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Article

Chalcogeno-urea Ligands on a Phosphadiazonium Lewis Acceptor: A New Synthetic Approach to Ch–P Bonds (Ch = O, S, Se)

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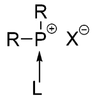
The isolation and characterization of the first intermolecular chalcogeno-urea complexes of iminophosphines are described. Trifluoromethylsulfonyloxy(2,4,6-tri-*tert*-butylphenylimino)phosphine, Mes*NPOTf, reacts quantitatively with chalcogenoimidazolines (ChIm, Ch = O, S, Se) and 1,3-dimethyldiphenylurea (OU) to give Lewis acid–base complexes, [Mes*NP•ChIm]OTf and [Mes*NP•OU]OTf. Single crystal X-ray diffraction studies indicate that the closest contact of the chalcogeno-urea donor occurs at phosphorus in all cases, representing compounds that contain examples of O–P, S–P, and Se–P coordinate bonds. In all complexes, coordination of the ligand causes significant displacement of the OTf anion, and the resulting cations $[\text{Mes*NP}\bullet\text{L}]^+$ are best described as complexes of a neutral ligand on a phosphadiazonium Lewis acceptor. As such, the complex ions $[\text{Mes*NP}\bullet\text{L}]^+$ are novel examples of cationic systems containing dicoordinate phosphorus centers. The complexes 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.

Introduction

The ligand designation used for phosphines in coordination chemistry is restrictive in the context of the developing chemistry of phosphorus(III) compounds as Lewis acids.[1−20] For phosphines bearing a sufficiently good leaving group (X), Lewis bases can effect nucleophilic displacement of an anion (X^-) with consequential formation of a cationic species involving a tricoordinate phosphorus(III) environment, **1**. The resulting donor−acceptor interactions are viewed as complexes of a neutral ligand on a phosphenium cation, and there are representative examples of arsenium[21,22] and stibenium[23] analogues.



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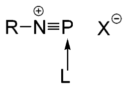

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We have now exploited this type of reaction to develop a series of cations containing dicoordinate phosphorus centers,

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(1) Burford, N.; Ragogna, P. J. *J. Chem. Soc., Dalton Trans.* **2002**, 4307−4315.
(2) Schultz, C. W.; Parry, R. W. *Inorg. Chem.* **1976**, *15*, 3046−3050.
(3) 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.
(4) Kuhn, N.; Göhner, M. *Z. Anorg. Allg. Chem.* **1999**, *625*, 1415−1416.
(5) Reed, R.; Réau, R.; Dahan, F.; Bertrand, G. *Angew. Chem.* **1993**, *105*, 464−465; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 399−401.
(6) Thomas, M. G.; Schultz, C. W.; Parry, R. W. *Inorg. Chem.* **1977**, *16*, 994−1001.
(7) Schmidpeter, A.; Lochschmidt, S.; Sheldrick, W. S. *Angew. Chem.* **1982**, *93*, 72−73; *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 63−64.
(8) Schmidpeter, A.; Lochschmidt, S.; Sheldrick, W. S. *Angew. Chem.* **1985**, *97*, 214−215; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 226−227.
(9) Shagvaleev, F., Sh.; Zykova, T. V.; Tarasova, R. I.; Sitdikova, T. Sh.; Moskva, V. V. *Zh. Obshch. Khim.* **1990**, *60*, 1775−1779.
(10) Kaukorat, T.; Neda, I.; Schmutzler, R. *Coord. Chem. Rev.* **1994**, *137*, 53−107.
(11) Bouhadir, G.; Reed, R. W.; Réau, R.; Bertrand, G. *Heteroat. Chem.* **1995**, *6*, 371−375.
(12) Alder, R. W.; Ellis, D. D.; Hogg, J. K.; Martín, A.; Orpen, A. G.; Taylor, P. N. *J. Chem. Soc., Chem. Commun.* **1996**, 537−538.
(13) Alder, R. W.; Ellis, D. D.; Orpen, A. G.; Taylor, P. N. *J. Chem. Soc., Chem. Commun.* **1996**, 539−540.
(14) Burford, N.; Losier, P.; Phillips, A. D.; Ragogna, P. J.; Cameron, T. S. *Inorg. Chem.* **2003**, *42*, 1087−1091.
(15) Gudat, D. *Coord. Chem. Rev.* **1997**, *163*, 71−106.

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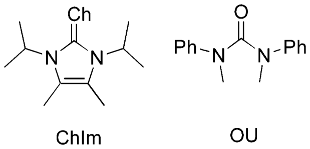
2. The iminophosphine Mes*NPOTf[24] (Mes* = 2,4,6-tri-*tert*-butylphenyl, OTf = OSO_2CF_3, trifluoromethanesulfonate) reacts with chalcogenoimidazolines (ChIm)[25-27] or 1,3-dimethyldiphenylurea (OU) to give ligand stabilized phosphadiazonium cations, which highlight a versatile new synthetic approach to the formation of Ch−P bonds.



ChIm
Ch = O, S, Se, Te

OU

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.[28] 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 using a syringe.

Solvents were dried and degassed using three freeze−pump−thaw cycles prior to use. Benzene 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 was dried over calcium hydride.

