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Ylidene→Iminophosphine Coordination Complexes and Reversible Dissociation of Dichlorophosphetidines

Neil Burford,*,† C. Adam Dyker,† Andrew D. Phillips,† Heather A. Spinney,† Andreas Decken,‡ Robert McDonald,§ Paul J. Ragogna,† and Arnold L. Rheingold||

Department of Chemistry, Dalhousie University, Halifax, Nova Scotia B3H 4J3, Canada, Department of Chemistry, University of New Brunswick, Fredericton, New Brunswick E3B 6E2, Canada, X-ray Crystallography Laboratory, Department of Chemistry, University of Alberta, Edmonton, Alberta T6G 2G2, Canada, and Department of Chemistry and Biochemistry, University of California, San Diego, 2040 Urey Hall Addition, 9500 Gilman Drive, MC 0332, La Jolla, California 92093-0332

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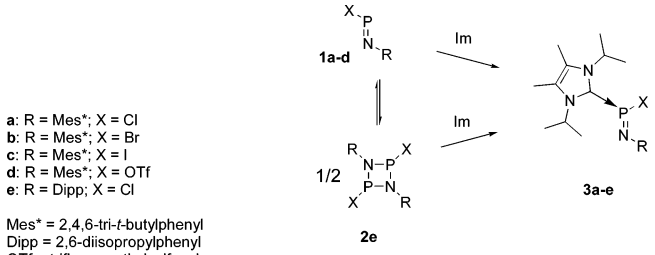
Chloro-, bromo-, iodo-, and trifluoromethylsulfonyloxy-(2,4,6-tri-*tert*-butylphenylimino)phosphines (Mes*NPX; X = Cl, Br, I, OTf) react quantitatively with 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (Im) to give Lewis acid–base complexes with the general formula Mes*NP(Im)X. The dichlorophosphetidine $(DippNPCl)_2$ (Dipp = 2,6-diisopropylphenyl) represents a formal cyclodimer of an iminophosphine and reacts with Im to give a similar complex. The process represents a ligand induced dissociation of the phosphetidine framework and is reversed by the introduction of an appropriate Lewis acid. Solid state structures of RNP(Im)X complexes show that the closest contact between acid and base occurs between phosphorus and carbon in all cases, highlighting them as compounds that contain examples of C→P coordinate bonds. Association of Im with phosphorus also effects a substantial increase in the P–X distance, but all derivatives maintain a short NP bond, indicating the presence of NP π-bonding.

Introduction

Compounds containing electron rich (lone pair bearing) phosphorus(III) centers are classic Lewis donors (ligands) in coordination chemistry. Nevertheless, complexes involving Lewis acceptor phosphorus(III) centers[1] are known with arene,[2] amine,[3,4] imine,[4−7] chalcogenourea,[8] phosphine,[9−21] and gallane[22] ligands, demonstrating the synthetic utility of coordinate element(donor)−phosphorus(acceptor) bond formation. In addition, a variety of phosphorus(III) Lewis acceptors form complexes[23−27] with the strongly Lewis basic imidazol-2-ylidenes.[28−31] We now show that 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (Im) forms complexes **3a**−**d** with iminophosphines **1a**−**d** effecting partial nucleophilic displacement of halide and sulfonyl units.[32] Moreover, the analogous displacement of an amide from a tricoordinate phosphorus center is implicated in the dissociation of phosphetidine **2e** to give the ligand-stabilized iminophosphine **3e**.



This new application of ligand−phosphine coordination chemistry represents a potentially versatile approach for

* To whom correspondence should be addressed. E-mail: neil.burford@dal.ca.
† Dalhousie University.
‡ University of New Brunswick.
§ University of Alberta.
|| University of California, San Diego.

(1) Burford, N.; Ragogna, P. J. *Dalton Trans.* **2002**, 4307−4315.
(2) Burford, N.; Clyburne, J. A. C.; Bakshi, P. K.; Cameron, T. S. *Organometallics* **1995**, *14*, 1578−1585.
(3) Kaukorat, T.; Neda, I.; Schmutzler, R. *Coord. Chem. Rev.* **1994**, *137*, 53−107.
(4) Burford, N.; Losier, P.; Phillips, A. D.; Ragogna, P. J.; Cameron, T. S. *Inorg. Chem.* **2003**, *42*, 1087−1091.
(5) Bouhadir, G.; Reed, R. W.; Réau, R.; Bertrand, G. *Heteroat. Chem.* **1995**, *6*, 371−375.
(6) Jones, V. A.; Sriprang, S.; Thornton-Pett, M.; Kee, T. P. *J. Organomet. Chem.* **1998**, *567*, 199−218.
(7) Burford, N.; Cameron, T. S.; Robertson, K. N.; Phillips, A. D.; Jenkins, H. A. *Chem. Commun.* **2000**, 2087−2088.
(8) Burford, N.; Phillips, A. D.; Spinney, H. A.; Robertson, K. N.; Cameron, T. S.; McDonald, R. *Inorg. Chem.* **2003**, *42*, 4949−4954.
(9) Schultz, C. W.; Parry, R. W. *Inorg. Chem.* **1976**, *15*, 3046−3050.

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transformations between iminophosphines and the ubiquitous phosphetidines for derivatives with appropriate steric loading.

Experimental Procedures

Schlenk techniques were used in the synthesis of starting materials and for recrystallization. All glassware was flame-dried under dynamic vacuum prior to use, and experiments were performed in an evacuated (10^{-3} Torr) reactor (unless otherwise stated).[33] Solids were manipulated in a glovebox with a nitrogen atmosphere (Braun; O_2, H_2O < 0.1 ppm) and stored in sealed glass tubes. Solvents and liquid reagents were transferred by reduced pressure distillation, or by using a syringe.

