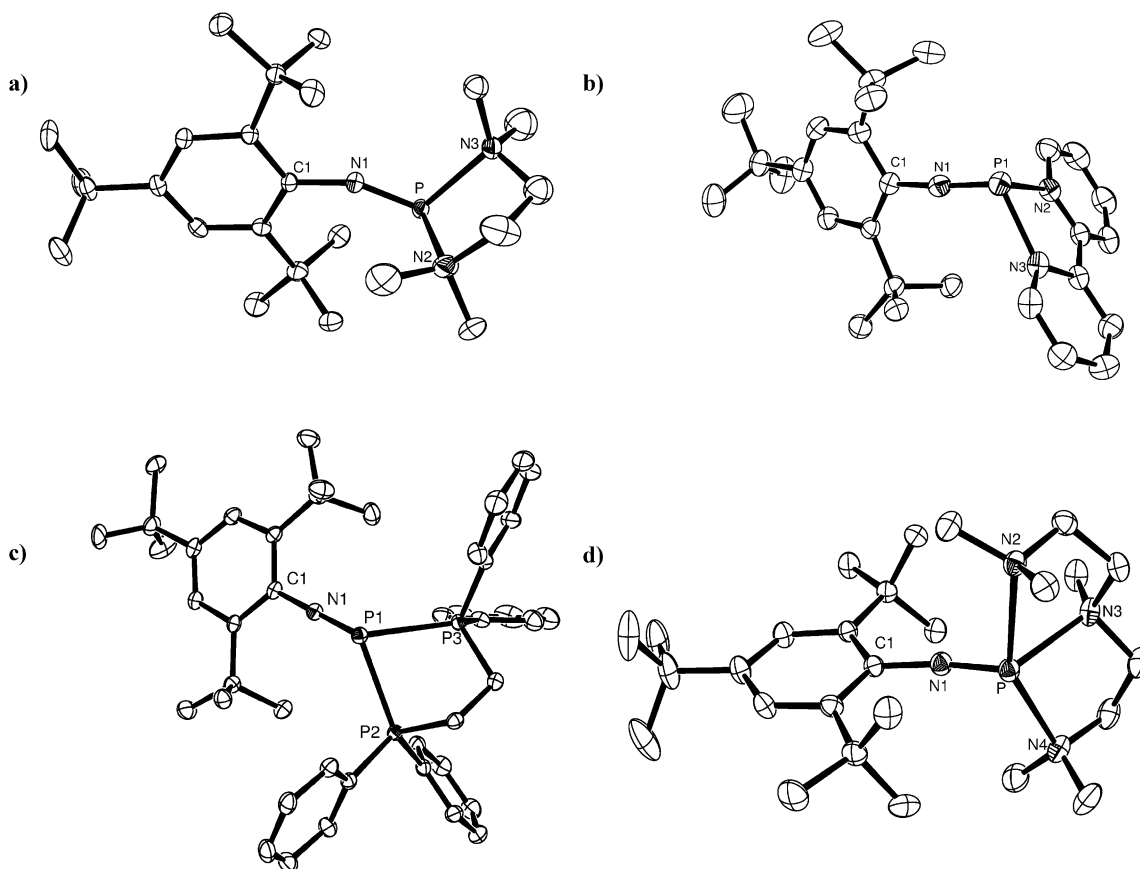
Mes\*NPOTf reacts rapidly at room temperature with the bifunctional ligands 2,2'-BIPY, TMEDA, DMPE, DEPE, and DIPHOS, and the trifunctional ligand PMDETA. The adducts, **2-BIPY**, **2-TMEDA**, **2-DIPHOS**, **2-DEPE**, and **3-PMDETA** have been isolated, independent of the imposed reaction stoichiometry, and **2-DMPE** has been identified by <sup>31</sup>P NMR spectroscopy. Although crystalline yields of the complexes are modest, <sup>31</sup>P NMR spectra of reaction mixtures confirm essentially quantitative reactions (>90%). Crystallographic data for **2-BIPY**, **2-TMEDA**, **2-DIPHOS**, and **3-PMDETA** are listed in Table 1, and a structural view of each cation is presented in Figure 1. Selected structural parameters and <sup>31</sup>P NMR chemical shifts are presented in Table 2 together with corresponding parameters for Mes\*NPOTf and related complexes of type **1**.