The following compounds were synthesized according to literature procedures: trifluoromethylsulfonyloxy-(2,4,6-tri-*tert*-butylphenylimino)phosphine (Mes*NPOTf),[24] 1,3-diisopropyl-4,5-dimethylimidazole-2(3*H*)-thione (SIm),[25] 1,3-diisopropyl-4,5-dimethylimidazole-2(3*H*)-selenone (SeIm),[26] and 1,3-diisopropyl-4,5-dimethylimidazole-2(3*H*)-tellurone (TeIm).[27] All other chemicals and reagents were obtained from Aldrich and used as received.

Samples for analysis by solution NMR spectroscopy were prepared in 5 mm (o.d.) flame-sealed Pyrex glass tubes. Chemical shifts are reported in ppm relative to a reference standard [100% $SiMe_4$ (^1H, ^{13}C), 10% CF_3Cl (^{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; ^{13}C, CD_2Cl_2, 54.00 ppm). Solution ^1H, ^{13}C, ^{19}F, and ^{31}P NMR spectra were collected at room temperature on a Bruker AC-250 NMR spectrometer. 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 AMX-400 NMR spectrometer.

Infrared spectra were collected on samples prepared as Nujol mulls on CsI plates using a Nicolet 510P FT-IR spectrometer. 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 using an electrothermal apparatus. Chemical analyses were performed by Beller Laboratories, Göttingen, Germany.

X-ray Crystallography. Crystals for single crystal X-ray diffraction studies were obtained by liquid−liquid diffusion. Approximately 50−100 mg of sample was dissolved in a small amount of solvent (CH_2Cl_2, 2−4 mL) in a 150 mm (14 mm o.d.) glass tube. A second solvent (hexane, 60−100 mL) was layered on to the solution using a syringe. The sealed tube (Ar) was left undisturbed for several weeks at room temperature. After deposition of crystals, the solution 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 a Rigaku AFC5R diffractometer equipped with a rotating anode source (SIm) or a Bruker P4/RA (P4 four-circle) diffractometer equipped with a rotating anode generator and a SMART 1000 CCD detector (all other structures).

All measurements were made with graphite monochromated Mo Kα radiation. The data were collected at room temperature (SIm) or 193 K (others) and were corrected for Lorentz and polarization effects. Absorption corrections were also applied to each structure. A secondary extinction parameter was refined for all structures save [Mes*NP·OU]OTf and [Mes*NP·SIm]OTf. 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.[29] Non-hydrogen atoms were refined anisotropically, except in the case of the solvent molecule in the structure of [Mes*NP·OIm]-OTf where the carbon atoms were left isotropic. Hydrogen atoms were included in geometrically calculated positions but were not refined. Disorder was encountered in several of the structures and was modeled by splitting the atoms in question over two positions each with 50% occupancy (SIm, isopropyl group; [Mes*NP·SeIm]-OTf, CF_3 group of OTf and ^{t}Bu group of Mes*; [Mes*NP·OIm]-OTf, solvent and ^{t}Bu group of Mes*). 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.

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(16) Burford, N.; Cameron, T. S.; LeBlanc, D. J.; Losier, P.; Sereda, S.; Wu, G. *Organometallics* **1997**, *16*, 4712−4717.

(17) Plack, V.; Münchenberg, J.; Thönnessen, H.; Jones, P. G.; Schmutzler, R. *Eur. J. Inorg. Chem.* **1998**, 865−875.

(18) Abrams, M. B.; Scott, B. L.; Baker, R. T. *Organometallics* **2000**, *19*, 4944−4956.

(19) Burford, N.; Cameron, T. S.; Robertson, K. N.; Phillips, A. D.; Jenkins, H. A. *J. Chem. Soc., Chem. Commun.* **2000**, 2087−2088.

(20) 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.

(21) Burford, N.; Parks, T. M.; Royan, B. W.; Borecka, B.; Cameron, T. S.; Richardson, J. F.; Gabe, E. J.; Hynes, R. *J. Am. Chem. Soc.* **1992**, *114*, 8147−8153.

(22) Burford, N.; Parks, T. M.; Bakshi, P. K.; Cameron, T. S. *Angew. Chem.* **1994**, *106*, 1332−1333; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1267−1268.

(23) Althaus, H.; Breunig, H. J.; Lork, E. *J. Chem. Soc., Chem. Commun.* **1999**, 1971−1972.

(24) Niecke, E.; Detsch, R.; Nieger, M.; Reichert, F.; Schoeller, W. W. *Bull. Soc. Chim. Fr.* **1993**, *130*, 25−31.

(25) Kuhn, N.; Kratz, T. *Synthesis* **1993**, 561−562.

(26) Kuhn, N.; Henkel, G.; Kratz, T. *Z. Naturforsch.* **1993**, *48b*, 973−977.

(27) Kuhn, N.; Henkel, G.; Kratz, T. *Chem. Ber.* **1993**, *126*, 2047−2049.

(28) Burford, N.; Muller, J.; Parks, T. M. *J. Chem. Educ.* **1994**, *71*, 807−809.