Solvents were dried and degassed using three freeze−pump−thaw cycles prior to use. Benzene, toluene, and *n*-hexane 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_2-Dichloromethane and d_6-benzene were dried over calcium hydride. Chemicals and reagents were obtained from Aldrich Chemical Co. 2,6-Diisopropylphenylaniline (Dip-pNH_2), and gallium trichloride were used as received. Phosphorus trichloride was distilled prior to use. Triethylamine was purified by fractional distillation from potassium hydroxide and then calcium hydride. Mes*NPCl (**1a**),[34] Mes*NPBr (**1b**),[34] Mes*NPI (**1c**),[34] Mes*NPOTf (**1d**),[35] $(DippNPCl)_2$ (**2e**),[36] and Im[37] were synthesized according to reported procedures.

Samples for analysis by solution NMR spectroscopy were prepared in 5 mm (o.d.) flame-sealed Pyrex glass tubes. Solution ^1H, ^{13}C, ^{19}F, and ^{31}P NMR spectra were collected at room temperature on Bruker AC-250 and Bruker Avance 500 NMR spectrometers. Chemical shifts are reported in ppm relative to an external reference standard [100% $SiMe_4$ (^1H, ^{13}C), 10% CCl_3F (^{19}F), and 85% H_3PO_4 (^{31}P)], and both ^1H and ^{13}C NMR were calibrated to an internal reference signal (^1H, $CHDCl_2$, 5.32 ppm, C_6D_5H, 7.16 ppm; ^{13}C, CD_2Cl_2, 54.00 ppm, C_6D_6, 128.5 ppm). NMR spectra of reaction mixtures were obtained by transferring an aliquot of the bulk solution to a 5 mm NMR tube, which was subsequently flame-sealed. Spectra were obtained within 1 day of sample preparation.

Solid state ^{31}P NMR spectra were obtained on powdered samples from ground crystalline solids. The samples were packed into zirconium oxide rotors and fitted with Vespel caps (4 mm o.d.). Chemical shifts are reported in ppm and referenced to external 85% aqueous H_3PO_4 by setting the isotropic peak of external solid $[NH_4][H_2PO_4]$ to 0.81 ppm. Solid state ^{31}P NMR spectra obtained with cross-polarization and magic-angle spinning (CP/MAS) were acquired using a Bruker MSL 200 spectrometer (**3a**, **3d**) or a Bruker AMX-400 NMR spectrometer (**3b**, **3c**, **3e**).

Infrared spectra were collected on samples prepared as Nujol mulls on CsI plates using Nicolet 510P FT-IR and 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. For all vibrational spectra, peaks are reported in wavenumbers (cm^{-1}) 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 by using an Electrothermal apparatus. Chemical analyses were performed by Beller Laboratories, Göttingen, Germany, or by Desert Analytics, Tucson, Arizona.

Unless otherwise stated, crystals for single crystal X-ray diffraction studies were obtained by liquid−liquid diffusion by dissolving a sample (0.05−0.10 g) in benzene (2 to 4 mL) in a 150 mm (14 mm o.d.) glass tube and layering hexane (15 to 20 mL) onto the solution using a syringe. The sealed tube (under argon) was left undisturbed for several weeks at room temperature. After deposition of crystals, the solvent was carefully removed using a syringe, and the crystals were coated with perfluoropolyether 216 (Riedel-de Haën). Single crystal X-ray diffraction data were collected using Siemens/Bruker P4 diffractometers fitted with Bruker SMART CCD detectors. All measurements were made with graphite monochromated Mo Kα radiation. 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^2 data using the program SHELX97.[38] Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in

(10) Thomas, M. G.; Schultz, C. W.; Parry, R. W. *Inorg. Chem.* **1977**, *16*, 994−1001.
(11) Schmidpeter, A.; Lochschmidt, S.; Sheldrick, W. S. *Angew. Chem., Int. Ed.* **1982**, *21*, 63−64.
(12) Schmidpeter, A.; Lochschmidt, S.; Sheldrick, W. S. *Angew. Chem., Int. Ed.* **1985**, *24*, 226−227.
(13) Shagvaleev, F. Sh.; Zykova, T. V.; Tarasova, R. I.; Sitdikova, T. Sh.; Moskva, V. V. *Zh. Obshch. Khim.* **1990**, *60*, 1775−1779.
(14) David, G.; Niecke, E.; Nieger, M.; Radseck, J.; Schoeller, W. W. *J. Am. Chem. Soc.* **1994**, *116*, 2191−2192.
(15) Romanenko, V. D.; Rudzevich, V. L.; Rusanov, E. B.; Chernega, A. N.; Senio, A.; Sotiropoulos, J. M.; Pfister-Guillouzo, G.; Sanchez, M. *Chem. Commun.* **1995**, 1383−1385.
(16) Burford, N.; Cameron, T. S.; Clyburne, J. A. C.; Eichele, K.; Robertson, K. N.; Sereda, S.; Wasylishen, R. E.; Whitla, W. A. *Inorg. Chem.* **1996**, *35*, 5460−5467.
(17) Burford, N.; Cameron, T. S.; LeBlanc, D. J.; Losier, P.; Sereda, S.; Wu, G. *Organometallics* **1997**, *16*, 4712−4717.
(18) Burford, N.; LeBlanc, D. J. *Inorg. Chem.* **1999**, *38*, 2248−2249.
(19) Abrams, M. B.; Scott, B. L.; Baker, R. T. *Organometallics* **2000**, *19*, 4944−4956.
(20) Burford, N.; Ragogna, P. J.; McDonald, R.; Ferguson, M. *J. Am. Chem. Soc.* **2003**, *125*, 14404−14410.
(21) Burford, N.; Ragogna, P. J.; McDonald, R.; Ferguson, M. J. *Chem. Commun.* **2003**, 2066−2067.
(22) Burford, N.; Ragogna, P. J.; Robertson, K. N.; Cameron, T. S.; Hardman, N. J.; Power, P. P. *J. Am. Chem. Soc.* **2002**, *124*, 382−383.
(23) Kuhn, N.; Fahl, J.; Bläser, D.; Boese, R. *Z. Anorg. Allg. Chem.* **1999**, *625*, 729−734.
(24) Hardman, N. J.; Abrams, M. B.; Pribisko, M. A.; Gilbert, T. M.; Martin, R. L.; Kubas, G. J.; Baker, R. T. *Angew. Chem., Int. Ed.* **2004**, *43*, 1955−1958.
(25) Arduengo, A. J.; Krafczyk, R.; Marshall, W. J.; Schmutzler, R. *J. Am. Chem. Soc.* **1997**, *119*, 3381−3382.
(26) Arduengo, A. J.; Dias, H. V. R.; Calabrese, J. C. *Chem. Lett.* **1997**, 143−145.
(27) Arduengo, A. J.; Calabrese, J. C.; Cowley, A. H.; Dias, H. V. R.; Goerlich, J. R.; Marshall, W. J.; Riegel, B. *Inorg. Chem.* **1997**, *36*, 2151−2158.
(28) Arduengo, A. J. *Acc. Chem. Res.* **1999**, *32*, 913−921.
(29) Bourissou, D.; Guerret, O.; Gabbaï, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39−91.
(30) Herrmann, W. A.; Köcher, C. *Angew. Chem., Int. Ed.* **1997**, *36*, 2162−2187.
(31) Kirmse, W. *Angew. Chem. Int. Ed.* **2004**, *43*, 1767−1769.
(32) Burford, N.; Cameron, T. S.; LeBlanc, D. J.; Phillips, A. D.; Concolino, T. E.; Lam, K. C.; Rheingold, A. L. *J. Am. Chem. Soc.* **2000**, *122*, 5413−5414.
(33) Burford, N.; Muller, J.; Parks, T. M. *J. Chem. Educ.* **1994**, *71*, 807−809.
(34) Niecke, E.; Nieger, M.; Reichert, F. *Angew. Chem., Int. Ed.* **1988**, *27*, 1715−1716.
(35) Niecke, E.; Detsch, R.; Nieger, M.; Reichert, F.; Schoeller, W. W. *Bull. Soc. Chim. Fr.* **1993**, *130*, 25−31.
(36) Burford, N.; Cameron, T. S.; Conroy, K. D.; Ellis, B.; Macdonald, C. L. B.; Ovans, R.; Phillips, A. D.; Ragogna, P. J.; Walsh, D. *Can. J. Chem.* **2002**, *80*, 1404−1409.
(37) Kuhn, N.; Kratz, T. *Synthesis* **1993**, 561−562.

