J. Am. Chem. Soc. **2000,** *122,* 5413−5414

Iminophosphide Bonding Environments from Carbene Complexes of Iminophosphines

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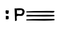
Received February 4, 2000

Stable compounds containing multiple bonding environments highlight important new directions in the diversification of phosphorus chemistry. While numerous examples of compounds containing **1**, **2**, and **3** have been identified,[1] other environments such as **4** have proven elusive. Salts of anions assigned as



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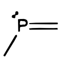

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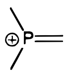

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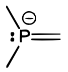

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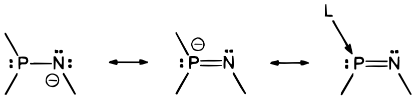
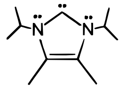


4a **4b** **4c**

iminophosphides **4b**[2] (also referred to as iminophosphoranides)[3] have solid-state structures best described as the corresponding phosphinoamides **4a**,[4] the relative stability of which has been theoretically modeled.[5] We have now exploited the coordination chemistry of unsaturated phosphorus(III) to prepare neutral systems represented by **4c**, involving a pyramidal tricoordinate phosphorus center with a lone pair and a distinctive N═P double bond. The new complexes involve the now routinely available carbenes,[6] which engage in substantially stronger donor−acceptor interactions with phosphorus[6c] than those observed with amines,[7,8] arenes,[9] or phosphines.[7,10]

^{31}P NMR spectroscopic studies of reaction mixtures containing equimolar amounts of imidazol-2-ylidene (carb, **5**) with Mes*NPCl **6a** (136 ppm) or Mes*NPOSO$_2$CF$_3$ **6b** (50 ppm) (Mes* = 2,4,6-tri-*tert*-butylphenyl) show almost quantitative (>85%) formation of the corresponding adducts **7a** (156 ppm) and **7b** (350 ppm), respectively. The complexes have been isolated and comprehensively characterized,[11a,b] and their structures are shown in Figure 1. Structural parameters are presented in Table 1, in comparison with those of the closely related complexes **7c** (^{31}P NMR 71 ppm)[11c] and **7d**,[10c] as well as lithium phosphinoamide derivatives.[4]



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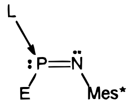

7

a: E = Cl, L = carb, **5**
b: E = OSO$_2$CF$_3$, L = carb, **5**
c: E = OSO$_2$CF$_3$, L = pyr
d: E = OSO$_2$CF$_3$, L = PPh$_3$

The N−P bond lengths for derivatives of **7** are in the range observed for iminophosphine and iminophosphorane derivatives (1.46−1.62 Å),[1d,14] and are substantially shorter than those observed for derivatives of phosphinoamides (1.66−1.67 Å).[4] The

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(1) For example: (a) Dillon, K. B.; Mathey, F.; Nixon, J. F. *Phosphorus: The Carbon Copy; From Organophosphorus to Phospha-organic Chemistry*; John Wiley and Sons: New York, 1998. *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O. J., Eds.; Georg Thieme Verlag: New York, 1990. (b) Cowley, A. H.; Kemp, R. A. *Chem. Rev.* **1985**, *85*, 367−382. (c) Niecke, E.; Gudat, D. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 217−237. (d) Power, P. *Chem. Rev.* **1999**, *99*, 3463−3503. (e) Loss, S.; Widauer, C.; Grützmacher, H. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 3329−3331. (f) Igau, A.; Baceiredo, A.; Grützmacher, H.; Pritzkow, H.; Bertrand, G. *J. Am. Chem. Soc.* **1989**, *111*, 6853−6854.