(29) Sheldrick, G. M. *SHELX-97*, version 97-2; University of Göttingen: Göttingen, Germany, 1997.

Table 1. Crystallographic Data for [Mes*NP·OIm]OTf, [Mes*NP·OU]OTf, [Mes*NP·SIm]OTf, SIm, and [Mes*NP·SeIm]OTf

	[Mes*NP·OIm]OTf·$(C_7H_8)_{0.5}$	[Mes*NP·OU]OTf	[Mes*NP·SIm]OTf	SIm	[Mes*NP·SeIm]OTf
formula	$C_{33.50}H_{53}F_3N_3O_4PS$	$C_{34}H_{45}F_3N_3O_4PS$	$C_{30}H_{49}F_3N_3O_3PS_2$	$C_{5.50}H_{10}NS_{0.50}$	$C_{30}H_{49}F_3N_3O_3PSSe$
molar mass	681.82	679.76	651.81	106.18	698.71
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	$C2/c$	$P2_1/c$
color	orange	orange	orange	colorless	orange
a/Å	9.5517(12)	24.569(2)	19.8669(14)	10.024(7)	19.8797(13)
b/Å	30.214(4)	11.2697(10)	10.4930(7)	11.298(7)	10.5398(7)
c/Å	13.180(2)	13.5349(12)	18.2872(14)	11.358(7)	18.0832(11)
α/deg	90	90	90	90	90
β/deg	95.816(3)	103.611(2)	114.911(2)	102.63(5)	113.840(1)
γ/deg	90	90	90	90	90
V/Å^3	3784.1(8)	3642.4(6)	3457.5(4)	1255(1)	3465.6(4)
T/K	193(2)	193(2)	193(2)	293(2)	193(2)
Z	4	4	4	8	4
R^a ($I > 2\sigma(I)$, all data)	0.0749, 0.2061	0.0491, 0.0615	0.0503, 0.0929	0.0433, 0.2557	0.0409, 0.0835
wR2^b ($I > 2\sigma(I)$, all data)	0.1656, 0.2111	0.1342, 0.1445	0.1229, 0.1386	0.1168, 0.1833	0.0827, 0.0924
GOF^c	0.882	1.020	0.929	0.936	0.881
$\Delta\rho$ max and min/e Å^{-3}	+ 0.500, −0.509	+ 0.530, −0.365	+ 0.365, −0.360	+ 0.177, −0.147	+ 0.398, −0.415

[a] $R = (\sum|F_o| - |F_c|)/(\sum|F_o|)$. [b] $wR2 = [(\sum w(F_o^2 - F_c^2)^2)/(\sum w(F_o^2)^2)]^{1/2}$. [c] $GOF = [(\sum w(F_o^2 - F_c^2)/(n - p)]^{1/2}$, where n = number of reflections, and p = number of parameters.

Preparation, Isolation and Characterization Data. 1,3-Diisopropyl-4,5-dimethyl-1,3-dihydro-2*H*-imidazol-2-one (OIm). 1,3-Diisopropylurea (0.96 g, 6.7 mmol) was combined with 3-hydroxy-2-butanone (0.61 g, 6.9 mmol) and 1-hexanol (10 mL) and heated at reflux for 12 h. After cooling to room temperature, the solvent was removed under reduced pressure (6 Torr) to leave a brown oil. Addition of *n*-hexane (15 mL) and its removal under reduced pressure (4.5 Torr) left a white solid (0.39 g, 2.0 mmol, 30%) that was sublimed under static vacuum. NMR: ^{1}H 1.3 (d, $^3J_{HH}$ = 7 Hz, 12H), 2.0 (s, 6H), 4.2 (septet, $^3J_{HH}$ = 7 Hz, 2H); ^{13}C{^{1}H} 9 (s) 21 (s), 42 (s), 113 (s), 152 (s). Isolation of OIm is difficult to reproduce, which has precluded isolation and comprehensive characterization of bulk samples of the complex.

[Mes*NP·OIm]OTf. A solution of OIm (0.11 g, 0.57 mmol) in benzene (10 mL) was added to a solution of Mes*NPOTf (0.25 g, 0.57 mmol) in benzene (30 mL) over a period of 20 min with stirring. The solvent was removed from the orange solution in vacuo leaving an orange-red oil. Addition of *n*-hexane (10 mL) resulted in precipitation of an orange solid, which was separated by decanting, washed with *n*-hexane (10 mL), and characterized as $C_{30}H_{49}F_3N_3O_4PS$ (0.28 g, 0.42 mmol, 74%). Crystals were obtained by liquid−liquid diffusion (see X-ray crystallography), mp 130 °C. IR: 1599(23), 1554(7), 1497(6), 1484(9), 1395(12), 1366(8), 1315(14), 1272(2), 1261(3), 1221(10), 1199(11), 1172(16), 1153(4), 1114(15), 1098(22), 1028(5), 1003(19), 906(17), 879(20), 872(21), 652(13), 637(1), 516(18). NMR: ^{1}H 1.3 (s, 9H), 1.5 (s, 18H), 1.6 (d, $^3J_{HH}$ = 7 Hz, 12H), 2.3 (s, 6H), 4.6 (septet, $^3J_{HH}$ = 7 Hz, 2H), 7.5 (d, $^5J_{PH}$ = 1 Hz, 2H); ^{13}C{^{1}H} 10 (s), 22 (s), 30 (s), 31 (s), 34 (s), 36 (s), 50 (s), 121 (q, $^1J_{FC}$ = 319 Hz), 123 (s), 129 (s), 135 (d, $^2J_{PC}$ = 39 Hz), 142 (s), 148 (d, $^3J_{PC}$ = 10 Hz), 153 (d, $^5J_{PC}$ = 1 Hz); ^{19}F{^{1}H} −78.8 (s, $^1J_{FC}$ = 319 Hz); ^{31}P{^{1}H} 77 (s).