Table 1. Crystal Data for Im, **3a**, **3b**, **3c**, **3d**, and **3e**

	Im	Mes*NP(Im)Cl	Mes*NP(Im)Br	Mes*NP(Im)I	Mes*NP(Im)OTf	DippNP(Im)Cl
compd label	Im	**3a**	**3b**	**3c**	**3d**	**3e**
formula	$C_{11}H_{20}N_2$	$C_{29}H_{49}N_3PCl$	$C_{29}H_{49}N_3PBr$	$C_{29}H_{49}N_3PI$	$C_{30}H_{49}N_3O_3F_3PS$	$C_{23}H_{37}ClN_3P$
mol wt (g/mol)	180.29	506.13	550.59	597.58	619.75	421.98
cryst syst	orthorhombic	monoclinic	triclinic	triclinic	orthorhombic	monoclinic
space group	*Pccn*	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	*Pbca*	$P2_1/c$
color	colorless	orange	orange	orange	purple	yellow
a/Å	9.1543(6)	21.8062(3)	8.531(5)	8.4383(5)	10.6688(2)	14.031(3)
b/Å	9.3381(6)	8.5184(1)	9.659(5)	9.5486(6)	15.2337(3)	9.522(3)
c/Å	13.4586(8)	17.8511(2)	21.359(11)	21.455(1)	42.5078(6)	17.977(5)
α/deg	90	90	77.668(11)	77.177(1)	90	90
β/deg	90	110.892(1)	79.791(10)	80.761(1)	90	105.198(5)
γ/deg	90	90	64.430(10)	65.159(1)	90	90
V/Å^3	1150.49(13)	3097.90(7)	1543.7(14)	1525.2(2)	6908.6(2)	2317.8(10)
T/K	193(2)	213(2)	293(2)	193(2)	213(2)	198(1)
Z	4	4	2	2	8	4
R^a ($I > 2\sigma(I)$, all data)	0.0400, 0.0438	0.0850, 0.1075	0.0623, 0.1208	0.0420, 0.0623	0.0892, 0.1360	0.0627, 0.0723
$wR_2{}^b$ ($I > 2\sigma(I)$, all data)	0.1096, 0.1128	0.2371, 0.2753	0.1314, 0.1529	0.0873, 0.0957	0.1502, 0.1699	0.1661, 0.1731
GOF[c]	1.092	1.082	0.958	1.049	1.342	1.065
$\Delta\rho$ max and min/e Å^{-3}	+0.239, −0.152	+0.644, −0.692	+0.499, −0.359	+1.060, −0.705	+0.444, −0.420	+0.929, −0.375

[a] $R = (\sum|F_o| - |F_c|)/(\sum|F_o|)$. [b] $wR_2 = [(\sum w(F_o^2 - F_c^2)^2)/(\sum w(F_o^2)^2)]^{1/2}$. [c] 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. ^{31}P NMR Chemical Shifts (ppm) in Solution, Selected Structural Parameters [Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg)] for Derivatives of **1**, **2**, and **3**, and Comparative Data for Related Complexes of Type **7**