In each complex, donor sites of the ligand interact primarily with the phosphorus acceptor site, effecting displacement of the triflate anion from Mes\*NPOTf. As for complexes involving a single donor site (complexes of type **1**),<sup>3,10,12,21</sup> the shortest P–O(OTf) contacts in derivatives of **2** and **3** are greater than the P–O distance in Mes\*NPOTf [1.923(3) Å],<sup>34</sup> and some derivatives can be designated as ionic. Consequently, the compounds represent bidentate chelate complexes (**2-BIPY**, **2-TMEDA**, and **2-DIPHOS**) and a tridentate complex (**3-PMDETA**) of the phosphadiazonium cation.<sup>39</sup>

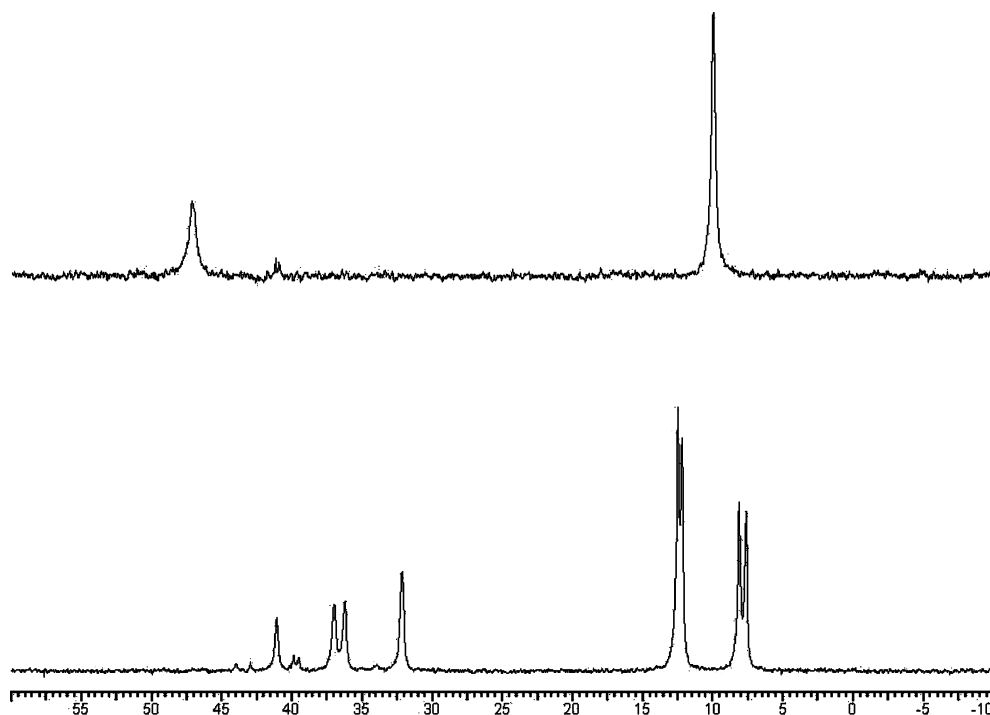


A symmetric bidentate coordinate interaction is observed in the solid-state structure of **2-BIPY** [N → P = 2.065(4) Å, 2.066(4) Å]. However, **2-TMEDA** [N → P = 2.090(2) Å, 2.154(3) Å] and **2-DIPHOS** [P → P = 2.5392(9) Å, 2.5708(9) Å] exhibit nonsymmetric chelation of the phosphadiazonium cation, analogous to complexes **4** [N → P = 2.025(3) Å, 1.939(1) Å (isomer 1); 2.239(5) Å, 1.918(5) Å (isomer 2)]<sup>8</sup> and **5** [P → P = 2.131-(2) Å, 2.126(2) Å].<sup>28</sup> The nonsymmetric interaction of diphosphinoethane ligands with Mes\*NP<sup>+</sup> is evidenced in the 298 K solution <sup>31</sup>P NMR spectra of complexes **2-DMPE** and **2-DEPE**, which exhibit an 8-line pattern. The signal corresponding to the phosphadiazonium center is a doublet of doublets due to nonequivalent coupling to the two donor phosphine centers. The donor phosphorus nuclei have slightly different chemical shifts but are not coupled to each other, so that the AMX spin system involves J<sub>MX</sub> = 0. Two broad peaks are observed in the solution <sup>31</sup>P NMR spectra of **2-DIPHOS** at 298 K, which resolve into an analogous 8-line pattern at 193 K (Figure 2). The solid-state <sup>31</sup>P CP-MAS NMR spectrum of **2-DIPHOS** provides coupling constants [<sup>1</sup>J<sub>(P1,P2)</sub> and <sup>1</sup>J<sub>(P2,P3)</sub>] that are consistent with those observed in solution, but the chemical shifts for the nonequivalent donor centers are more distinct in the solid state (Δδ<sub>(P2,P3)</sub> = 30 ppm) than in solution (Δδ<sub>(P2,P3)</sub> = 0.1 ppm) (Figure 3).