[Mes*NP·OU]OTf. A solution of OU (0.24 g, 1.0 mmol) in benzene (15 mL) was added to a solution of Mes*NPOTf (0.44 g, 1.0 mmol) in benzene (20 mL) over a period of 5 min with stirring. The solvent was removed from the orange solution in vacuo leaving an orange oil. Addition of *n*-hexane (20 mL) resulted in precipitation of an orange solid, which was separated by decanting, washed with *n*-hexane (20 mL), and characterized as $C_{34}H_{45}F_3N_3O_4PS$ (0.41 g, 0.61 mmol, 61%). Crystals were obtained by liquid−liquid diffusion (see X-ray crystallography) and were spectroscopically identical to the powder, mp 147 °C. Anal. Calcd for 679.76 g/mol (Found): C 60.1 (58.6), H 6.7 (6.8), N 6.2 (5.8)%. IR: 1673(15), 1600(12), 1563(11), 1495(6), 1405(5), 1300(8), 1280(2), 1247(1), 1224(7), 1174(10), 1157(4); 1129(14), 1109(16), 1079 (19), 1029(3), 1003(22), 941(20), 879(23), 753(21), 740(17), 712(13), 694(18), 638(9), 517(24). Raman: 3067(3), 3007(11), 2964(2), 2929(4), 2907(5), 2879(7), 1600(6), 1513(1), 1481(9), 1294(13), 1029(12), 1003(8), 123(10). NMR: ^{1}H 1.3 (s, 9H), 1.4 (s, 18H), 3.3 (s, 6H), 7.3−7.5 (m, 12H); ^{13}C{^{1}H} 30 (s), 31 (s), 34 (s), 35.8 (s), 36.2 (s), 37 (s), 43 (s), 121 (q, $^1J_{FC}$ = 320 Hz), 123 (s), 124 (s), 127 (s), 129 (s), 131 (s), 134 (d, $^2J_{PC}$ = 42 Hz), 143 (s), 147 (d, $^3J_{PC}$ = 10 Hz), 152 (d, $^5J_{PC}$ = 7 Hz), 160 (s); ^{19}F{^{1}H} −78.6 (s); ^{31}P{^{1}H} 62 (s); CP-MAS ^{31}P 73.

[Mes*NP·SIm]OTf. A solution of SIm (0.14 g, 0.68 mmol) in benzene (10 mL) was added to a solution of Mes*NPOTf (0.30 g, 0.68 mmol) in benzene (20 mL) over a period of 40 min with stirring. The solvent was removed from the red solution in vacuo giving a pink solid, which was separated by decanting, washed with benzene (20 mL), and characterized as $C_{30}H_{49}F_3N_3O_3PS_2$ (0.23 g, 0.35 mmol, 52%). Crystals were obtained by liquid−liquid diffusion (see X-ray crystallography) and were spectroscopically identical to the powder; mp 161 °C. Anal. Calcd for 651.81 g/mol (Found): C 55.3 (54.2), H 7.6 (7.5), N 6.5 (6.2)%. IR: 1598(11), 1417(7), 1394(8), 1365(4), 1266(1), 1223(6), 1147(5), 1113(10), 1090(13), 1061(15), 1031(2), 978(18), 884(17), 751(14), 638(3), 517(12), 371(9), 303(16). Raman: 2969(6), 2931(7), 1597(2), 1452(1), 1412(4), 1363(3), 1292(5), 1136(8), 1061(9), 117(10). NMR: ^{1}H 1.3 (s, 9H), 1.5 (s, 18H), 1.6 (d, 12H, $^3J_{HH}$ = 7 Hz), 2.4 (s, 6H), 5.2 (septet, 2H, $^3J_{HH}$ = 7 Hz), 7.5 (d, 2H, $^5J_{PH}$ = 1 Hz); ^{13}C{^{1}H} 11 (s), 22 (s), 31 (d, $^5J_{PC}$ = 2 Hz), 31 (s), 34 (d, $^4J_{PC}$ = 3 Hz), 36 (d, $^6J_{PC}$ = 1 Hz), 53 (s), 121 (q, $^1J_{FC}$ = 319 Hz), 123 (d, $^4J_{PC}$ = 3 Hz), 129 (s), 130 (s), 138 (d, $^2J_{PC}$ = 41 Hz), 145 (d, $^3J_{PC}$ = 12 Hz), 153 (d, $^5J_{PC}$ = 7 Hz); ^{19}F{^{1}H} −78.8 (s); ^{31}P{^{1}H} 156 (s); CP-MAS ^{31}P 165.