compd	label	^{31}P δ[a]	C−P	N1−C	N2−C	N1−C−N2	C−N3−P	N1−C−P	N2−C−P	P−X	N3−P	C−N3−P−C	Σ∠P	ref
Im	Im			1.360(1)	1.398(1)	113.09(9)								this work
$(DippNPCl)_2$	**2e**	211[a,b]								2.071(8)	1.69(2)			36
										2.085(8)	1.73(1)			
DippNP(Im)Cl	**3e**	128,[b,c] 130[c,d]	1.902(2)	1.343(3)	1.339(3)	106.6(2)	142.9(2)	120.5(2)	132.6(2)	2.318(1)	1.543(2)	−18.7(3)	310.5	this work
Mes*NPCl	**1a**	132					154.8(4)			2.142(4)	1.495(4)			34
Mes*NP(Im)Cl	**3a**	172	1.886(5)	1.365(7)	1.370(7)	106.7(4)	120.2(4)	120.5(4)	132.8(4)	2.471(2)	1.585(5)	−162.0(4)	301.2	this work[32]
		154[b]												
		156[d]												
Mes*NPBr	**1b**	146					159.5(4)			2.337(2)	1.498(4)			50
Mes*NP(Im)Br	**3b**	199	1.881(5)	1.369(6)	1.353(6)	106.1(4)	116.1(3)	119.7(4)	134.2(4)	2.674(2)	1.578(4)	−165.8(3)	304.2	this work
Mes*NPI	**1c**	206					172.5(3)			2.895(1)	1.480(3)			51
Mes*NP(Im)I	**3c**	214	1.874(3)	1.347(1)	1.340(4)	107.5(3)	116.2(2)	119.1(2)	133.3(2)	2.907(1)	1.574(3)	−166.6(2)	306.6	this work
		189[b]												
Mes*NPOTf	**1d**	50					176.4(3)			1.923(3)	1.467(4)			35
Mes*NP(Im)OTf	**3d**	339	1.852(5)	1.355(5)	1.347(6)	107.5(4)	116.2(3)	119.7(3)	132.8(3)	2.951(5)	1.574(4)	−170.1(4)	298.3	this work[32]
		350[d]												
$Ph_2P(Im)AlCl_4$	**4**	−27	1.813(7)	1.358(8)	1.369(8)	105.6(6)		122.7(5)	131.4(5)				310.1	23
$PhF_4P(Im')$[e]	**5**	−141	1.910(4)	1.355(4)	1.351(4)	105.0(3)		126.1(3)	128.9(3)					25
PhP(Im′)[e]	**6**	−54	1.794(3)	1.365(4)	1.361(4)	104.7(2)		124.7(2)	130.2(2)					26
Mes*NP(pyr)OTf	**7z**	71					161.7(7)			2.712(7)	1.472(8)		307.3	4
Mes*NP(quin)OTf	**7y**	144					143.9(2)			2.697(3)	1.519(2)		302.2	4
$Mes*NP(PPh_3)OTf$	**7x**	−5,					169.5(4)			2.298(4)	1.486(4)		305.9	16
		52[f]												
Mes*NP(OU)OTf	**7w**	62					166.2(2)			2.942(2)	1.486(2)		308.6	8
Mes*NP(OIm)OTf	**7v**	77					159.7(3)			2.774(4)	1.494(3)		312.0	8
Mes*NP(SIm)OTf	**7u**	156					174.4(2)			*g*	1.498(2)		*g*	8
Mes*NP(SeIm)OTf	**7t**	182					175.5(2)			*g*	1.500(2)		*g*	8

[a] In CH_2Cl_2. [b] In toluene. [c] Dynamic behavior. [d] In benzene. [e] Im′ = 1,3-mesitylimidazol-2-ylidene. [f] Chemical shifts for fully dissociated acceptor and ligand. [g] P−O distance is greater than the sum of the van der Waals' radii.

geometrically calculated positions, but were not refined. Refinement details are summarized in Table 1, and important geometrical parameters are listed in Table 2. The full set of crystallographic results has been deposited.

Isolation Procedures and Characterization Data. Mes*NP(Im)Cl, 3a. A solution of Im (0.16 g, 0.89 mmol) in benzene (9 mL) was added to Mes*NPCl (0.30 g, 0.92 mmol) in benzene (13 mL). The reaction mixture was stirred for 1 h, and the solvent was removed in vacuo to a volume of 3 mL. Crystals were washed 3 times with 5 mL portions of benzene and characterized as $C_{29}H_{49}ClN_3P$ (506.15 g/mol); yield 0.11 g, 0.22 mmol, 25%, mp 178 °C. Anal. Calcd % (Found): C 68.8 (69.1), H 9.8 (9.8), N 8.3 (8.4). IR: 1414(1), 1391(5), 1367(6), 1360(4), 1352(10), 1286(15), 1260(2), 1251(3), 1240(7), 1213(8), 1188(13), 1172(20), 1138(16), 1124(9), 1115(14), 1083(19), 1020(21), 877(11), 793(12), 692(18), 400(17). NMR (CD_2Cl_2): ^{1}H 1.3 (s, 9H), 1.4 (s, 18H), 1.6 (d, $^3J_{HH}$ = 7 Hz, 12H), 2.4 (s, 6H), 6.2 (m, 2H), 7.3 (d, $^5J_{PH}$ = 1.5 Hz, 2H); ^{13}C{^{1}H} 11 (s), 22 (s), 32 (s), 33 (s), 35 (s), 37 (s), 51 (d, $^4J_{PC}$ = 20 Hz), 122 (s), 127 (s), 140 (d, $^4J_{PC}$ = 12 Hz), 141 (s), 147 (d, $^2J_{PC}$ = 25 Hz), 154 (d, $^1J_{PC}$ = 115 Hz); ^{31}P{^{1}H}172 (s). CP-MAS ^{31}P: 193; crystals are spectroscopically identical to the powder.