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(11) Preparative procedures for derivatives of **7:** A benzene solution of the neutral ligand was slowly added to a stirred benzene solution of **6**. After 1 h, the solvent was removed in vacuo giving crystalline material, which was washed with benzene. Samples for X-ray diffraction studies were recrystallized by slow diffusion of hexane into a saturated benzene solution (**7a** and **7b**) or by slow evaporation of a 1:1 CH$_2$Cl$_2$/hexane solution (**7c**). (a) **7a**:**5**, 0.16 g, 0.89 mmol; **6a**, 0.30 g, 0.92 mmol; orange crystals, 0.11 g, 0.22 mmol, 25%; mp 177−178 °C dec. Anal. Calcd: C, 68.82; H, 9.76; N, 8.30. Found: C, 69.08; H, 9.82; N, 8.36. IR (cm^{-1}, rel intensity): 1623m, 1596w, 1415s, 1392s, 1384s, 1361s, 1351m, 1319w, 1286m, 1260s, 1250s, 1240s, 1188m, 1172m, 1138m, 1123m, 1115m, 1084m, 1020m, 977w, 952w, 936w, 922w, 906m, 888w, 877m, 824w, 793m, 783w, 774m, 756m, 708w, 692m, 674w, 656w, 643w, 551w, 514w, 496w, 400m, 363w. ^{1}H and ^{13}C NMR details are consistent with other derivatives of Mes*NP and **7**: ^{31}P NMR (CD$_2$Cl$_2$) 172 ppm ($^{1}J_{PC}$ = 115 Hz); crystal data, C$_{29}$H$_{49}$ClN$_3$P, $M = 506.13$, monoclinic, $P2_1/c$, $a = 21.8062(3)$ Å, $b = 8.5184(1)$ Å, $c = 17.8511(2)$ Å, $\beta = 110.892(1)°$, $V = 3097.90(7)$ Å^3, $T = 213(2)$ K, $Z = 4$, μ(Mo Kα) = 0.195 mm^{-1}, 9422 measured reflections, 4217 independent reflections, 3497 reflections with $I > 2\sigma(I)$, 307 refined parameters, $R[F^2 > 2\sigma(F^2)] = 0.085$, $wR(F^2) = 0.2753$, $S = 1.082$. (b) **7b**:**5**, 0.12 g, 0.67 mmol; **6b**, 0.31 g, 0.70 mmol; purple crystals; 0.16 g, 0.26 mmol, 38%; mp 149−151 °C dec. Anal. Calcd: C, 58.14; H, 7.97; N, 6.78. Found: C, 58.20; H, 7.82; N, 6.85. IR (cm^{-1}, rel. intensity): 1611w, 1596w, 1418m, 1280s, 1246s, 1229s, 1221s, 1159m, 1122s, 1090w, 1026m, 909w, 877w, 795m, 754w, 693w, 549w, 517m, 499w, 452w, 400w, 346w. ^{1}H and ^{13}C NMR details are consistent with other derivatives of Mes*NP and **7**; ^{31}P NMR (CD$_2$Cl$_2$) 339 ppm ($^{1}J_{PC}$ = 132 Hz); ^{19}F NMR (CD$_2$Cl$_2$) −78.6 ppm ($^{1}J_{FC}$ = 321 Hz); crystal data, C$_{30}$H$_{49}$F$_3$N$_3$O$_3$PS, $M = 619.75$, orthorhombic, *Pbca*, $a = 10.6688(2)$ Å, $b = 15.2337(3)$ Å, $c = 42.5078(6)$ Å, $V = 6908.6(2)$ Å^3, $T = 213(2)$ K, $Z = 8$, μ(Mo Kα) = 0.189 mm^{-1}, 23185 measured reflections, 5361 independent reflections, 3752 reflections with $I > 2\sigma(I)$, 370 refined parameters, $R[F^2 > 2\sigma(F^2)] = 0.0892$, $wR(F^2) = 0.1699$, $S = 1.215$. (c) **7c**:pyridine complexes of iminophosphines have been previously mentioned [Blättner, M.; Ruban, A.; Gudat, D.; Nieger, M.; Niecke, E. *Phosphorus, Sulfur Silicon* **1999**, *147*, 31]. Pyridine, 0.13 g, 1.64 mmol; **6b**, 0.30 g, 0.69 mmol; orange-red crystals,0.11 g, 0.22 mmol, 31%; mp 118−120 °C. Anal. Calcd: C, 55.59; H, 6.61; N, 5.40. Found: C, 55.04; H, 6.95; N, 5.42. IR (cm^{-1}, rel. intensity): 1611w, 1597w, 1540w, 1496m, 1481m, 1397w, 1367m, 1362m, 1288s, 1265m, 1234s, 1211w, 1167m, 1161m, 1060m, 1024s, 1008m, 887w, 880w, 771m, 758w, 692w, 651w, 638s, 520w, 429w, 379w. ^{1}H and ^{13}C NMR details are consistent with other derivatives of Mes*NP and pyridine: ^{31}P NMR (CD$_2$Cl$_2$) 71 ppm; ^{19}F NMR (CD$_2$Cl$_2$) −78.9 ppm ($^{1}J_{FC}$ = 320 Hz); crystal data, C$_{24}$H$_{34}$F$_3$N$_2$O$_3$PS, $M = 518.56$, triclinic, $P\bar{1}$, $a = 10.298(3)$ Å, $b = 16.842(4)$ Å, $c = 8.835(2)$ Å, $\alpha = 95.69(2)°$, $\beta = 112.24(2)°$, $\gamma = 80.66(2)°$, $V = 1398.4(6)$ Å^3, $T = 296(2)$ *K*, $Z = 2$, μ(Cu Kα) = 19.72 cm^{-1}, 3143 measured reflections, 2932 independent reflections, 1354 reflections with $I > 3\sigma(I)$, 228 refined parameters, $R = 0.057$, $Rw = 0.060$, $S = 1.95$.