[Mes*NP·SeIm]OTf. A solution of SeIm (0.18 g, 0.69 mmol) in benzene (15 mL) was added to a solution of Mes*NPOTf (0.30 g, 0.68 mmol) in benzene (20 mL) over a period of 25 min with stirring. The solvent was removed from the red solution in vacuo giving a red solid, which was separated by decanting, washed with benzene (20 mL), and characterized as $C_{30}H_{49}F_3N_3O_3PSSe$, (0.23 g, 0.33 mmol, 48%). Crystals were obtained by liquid−liquid diffusion (see X-ray crystallography) and were spectroscopically identical to the powder; mp 139 °C. Anal. Calcd for 698.71 g/mol (Found): C 51.6 (51.9), H 7.1 (6.8), N 6.0 (6.0)%. IR: 1597(11), 1413(7), 1393(9), 1364(5), 1265(1), 1221(6), 1146(4), 1112(8), 1083(13), 1060(18), 1031(3), 972(14), 927(19), 904(17), 884(10),

Table 2. Selected Bond Lengths (Å), Angles (deg), and Torsion Angles (deg) for [Mes*NP·OIm]OTf, [Mes*NP·OU]OTf, [Mes*NP·SIm]OTf, SIm, [Mes*NP·SeIm]OTf, and SeIm[26]

[Mes*NP·OIm]OTf		[Mes*NP·OU]OTf		[Mes*NP·SIm]OTf		SIm		[Mes*NP·SeIm]OTf		SeIm[26]	
P(1)−N(1)	1.494(3)	P(1)−N(1)	1.486(2)	P(1)−N(1)	1.498(2)			P(1)−N(1)	1.500(2)		
P(1)−O(1)	1.773(3)	P(1)−O(1)	1.790(2)	P(1)−S(1)	2.266(1)			P(1)−Se(1)	2.407(9)		
P(1)−O(4)	2.774(4)	P(1)−O(4)	2.942(3)								
N(2)−C(19)	1.330(5)	N(2)−C(19)	1.331(3)	N(2)−C(19)	1.346(3)	N(1)−C(1)	1.357(4)	N(2)−C(19)	1.345(3)	N(1)−C(1)	1.357(3)
N(3)−C(19)	1.336(5)	N(3)−C(19)	1.334(3)	N(3)−C(19)	1.358(3)	N(1A)−C(1)	1.357(4)	N(3)−C(19)	1.355(3)	N(1A)−C(1)	1.357(3)
N(1)−C(1)	1.404(5)	N(1)−C(1)	1.405(3)	N(1)−C(1)	1.382(3)			N(1)−C(1)	1.381(3)		
O(1)−C(19)	1.342(5)	O(1)−C(19)	1.317(3)	S(1)−C(19)	1.736(3)	S(1)−C(1)	1.690(5)	Se(1)−C(19)	1.889(3)	Se(1)−C(1)	1.853(4)
C(1)−N(1)−P(1)	159.7(3)	C(1)−N(1)−P(1)	166.2(2)	C(1)−N(1)−P(1)	174.4(2)			C(1)−N(1)−P(1)	175.5(2)		
N(1)−P(1)−O(1)	107.5(2)	N(1)−P(1)−O(1)	105.72(9)	N(1)−P(1)−S(1)	114.11(9)			N(1)−P(1)−Se(1)	115.35(9)		
N(2)−C(19)−N(3)	110.9(4)	N(2)−C(19)−N(3)	122.9(2)	N(2)−C(19)−N(3)	107.5(2)	N(1)−C(1)−N(1A)	106.3(4)	N(2)−C(19)−N(3)	108.1(2)	N(1)−C(1)−N(1A)	106.4(3)
C(19)−O(1)−P(1)	120.5(3)	C(19)−O(1)−P(1)	124.8(13)	C(19)−S(1)−P(1)	91.78(9)			C(19)−Se(1)−P(1)	88.29(8)		
N(2)−C(19)−O(1)	126.0(4)	N(2)−C(19)−O(1)	120.5(2)	N(2)−C(19)−S(1)	125.6(2)	N(1)−C(1)−S(1)	126.9(2)	N(2)−C(19)−Se(1)	125.4(2)	N(1)−C(1)−Se(1)	126.8(1)
N(3)−C(19)−O(1)	123.1(4)	N(3)−C(19)−O(1)	116.6(2)	N(3)−C(19)−S(1)	126.7(2)	N(1A)−C(1)−S(1)	126.9(2)	N(3)−C(19)−Se(1)	126.4(2)	N(1A)−C(1)−Se(1)	126.8(1)
P(1)−O(1)−C(19)−N(2)	60.7(5)	P(1)−O(1)−C(19)−N(2)	−44.2(3)	P(1)−S(1)−C(19)−N(2)	−97.0(2)			P(1)−Se(1)−C(19)−N(2)	97.8(2)		
P(1)−O(1)−C(19)−N(3)	−120.4(4)	P(1)−O(1)−C(19)−N(3)	136.2(2)	P(1)−S(1)−C(19)−N(3)	77.4(2)			P(1)−Se(1)−C(19)−N(3)	−76.3(2)		
N(1)−P(1)−O(1)−C(19)	170.4(3)	N(1)−P(1)−O(1)−C(19)	−178.6(2)	N(1)−P(1)−S(1)−C(19)	168.6(1)			N(1)−P(1)−Se(1)−C(19)	−171.9(1)		
C(1)−N(1)−P(1)−O(1)	−5.3(10)	C(1)−N(1)−P(1)−O(1)	14.4(8)	C(1)−N(1)−P(1)−S(1)	−148(2)			C(1)−N(1)−P(1)−Se(1)	148(3)		