Mes*NP(Im)Br, 3b. A solution of Im (0.15 g, 0.81 mmol) in benzene (5 mL) was added dropwise to a stirred solution of Mes*NPBr (0.30 g, 0.81 mmol) in benzene (4 mL) over a period of 5 min in a 20 mL glass vial in the glovebox. The reaction mixture was stirred for 45 min, and the solvent was removed in vacuo to a volume of approximately 3 mL. The orange powder was separated

(38) Sheldrick, G. M. *SHELXL-97, Program for crystal structure determination*; University of Göttingen: Göttingen, Germany 1997.

from the red supernatant solution using a needle and syringe, washed with 2 × 4 mL portions of hexane, dried under dynamic vacuum, and characterized as $C_{29}H_{49}BrN_3P$ (550.60 g/mol); yield 0.35 g, 0.63 mmol, 78%, decomp point 170 °C. Anal. Calcd % (Found): C 63.2 (62.8); H 9.0 (8.5); N 7.6 (7.7). IR: 3049(22), 1621(13), 1418(2), 1395(6), 1375(3), 1361(5), 1285(14), 1266(8), 1238(1), 1214(4), 1188(10), 1171(19), 1155(16), 1139(12), 1121(7), 1082(21), 1018(15), 905(17), 878(18), 795(9), 756(20), 697(11) 397(23). Raman: 3052(11), 2968(1), 2924(2), 2765(11), 1622(9), 1596(6), 1452(5), 1363(7), 1293(4), 1243(3), 1147(10), 1020(11), 822(11), 264(12), 143(11), 124(8). NMR (CD_2Cl_2): ^{1}H 1.3 (s, 9H), 1.4 (s, 18H), 1.6 (d, $^3J_{HH}$ = 8 Hz, 12H), 2.4 (s, 6H), 6.0 (septet, $^3J_{HH}$ = 8 Hz, 2H), 7.3 (d, $^5J_{PH}$ = 1 Hz, 2H); ^{13}C{^{1}H} 11 (s), 21(s), 23 (s), 32 (s), 33 (s), 35(s), 37(s), 51 (d, $^4J_{PC}$ = 18 Hz), 123 (s), 126 (s), 128 (s), 129 (s), 139 (d, $^3J_{PC}$ = 12 Hz), 142 (s), 147 (d, $^2J_{PC}$ = 20 Hz), 152 (d, $^1J_{PC}$ = 123 Hz); ^{31}P{^{1}H} 199. CP-MAS ^{31}P: 212, 215; crystals are spectroscopically identical to the powder.

Mes*NP(Im)I, 3c. A solution of Im (0.11 g, 0.61 mmol) in benzene (5 mL) was added dropwise to a stirred solution of Mes*NPI (0.27 g, 0.61 mmol) in benzene (4 mL) over a period of 5 min in a 20 mL glass vial in the glovebox. The reaction mixture was stirred for 45 min, and the solvent was removed in vacuo to a volume of approximately 3 mL. The red powder was separated from the red supernatant solution using a needle and syringe, washed with 2 × 4 mL portions of hexane, dried under dynamic vacuum, and characterized as $C_{29}H_{49}N_3PI$ (597.60 g/mol), yield 0.32 g, 0.54 mmol, 89%, mp 209−210 °C. Anal. Calcd % (Found): C 58.3 (58.5); H 8.3 (8.3); N 7.0 (7.1). IR: 1620(12), 1411(2), 1377(3), 1361(4), 1307 (19), 1285(16), 1265(7), 1234(1), 1214(5), 1153(13), 1136(8), 1119(6), 1081(15), 1012(10), 903(17), 878(14), 794(9), 770(20), 756(18), 694(11), 396(21). Raman: 3049(15), 2968(1), 2930(2), 1621(8), 1597(7), 1473(5), 1451(6), 1422(6), 1399(12), 1360(7), 1291(4), 1265(10), 1237(3), 1198(11), 1146(9), 1121(15), 1012(10), 822(14), 262(15), 223(14), 161(14), 145(13), 123(8). NMR (CD_2Cl_2): ^{1}H 1.3 (s, 9H), 1.4 (s, 12H), 1.6 (d, $^3J_{HH}$ = 7 Hz, 12H), 2.4 (s, 6H), 5.9 (septet, $^3J_{HH}$ = 7 Hz, 2H), 7.3 (d, $^5J_{PH}$ = 1 Hz, 2H); ^{13}C{^{1}H} 11 (s), 21 (s), 23 (s), 32 (s), 33 (s), 35 (s), 37 (s), 51 (d, $^4J_{PC}$ = 17 Hz), 123 (s), 127 (s), 128 (s), 129 (s), 132 (s), 138 (d, $^3J_{PC}$ = 13 Hz), 142 (s), 146 (d, $^2J_{PC}$ = 16 Hz), 151 (d, $^1J_{PC}$ = 129 Hz); ^{31}P{^{1}H} 214. CP-MAS ^{31}P: 223; crystals are spectroscopically identical to the powder.

Mes*NP(Im)OTf, 3d. A solution of Im (0.13 g, 0.70 mmol) in benzene (7 mL) was added to a stirred solution of Mes*NPOTf (0.31 g, 0.70 mmol) in benzene (11 mL). The reaction mixture was stirred for 1 h, and the solvent was removed in vacuo to a volume of 3 mL. Crystals were washed 3 times with 5 mL portions of benzene and characterized as $C_{30}H_{49}F_3N_3PO_3$ (619.77 g/mol); yield: 0.16 g, 0.26 mmol, 37%, mp 145 °C. Anal. Calcd % (Found): C 58.1 (58.2), H 8.0 (7.8), N 6.8 (6.8). IR: 1610(21), 1419(9), 1280(1), 1246(2), 1229(5) 1221(6), 1159(8), 1147(7), 1122(10), 1090(14), 1026(4), 909(18), 889(20), 877(15), 795(12), 754(16), 637(3), 628(13), 572(17), 549(19), 517(11). NMR (CD_2Cl_2): ^{1}H 1.3 (s, 9H), 1.4 (s, 18H), 1.7 (d, $^3J_{HH}$ = 7 Hz, 12H), 2.5 (s, 6H), 5.9 (m, $^3J_{HH}$ = 7 Hz, $^5J_{PH}$ = 1 Hz, 2H), 7.5 (d, $^5J_{PH}$ = 1 Hz, 2H); ^{13}C{^{1}H} 12 (s), 22 (s), 32 (s), 33 (s), 35 (s), 37 (s), 53 (d, $^4J_{PC}$ = 9 Hz), 121 (q, $^1J_{FC}$ = 321 Hz), 123 (s), 132 (s), 136 (d, $^2J_{PC}$ = 12 Hz), 143 (d, $^3J_{PC}$ = 6 Hz), 146 (d, $^1J_{PC}$ = 132 Hz) 148 (d, $^5J_{PC}$ = 2 Hz); ^{19}F{^{1}H} −79 (s); ^{31}P{^{1}H} 339 (s). CP-MAS ^{31}P 366; crystals are spectroscopically identical to the powder.