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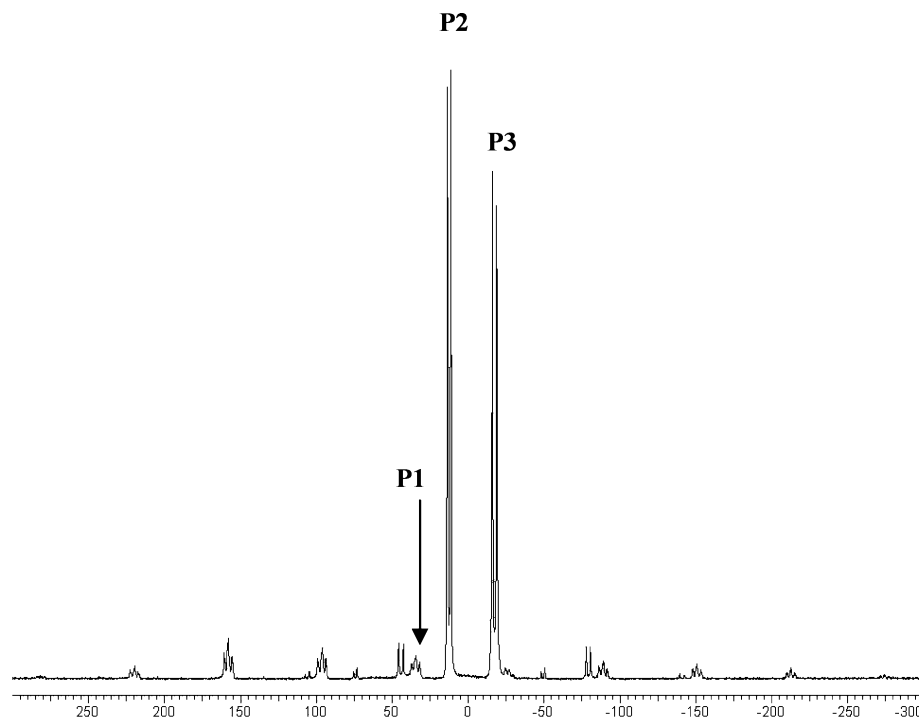
**Figure 1.** Structural views of the cation in the solid state for (a) **2-TMEDA**, (b) **2-BIPY**, (c) **2-DIPHOS**, and (d) **3-PMDETA** drawn with 30% probability displacement ellipsoids. Hydrogen atoms and anions have been omitted. The *p-tert*-butyl group of Mes\* in **2-DIPHOS** and part of the TMEDA ligand in **2-TMEDA** are disordered over two positions (not shown).



**Figure 2.** Solution  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of **2-DIPHOS** at 298 K (top) and at 193 K (bottom).

The central  $\text{N}(3) \rightarrow \text{P}$  coordinate bond [2.263(2) Å] in **3-PMDETA** is slightly shorter than those achieved by the

terminal nitrogen donors of the ligand [ $\text{N}(2) \rightarrow \text{P} = 2.436(2)$  Å;  $\text{N}(4) \rightarrow \text{P} = 2.524(2)$  Å], and together with  $\text{N}(1)$  they impose



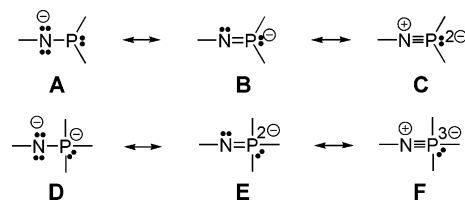
**Figure 3.** Solid-state  $^{31}\text{P}\{^1\text{H}\}$  CP-MAS NMR spectrum of **2-DIPHOS** at 298 K, showing the isotropic chemical shifts of P1 (phosphadiazonium), P2 (donor), and P3 (donor).

a distorted disphenoidal geometry at phosphorus, in which N(2) and N(4) occupy axial positions. The ligand is conformationally similar to those in complexes of  $[\text{AlH}_2^+]$ <sup>40</sup> and  $[\text{AlMe}_2^+]$ ,<sup>41</sup> where the aluminum centers adopt a distorted trigonal bipyramidal geometry with the terminal nitrogen atoms of the ligand occupying the axial sites. In this context, the disphenoidal geometry of the phosphorus center in **3-PMDETA** reveals the stereochemical presence of the lone pair at the acceptor site.