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Table 1. Structural Parameters for Mes*NPCl and Mes*NPOSO$_2$CF$_3$, and Their Complexes with **5**, Pyridine, and Triphenylphosphine (E and D are the donor atoms of the anionic and neutral ligands, respectively) and Lithium Phosphinoamide Derivatives

compd	N−P (Å)	P−E (Å)	P−D (Å)	C−N−P (deg)	ref
Mes*NPCl (**6a**)	1.509(2)	(E = Cl) 2.127(1)		146.4(2)	12
Mes*NP(carb)Cl (**7a**)	1.585(5)	(E = Cl) 2.471(2)	(D = C) 1.886(5)	120.2(4)	this work
Mes*NPOSO$_2$CF$_3$ (**6b**)	1.467(4)	(E = O) 1.923(3)		176.4(3)	13
Mes*NP(PPh$_3$)OSO$_2$CF$_3$ (**7d**)	1.486(4)	(E = O) 2.298(4)	(D = P) 2.625(2)	169.5(4)	10c
Mes*NP(pyr)OSO$_2$CF$_3$ (**7c**)	1.472(8)	(E = O) 2.712(7)	(D = N) 1.958(8)	161.7(7)	this work
Mes*NP(carb)OSO$_2$CF$_3$ (**7b**)	1.574(4)	(E = O) 2.951(5)	(D = C) 1.852(5)	116.2(3)	this work
[Li(RNPPh$_2$)(OEt$_2$)]$_2$ (R = Ph, Np, ^{i}Pr, Mes*)	1.659(4)−1.672(2)			116.3(2)−121.7(1)	4

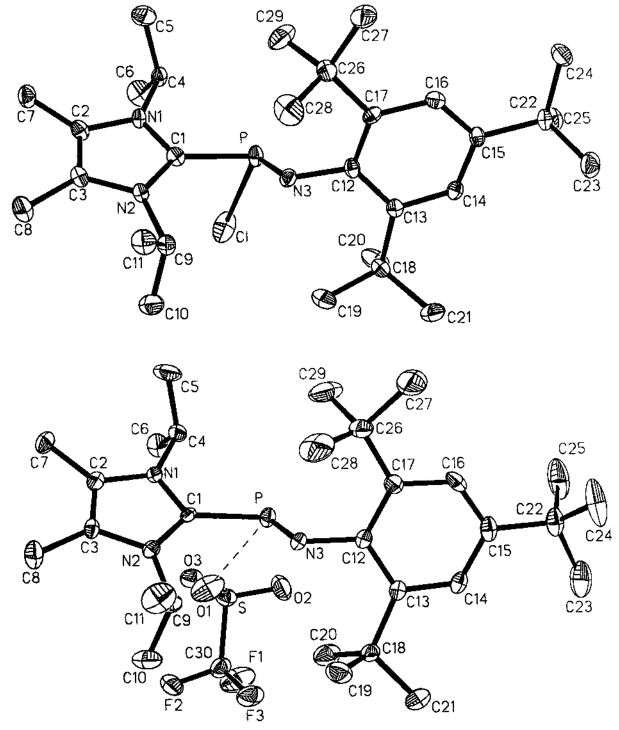
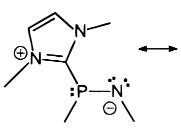


Figure 1. Crystal structures of **7a** and **7b** drawn with 30% probability displacement ellipsoids. Hydrogen atoms have been omitted for clarity.

CNP bond angles and P−E bond lengths (E = Cl or O) correlate with the basicity trends of both the neutral ligands (PPh$_3$ < pyr < carb[15]) and the anionic ligands (OSO$_2$CF$_3^-$ < Cl$^-$). In this context, the increasing O−P bond length trend in **6b**, **7d**, **7c**, and **7b** can be viewed in terms of the complexes demonstrating incipient anionic ligand displacement (cf. sum of the van der Waals radii for O−P, 3.3 Å).[16] The ^{13}C NMR chemical shifts of the methylene centers in **7a** (158 ppm) and **7b** (147 ppm) are in the range observed for other main-group derivatives of **5** (e.g., 126 [(carb)S(O)Cl$_2$][17] to 181 ppm [(carb)SnCl$_2$][18]).

Imidazol-2-ylidenes[6,19] have been previously exploited to obtain new phosphoranes,[20] cationic phosphines,[21] and phosphaalkenes,[22] which are now complemented by the new complexes **7a** and **7b**. More importantly, **7a** represents a definitive example of the iminophosphide bonding environment **8b** (**4b**), the relative stability of which (with respect to the phosphinoamide **8a** (**4a**)) was theoretically predicted[5] in terms of the presence of an electronegative substituent (Cl) at phosphorus. The interesting isomeric relationship of **8b** with the methylene(imino)phosphorane bonding arrangement **9**, which has been observed with substituents other than imidazole,[23] implies that the π-interaction between the nitrogen centers and the methylene center is favored over that between a planar phosphorus center and methylene center.



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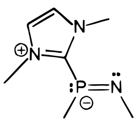

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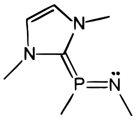

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Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada (N.B., T.S.C.) and the Killam Foundation (N.B.) for funding, the Walter Sumner Foundation for a scholarship (A.D.P.), the Atlantic Regional Magnetic Resonance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

Supporting Information Available: Thermal ellipsoid diagram of **7c**, tables of crystallographic data, atomic coordinates, isotropic and anisotropic displacement parameters, and bond lengths and angles for **7a**, **7b** and **7c** (PDF) and a CIF file for **7a** and **7b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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