DippNP(Im)Cl, 3e. A solution of Im (0.32 mmol) in toluene (2 mL) was added to a stirred solution of $(DippNPCl)_2$ (0.16 mmol) in toluene (3 mL). The reaction mixture was stirred for 30 min and filtered, and the solvent was removed in vacuo with heating (∼70 °C). The resulting yellow solid was washed with 2−3 mL of hexane, pumped to dryness, and characterized as $C_{23}H_{37}ClN_3P$ (421.98 g/mol), yield 0.081 g, 0.19 mmol, 60%, decomp point 150−164 °C. Anal. Calcd (Found): C 65.5 (65.2); H 8.9 (8.8); N 10.0 (9.3). IR: 1621(6), 1586(7), 1553(10), 1403(15), 1366(2), 1300(14), 1255(8), 1216(9), 1111(5), 1055(12), 1025(11), 796(4), 768(13), 746(1), 376(5), 267(3). Raman: 3050(8), 2974(5), 2946(1), 2868(6), 1622(9), 1587(3), 1438(2), 1370(4), 1301(7), 884(10). NMR (C_6D_6): ^{1}H 2.1 (broad s), 2.3 (broad s), 2.4 (d, $^3J_{HH}$ = 7 Hz, 12H), 4.9 (septet, $^3J_{HH}$ = 7 Hz, 2H) 8−8.3 (m, 3H); ^{31}P{^{1}H} 130 (s, exhibits dynamic behavior down to −80 °C). CP-MAS ^{31}P: 62 ppm; crystals suitable for X-ray diffraction were obtained from a toluene solution by slow evaporation and are spectroscopically identical to the powder.

^{31}P NMR Studies of Equimolar (∼0.02 M) Combinations in Toluene. $GaCl_3$ was added to DippNP(Im)Cl and a signal at 211 ppm assigned to $(DippNPCl)_2$ **2e**. $GaCl_3$ was added to Mes*NP(Im)Cl and a signal at 353 ppm assigned to [Mes*NP(Im)][$GaCl_4$], which decomposes slowly (>1 week) to Mes*NPCl **1a**. Mes*NPCl was added to DippNP(Im)Cl and signals of comparable intensity at 211 ppm assigned to $(DippNPCl)_2$ **2e**, and 156 ppm assigned to **3a**.

Results and Discussion

The isolation and stability of iminophosphine compounds **1** usually depend on the presence of sterically bulky substituents, which counter the thermodynamic preference for N—P single bonds over multiple N═P bonding.[39] Some derivatives of **1** undergo reversible dimerization reactions,[40−42] and in one case, both the monomer **1d** and dimer **2d** have been isolated and structurally characterized.[43] We now show that the phosphetidine **2e**, involving major, but not dominant, steric loading (R = Dipp) is susceptible to dissociation on interaction with the strong Lewis base Im.

Equimolar mixtures of Im with halo(imino)phosphines **1a**−**d** react rapidly at room temperature to give Lewis acid−base adducts **3a**−**d**, which have been definitively characterized. Although isolation yields are modest for **3a** and **3d**, solution ^{31}P NMR spectra of reaction mixtures show them to be essentially quantitative (>85%). Reaction of phosphetidine **2e** with 2 equivalents of Im gives the analogous adduct **3e**, representing a ligand stabilized monomer resulting from dissociation of the corresponding dimer **2e**. The ^{31}P NMR chemical shift of **3e** in the solid state (62 ppm) is dramatically different from that observed in benzene solution (130 ppm), indicating substantial structural differences between the species in solution and in the solid state.

Crystallographic data for compounds **3a**−**e** are listed in Table 1, the solid state structures are illustrated in Figure 1, and selected structural parameters are presented in Table 2, together with analogous parameters for **1a**−**d** and related

(39) Burford, N.; Clyburne, J. A. C.; Chan, M. S. W. *Inorg. Chem.* **1997**, *36*, 3204−3206.
(40) Niecke, E.; Rüger, R.; Krebs, B.; Dartmann, M. *Angew. Chem., Int. Ed.* **1983**, *22*, 552−553.
(41) Niecke, E.; Lysek, M.; Symalla, E. *Chimia* **1986**, *40*, 202−205.
(42) Niecke, E.; Rüger, R.; Schoeller, W. W. *Angew. Chem., Int. Ed.* **1981**, *20*, 1034−1036.
(43) Burford, N.; Cameron, T. S.; Conroy, K. D.; Ellis, B.; Lumsden, M. D.; Macdonald, C. L. B.; McDonald, R.; Phillips, A. D.; Ragogna, P. J.; Schurko, R. W.; Walsh, D.; Wasylishen, R. E. *J. Am. Chem. Soc.* **2002**, *124*, 14012−14013.