The N  $\rightarrow$  P distances in complexes of type **1**, **2**, and **3** involving nitrogen donors exhibit a predictable trend corresponding to the number of donor sites interacting with phosphorus. The single-donor ligands in **1-PYR** [1.958(8) Å] and **1-QUIN** [1.933(2) Å] engage the phosphorus center more effectively than those in the chelate complexes **2-BIPY** [2.065(4) Å, 2.066(4) Å] and **2-TMEDA** [2.090(2) Å, 2.154(3) Å], and the longest coordinate interactions are observed in **3-PMDETA** [2.263(2) Å, 2.436(2) Å, 2.524(2) Å]. A contrasting trend is observed for the P  $\rightarrow$  P coordinate bonds, with those in **2-DIPHOS** [2.5392(9) Å, 2.5708(9) Å] shorter than that observed in **1-PHOS** [2.625(2) Å],<sup>21</sup> perhaps reflecting the greater basicity of the phosphorus donors in **DIPHOS**. Nevertheless, all of these P  $\rightarrow$  P distances are substantially longer than the narrow range [2.13–2.31 Å] observed in phosphine–phosphenium complexes.<sup>27</sup>

The (Mes\*)N(1)–P(1) bond lengths in derivatives of **2** and **3** are only slightly longer than that in the free acid Mes\*NPOTf, consistent with observations for derivatives of **1**. Moreover, the C(1)–N(1)–P(1) angles are only slightly more acute than the almost linear geometry for nitrogen in Mes\*NPOTf, indicating that interaction of the phosphorus acceptor site with one, two, or three donors effects minimal disruption of the N–P  $\pi$ -bond-

ing in the phosphadiazonium cation. The pyramidal geometry of phosphorus in derivatives of **2** and the disphenoidal geometry of phosphorus in **3-PMDETA** illustrate retention of a nonbonding pair (lone pair) of electrons at phosphorus in these complexes. In this context, we invoke bonding models for **2** and **3** that involve an N–P bond order of two (represented by **B** and **E**) or three (represented by **C** and **F**) and consider the more familiar resonance structures **A** and **D**<sup>42–44</sup> as minor contributors.



Bonding models **B**, **C**, **E**, and **F** impose unusual hypervalent, low-coordinate environments for phosphorus. Prototypical compounds such as  $\text{PF}_5$  and  $\text{PF}_6^-$  represent examples of 10 and 12 valent environments, respectively, with high coordination numbers, and  $\sigma$ -bonded frameworks such as derivatives of 5-aza-2,8-dioxo-1-phosphabicyclo[3.3.0]octa-2,4,6-triene **6<sup>45</sup>** contain a 10 valence electron, tricoordinate phosphorus center.<sup>46</sup> In comparison, derivatives of **2** can be considered as examples of 12-valent, tricoordinate phosphorus centers, and the environment for phosphorus in **3-PMDETA** represents a 14-valent, tetra-coordinate phosphorus center.

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## Conclusion

Mes\*NPOTf reacts with bifunctional or trifunctional ligands to give chelate complexes of the phosphadiazonium cation, containing three- and four-coordinate phosphorus centers, respectively. Solid-state structures and spectroscopic data indicate retention of the (Mes\*)NP  $\pi$ -bonding and the presence of a stereochemically active lone pair at phosphorus, highlighting new hypervalent, low-coordinate P(III) bonding environments.

**Acknowledgment.** We thank the Natural Sciences and Engineering Research Council of Canada, the Killam Foundation of the Canada Council for the Arts, the Canada Research Chairs Program, the Canada Foundation for Innovation, the Nova Scotia Research and Innovation Trust Fund, and the Walter C. Sumner

Foundation for funding, Meaghan N. Grundy for performing preliminary experimental work, the Atlantic Region Magnetic Resonance Centre for use of instrumentation, and Dr. Hilary Jenkins for X-ray data collection (**2-BIPY**).

**Supporting Information Available:** Crystallographic information files (CIF) for **2-TMEDA**, **2-DIPHOS**, and **3-PM-DETA**. This material is available free of charge via the Internet at <http://pubs.acs.org>. Please note that the CIF for **2-BIPY** has already been deposited to the Cambridge structural database (CCDC registry number: 182/1780; CCDC reference code: QOCBOZ).

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