775(16), 751(12), 637(2), 571(20) 516(15). Raman: 2995(8), 2970(3), 2932(4), 2882(9), 1597(2), 1451(1), 1412(7), 1376(11), 1357(5), 1284(6), 1204(12), 1136(9), 1061(10), 1031(13), 286(14). NMR: ^{1}H 1.3 (s, 9H), 1.4 (s, 18H), 1.6 (d, 12H, $^{3}J_{HH} = 7$ Hz), 2.5 (s, 6H), 5.2 (m, 2H, $^{3}J_{HH} = 7$ Hz), 7.4 (d, $^{5}J_{PH} = 1$ Hz); ^{13}C{^{1}H} 11 (s), 22 (s), 30 (s), 31 (s), 36 (s), 36 (s), 55 (s), 121 (q, $^{1}J_{FC} = 321$ Hz), 123 (s), 129 (s), 131 (s), 138 (d, $^{2}J_{PC} = 32$ Hz), 145 (d, $^{3}J_{PC} = 12$ Hz), 154 (d, $^{5}J_{PC} = 7$ Hz); ^{19}F{^{1}H} −78.7 (s); ^{31}P{^{1}H} 181; CP-MAS ^{31}P 195.

Mes*NPOTf + TeIm. A solution of TeIm (0.09 g, 0.30 mmol) in benzene (25 mL) was added to a solution of Mes*NPOTf (0.13 mg, 0.31 mmol) in benzene (20 mL) over a period of 1 h with stirring. The reaction mixture was filtered through a fine frit to give a purple solution and black precipitate. NMR reaction mixture: ^{31}P{^{1}H} 350 assigned to [Mes*NP·Im]OTf.[20]

Results and Discussion

Many low oxidation state nonmetal centers exhibit substantial Lewis acidity despite the presence of nonbonding electrons (lone pairs). Phosphines, as “classic” ligands, are perhaps the most interesting Lewis acids, and their acceptor ability offers a versatile new synthetic approach in phosphorus chemistry, demonstrated here by the isolation and characterization of the first intermolecular chalcogeno-urea complexes of an iminophosphine.

Mes*NPOTf reacts rapidly at room temperature with chalcogenoimidazolines (ChIm, Ch = O, S, Se) and 1,3-dimethyldiphenylurea (OU). Solution ^{31}P NMR spectra of the reaction mixtures show primary components (>90%) that correspond to the isolated products characterized as [Mes*NP·ChIm]OTf and [Mes*NP·OU]OTf, respectively. Attempts to synthesize [Mes*NP·TeIm]OTf using similar procedures resulted in precipitation of a black solid that is speculated to be elemental tellurium, and a signal in the ^{31}P NMR spectrum of the reaction mixture is assigned to the previously reported carbene complex, [Mes*NP·Im]OTf.[20]

The solid state structures of [Mes*NP·ChIm]OTf (Ch = O, S, Se) and [Mes*NP·OU]OTf (Table 1) confirm their formulations as adducts of Mes*NPOTf. As shown in Figure 1 and quantified in Table 2, the closest contact of the donor occurs at phosphorus in all cases, so that the structures represent compounds that contain examples of O−P, S−P, and Se−P coordinate bonds. The trifluoromethanesulfonate unit is structurally similar in each complex but is modified from that in the starting iminophosphine,[24] presumably due to the significant displacement of the anion [OTf]$^{-}$ from the cation [Mes*NP·L]$^{+}$. In the case of [Mes*NP·SIm]OTf and [Mes*NP·SeIm]OTf, the closest P−OTf contacts are greater than the sum of the van der Waals radii (P−O = 3.3 Å), and the P−OTf contacts for [Mes*NP·OIm]OTf and [Mes*NP·OU]OTf [2.774(4) Å and 2.942(3) Å, respectively] are substantially greater than in the free acid [Mes*NPOTf, P−O 1.923(3) Å].[24] Accordingly, we assign an ionic formulation to all adducts and consider them ligand stabilized phosphadiazonium salts. In this context, the complexes are distinct from the phosphadiazonium dichalcogenophosphinate