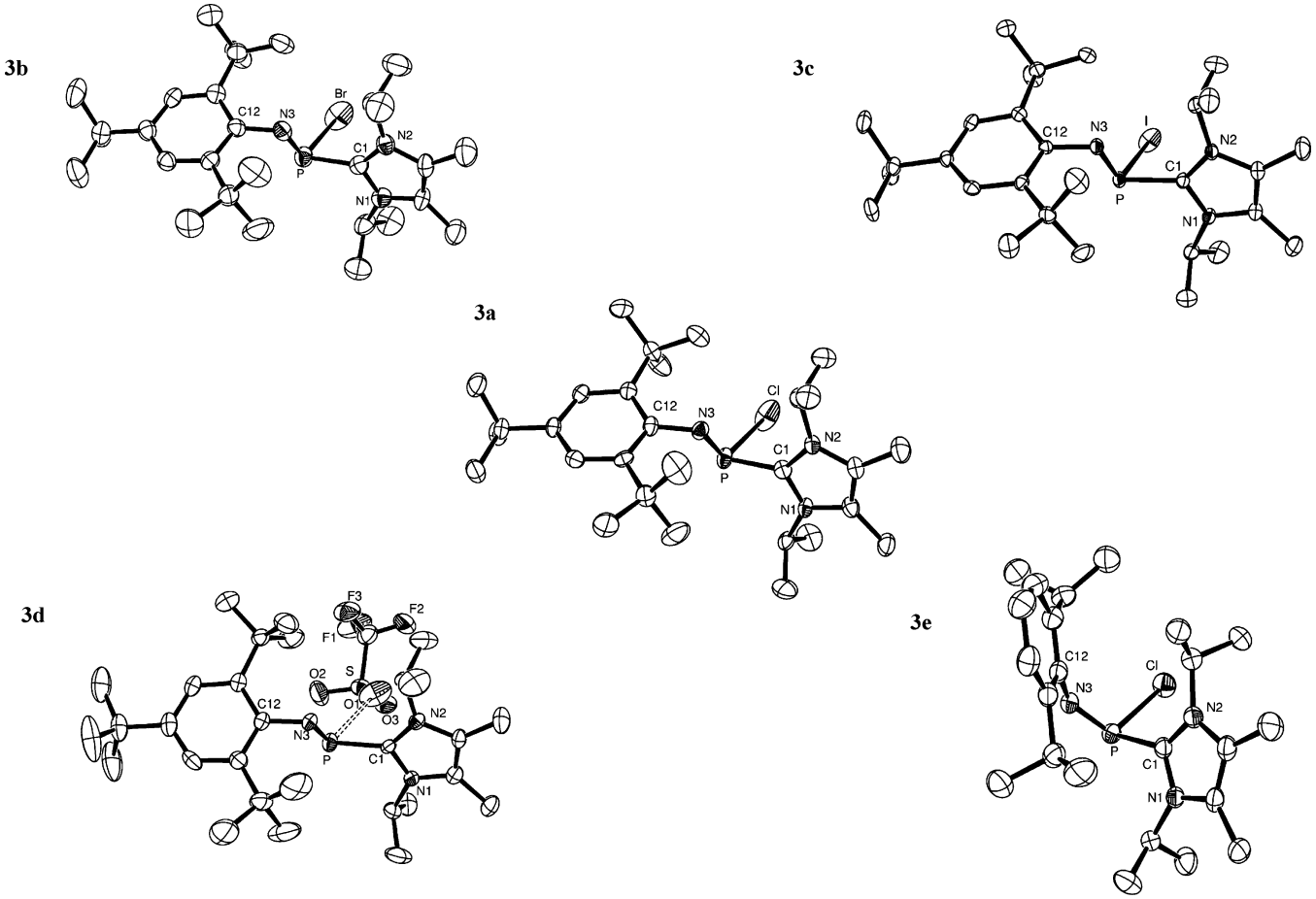
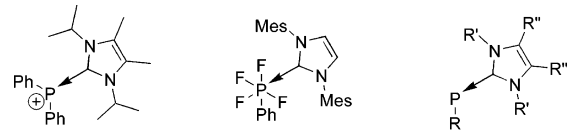


Figure 1. Structural views of the solid state structures of Mes*NP(Im)Cl **3a**, Mes*NP(Im)Br **3b**, Mes*NP(Im)I **3c**, Mes*NP(Im)OTf **3d**, and DippNP(Im)Cl **3e**, drawn with 50% probability displacement ellipsoids. Hydrogen atoms are not shown.

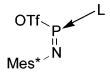
complexes of type **4**, **5**, **6**, and **7**. In all derivatives of **3a**−**e**, the closest contact between **1a**−**e (1e** is the formal monomer of **2e**) and Im involves the phosphorus center and the unique carbon center, respectively. The P−C distances are crystallographically indistinguishable between derivatives of **3a**−**e** despite the variation in X and R and are comparable in length with C−P bonds in alkylphosphines [average, 1.855(19) Å].[44] Nevertheless, a range of C−P distances is observed for imidazolylidene complexes of diphenylphosphenium **4** [1.813(7) Å],[23] tetrafluorophenylphosphorane **5** [1.910(4) Å],[25] and phosphinidenes **6a** [R = Ph, R′ = R″ = Me, 1.794(3) Å;[26] R = Ph, R′ = Mes, R″ = H, 1.763(6) Å; R = CF_3, R′ = Mes, R″ = H, 1.784(2) Å[27]].



4 **5** **6**

The planar five-membered ring of the Im unit is structurally similar to that in the free ligand (Im), and contraction (6−7°) of the N−C−N angle represents the only substantive adjustment within the ligand as a result of coordination. The orientation of the ligand with respect to the acceptor phosphorus center is nonsymmetric. In all complexes **3a**−**e**, the N1−C−P angle is uniformly smaller than N2−C−P (ΔN−C−P = difference between N1−C−P and N2−C−P = 12−15°) (Table 2) due to the eclipsed conformation of N2 and N3. A nonsymmetric interaction of the ylidene with phosphorus is also apparent in complexes **4** (ΔN−C−P = 8.7°) and **6** (ΔN−C−P = 5.5°).

z: L = pyridine
y: L = quinuclidine
x: L = PPh_3
w: L = 1,3-dimethyldiphenylurea
v: L = 1,3-diisopropyl-4,5-dimethylimidazol-2-one
u: L = 1,3-diisopropyl-4,5-dimethylimidazol-2-thione
t: L = 1,3-diisopropyl-4,5-dimethylimidazol-2-selenone

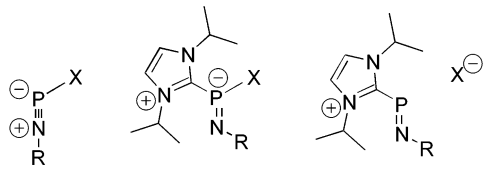


7

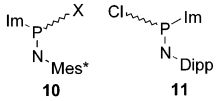
The N3−P distances in complexes **3a**−**d** are comparable to those in alkyliminophosphines [e.g., Mes*NPCEt$_3$, N−P = 1.566(2) Å, C−N−P = 124.8(2)°][45] and are longer than those in the corresponding free Lewis acceptors **1a**−**d**. The elongation of N3−P on interaction with Im is significantly greater than that observed in complexes of **1d** with pyridine **7z**, quinuclidine **7y**,[7,46] triphenylphosphine **7x**,[16] and chalcogenourea **7(w,v,u,t)**[8] ligands (Table 2). In addition, the C12−N3−P bond angles in **3a**−**d** are all substantially less than the almost linear C−N−P fragments in the corresponding halo(imino)phosphines **1a**−**d** (Table 2). We conclude that coordination of the relatively strong base Im (cf., pK_a