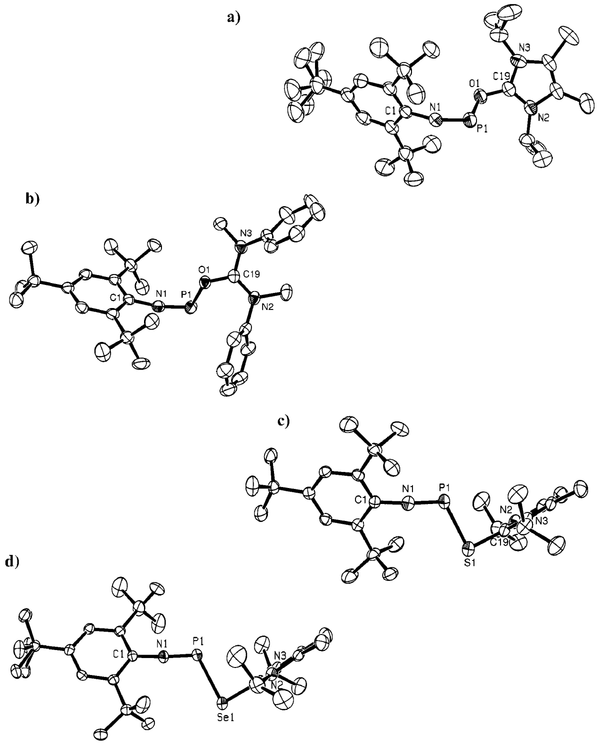

Figure 1. Structural view of the cation in the solid state structures of (a) [Mes*NP·OIm]OTf, (b) [Mes*NP·OU]OTf, (c) [Mes*NP·SIm]OTf, and (d) [Mes*NP·SeIm]OTf drawn with 50% probability displacement ellipsoids. Hydrogen atoms have been omitted for clarity. The *p-tert*-butyl group of the Mes* substituent is disordered between two positions in [Mes*NP·OIm]-OTf and [Mes*NP·SeIm]OTf.

salts [Mes*NP][$S_2P(^tBu)_2$][30] and [Mes*NP][$Se_2P(^tBu)_2$],[31] which exhibit long P−Ch cation−anion contacts.

A consistently short N(1)−P(1) bond length is observed for all complexes [OIm, N−P 1.494(3) Å; OU, N−P 1.486(2) Å; SIm, N−P 1.498(2) Å; SeIm, N−P 1.500(2) Å]. It is only slightly longer than that in the free acceptor [N−P 1.467(4) Å],[24] and much less than that observed for the carbene complex, [Mes*NP·Im]OTf [N−P 1.574(4) Å].[20] Retention of N−P multiple bonding in the complexes is also evidenced by the intense band observed in the Raman spectra at approximately 1450 cm^{-1}.[32] The C(1)−N(1)−P(1) angles [OIm, C−N−P 159.7(3)°; OU, C−N−P 166.2(2)°; SIm, C−N−P 174.4(2)°; SeIm, C−N−P 175.5(2)°] are all more acute than that of the free Lewis acid Mes*NPOTf [C−N−P 176.4(3)°].[24] However, the angular adjustments on coordination of ChIm and OU are not as dramatic as that observed for coordination of the carbene in [Mes*NP·Im]OTf [C−N−P 116.2(3)°].[20]

A summary of N−P bond lengths and C−N−P bond angles for all reported complexes [Mes*NP·L]OTf is presented in Table 3. It is clear that in most cases the ligand causes little distortion in the Mes*NPOTf framework; the complexes retain very short N−P bond lengths and large C−N−P angles. [Mes*NP·Im]OTf is anomalous with a long N−P bond and a narrow angle at nitrogen, which may be related to the relatively high basicity of the ligand (cf. pK_a $ImH^+ = 24$,[33] pK_a pyridine$H^+ = 5.8$[34]).

Table 3. Selected Bond Lengths (Å) and Angles (deg) in Complexes [Mes*NP·L]OTf

ligand (L)	N(1)−P(1)	P(1)−OTf	C(1)−N(1)−P(1)	ref
none	1.467(4)	1.923(3)	176.4(3)	24
pyridine	1.472(8)	2.712(7)	161.7(7)	14
PPh_3	1.486(4)	2.298(4)	169.5(4)	44
OU	1.486(2)	2.942(3)	166.2(2)	this work
OIm	1.494(3)	2.774(4)	159.7(3)	this work
2,2′-bipyridine	1.497(4)		169.4(4)	19
SIm	1.498(2)		174.4(2)	this work
SeIm	1.500(2)		175.5(2)	this work
quinuclidine	1.519(2)	2.697(3)	143.9(2)	14
Im	1.574(4)	2.952(5)	116.2(3)	20

The structural features of the imidazole fragments in all [Mes*NP·ChIm]OTf compounds are identical to, or differ only slightly from, those of the corresponding free ligands. Coordination effects slight elongation of the C−Ch bonds [C−S, 1.736(3) Å, cf. 1.690(5) Å; C−Se, 1.889(3) Å, cf. 1.853(4) Å[26]], which are shorter than typical C−Ch single bonds [C−S, 1.819(19) Å; C−Se,1.970(32) Å][35] and identical to those reported for ChIm−pentacarbonylchromium complexes [SIm 1.737(5) Å; SeIm 1.892(17) Å].[36]