(44) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin. Trans. 2* **1987**, S1−S19.
(45) Barion, D.; Gärtner-Winkhaus, C.; Link, M.; Nieger, M.; Niecke, E. *Chem. Ber.* **1993**, *126*, 2187−2195.

imidazolium = 24,[47] pK_a pyridinium = 5.8[48]) imposes the greatest disruption on N−P π-bonding in **1a**−**d**, for which we apply representation **8** as the most appropriate bonding description. The partial nucleophilic displacement of X^- by the ligand in **3a**−**d** prompts bonding model **9b**; however, the P−X distances are substantially less than the sum of van der Waals' radii so that a covalent zwitterionic model **9a** is preferred.

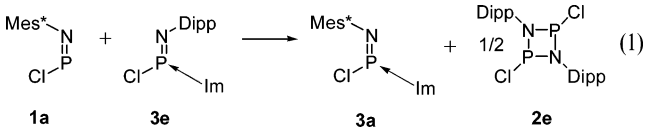


Dissociation of the dimer **2e** on reaction with Im can be considered as a nucleophilic displacement of an amide (rather than a halide) from the tricoordinate phosphorus center. The crystallographically characterized Im−iminophosphine complex **3e** has an N−P distance that is consistent with those in **3a**−**d** and is substantially shorter than that in the phosphetidine **2e**.



All derivatives of Mes*NP(Im)X **3a**−**d** adopt a *trans* configuration **10** of Mes* and Im about the P═N vector (torsion angles C−N3−P−C 162−170°; Table 2). In contrast, Dipp and Im are observed in a *cis* configuration [C−N3−P−C = 18.7(3)°] (**11**) in the solid state structure of **3e**, likely due to the steric distinction between Mes* and Dipp substituents. Nevertheless, the steric strain imposed by Dipp (**3e**) is accommodated in the *cis* configuration by adjustment of C−N3−P, which is distinctly large for DippNP(Im)Cl **3e** [142.9(2)°] in comparison to all *trans*-configured derivatives of Mes*NP(Im)X (116−120° for **3a**−**d**).

^{31}P NMR spectra of the reaction between **1a** and **3e** show quantitative ligand exchange of Im to give **3a** and **2e** (eq 1). This preference for adduct formation by the more sterically loaded iminophosphine **1a** is enthalpically driven by the N−P bond formation in the phosphetidine **2e**. ^{31}P NMR spectra of the reaction between **3e** and $GaCl_3$ show rapid and quantitative reformation of the corresponding phosphetidine **2e**. We interpret these observations in terms of Im−$GaCl_3$ adduct formation and dimerization of the released iminophosphine **1e**, which is a weaker Lewis acid than $GaCl_3$. A similar process has been observed for ylidene−phosphinidene complexes, which form oligophosphines in the presence of stronger Lewis acids.[49] In contrast to **3e**, the reaction of **3a** with $GaCl_3$ shows a ^{31}P NMR signal at 353 ppm, which we assign to [Mes*NP(Im)][$GaCl_4$] (cf. triflate derivative **3d**: ^{31}P, 350 ppm),[3] a kinetic product that slowly decomposes to **1a**, presumably by loss of Im−$GaCl_3$. Chloride ion abstraction from **3a** and retention of the Im−P coordinate bond in the presence of $GaCl_3$ (rather than Im abstraction) is a consequence of the steric preclusion of phosphetidine **2a** by the Mes* substituent, and we designate Mes* as imposing a "dominant steric influence". The slightly lower steric imposition of the Dipp substituent and the expected exothermicity associated with exchange of two N═P bonds for four N−P bonds allows for dimerization of **1e** (to **2e**). Nevertheless, the "major steric influence" of the Dipp substituent restricts other possible reaction pathways, and the phenyl derivative of **2** reacts with Im to give multiple phosphorus containing products that have not been identified.



Conclusions

The strong Lewis base Im forms complexes with a series of halo(imino)phosphines Mes*NPX (X = Cl, Br, I, OTf), which retain the short N−P bonds that are characteristic of the corresponding free acids. Association with the ligand does impose significant adjustments in the angle at nitrogen and partially displaces the leaving group (X). Major steric loading on the phosphetidine framework $(DippNPCl)_2$ influences formation of analogous adducts on reaction with Im, representing dissociation of the dimer and ligand stabilization of the iminophosphine. Reversal of this process can be accomplished by removal of the ligand on reaction with a stronger Lewis acid.

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Supporting Information Available: Crystallographic information files (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(46) Burford, N.; Macdonald, C. L. B.; LeBlanc, D. J.; Cameron, T. S. *Organometallics* **2000**, *19*, 152−155.
(47) Alder, R. W.; Allen, P. R.; Williams, S. J. *Chem. Commun.* **1995**, 1267−1268.
(48) Benoit, R. L.; Mackinnon, M. J.; Bergeron, L. *Can. J. Chem.* **1981**, *59*, 1501−1504.
(49) Arduengo, A. J.; Carmalt, C. J.; Clyburne, J. A. C.; Cowley, A. H.; Pyati, R. *Chem. Commun.* **1997**, 981−982.
(50) Chernega, A. N.; Korkin, A. A.; Aksinenko, N. E.; Ruban, A. V.; Romanenko, V. D. *Zh. Obshch. Khim.* **1990**, *60*, 2462−2469.
(51) Niecke, E.; Gudat, D. *Angew. Chem., Int. Ed.* **1991**, *30*, 217−237.