Solid state structures of OIm and OU have not been determined, but the crystal structures of tetramethylurea [C−O 1.226(2) Å],[37] 1,3-diethyldiphenylurea [C−O 1.217(6) Å],[38] and related cyclic saturated ureas [e.g., $OC(NCH)CH_2)_2$ C−O 1.262(4) Å][39,40] provide a database of C−O bonds that are substantially shorter than those in [Mes*NP·OIm]OTf [1.342(5) Å] and [Mes*NP·OU]OTf [1.317(3) Å]. The C−O bond lengths in [Mes*NP·OIm]OTf and [Mes*NP·OU]OTf are closer in length to the value observed in the tetramethylurea−$AlCl_3$ complex [C−O 1.302(3) Å].[41] The OU ligand has previously been used in the coordination chemistry of the actinide elements thorium and uranium. The OU complexes $Th(OU)_3Cl_4$,[42] $U(OU)_2Cl_4$,[43] and $U(OU)_2Br_4$[43] exhibit a range of C−O bond lengths [1.24(1)−1.31(2) Å].[42,43]

The P−Ch bonds in [Mes*NP·ChIm]OTf [P−O 1.773(3) Å; P−S 2.266(1) Å; P−Se 2.407(1) Å] are longer than those

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(30) Niecke, E. In *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O. J., Eds.; Georg Thieme Verlag: New York, 1990; pp 293−320.

(31) Niecke, E.; Nieger, M.; Reichert, F.; Schoeller, W. W. *Angew. Chem.* **1988**, *100*, 1779−1780; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1713−1716.

(32) Burford, N.; Clyburne, J. A. C.; Silvert, D.; Warner, S.; Whitla, W. A.; Darvesh, K. V. *Inorg. Chem.* **1997**, *36*, 482−484.

(33) Alder, R. W.; Allen, P. R.; Williams, S. J. *J. Chem. Soc., Chem. Commun.* **1995**, 1267−1268.

(34) Benoit, R. L.; Mackinnon, M. J.; Bergeron, L. *Can. J. Chem.* **1981**, *59*, 1501−1504.

(35) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin. Trans. 2* **1987**, S1−S19.

(36) Kuhn, N.; Fawzi, R.; Kratz, T.; Steimann, M.; Henkel, G. *Phosphorus, Sulfur Silicon Relat. Elem.* **1996**, *108*, 107−119.

(37) Frampton, C. S.; Parkes, K. E. B. *Acta Crystallogr.* **1996**, *C52*, 3246−3248.

(38) Ganis, P.; Avitabile, G.; Benedetti, E.; Pedone, C.; Goodman, M. *Proc. Natl. Acad. Sci. U.S.A.* **1970**, *67*, 426−433.

(39) Kapon, M.; Reisner, G. M. *Acta Crystallogr.* **1989**, *C45*, 780−782.

(40) Ueda, H.; Onishi, H.; Nagai, T. *Acta Crystallogr.* **1986**, *C42*, 462−464.

(41) Bittner, A.; Männig, D.; Nöth, H. *Z. Naturforsch.* **1986**, *41b*, 587−591.

(42) Bagnall, K. W.; Al-Daher, A. G. M.; Bombieri, G.; Benetollo, F. *Inorg. Chim. Acta* **1986**, *115*, 229−236.

(43) de Wet, J. F.; Caira, M. R. *J. Chem. Soc., Dalton Trans.* **1986**, 2035−2041.

in typical tris(chalcogeno)phosphines [e.g., $P(OC_6H_4OMe\text{-}2)_3$, P−O 1.624(4) Å;[45] $P(SC_6H_5)_3$, P−S 2.122(1) Å;[46] $P(SeC_6H_5)_3$, P−Se 2.271(2) Å[47]] and *P*-chalcogeno-iminophosphines [e.g., Mes*NPOR, P−O 1.585(3) Å ($R = SiMe_3$) to 1.728(3) Å ($R = OSO_2C_6H_4(Me)\text{-}4$);[24;48−52] Mes*NPS^{t}Bu, P−S 2.098(1) Å[53]]. Nevertheless, the P−Ch bonds in [Mes*NP•SIm]OTf (P−S 2.266(1) Å) and [Mes*NP•SeIm]OTf (P−Se 2.407(1) Å) are substantially shorter than those in the phosphadiazonium salts [Mes*NP][$S_2P(^tBu)_2$] [P−S 2.442(2), 2.739(2) Å][30] and [Mes*NP][$Se_2P(^tBu)_2$] [P−Se 2.636(5), 2.788(5) Å],[31] as would be expected in comparing P−Ch coordinate bonds to P−Ch cation−anion contacts.

The complexes [Mes*NP•SIm]OTf and [Mes*NP•SeIm]OTf are isostructural, with nearly identical unit cell parameters. [Mes*NP•OIm]OTf and [Mes*NP•OU]OTf also exhibit similar structural and spectroscopic features distinct from those of the sulfur and selenium compounds. For instance, the P−Ch−C bond angles are substantially larger in [Mes*NP•OIm]OTf [120.5(3)°] and [Mes*NP•OU]OTf [124.8(1)°] than in [Mes*NP•SIm]OTf [91.8(1)°] and [Mes*NP•SeIm]OTf [88.3(1)°]. Moreover, the ureas OIm and OU behave as in-plane donors, while the plane of the thio- and seleno-ureas are perpendicular to the axis of the phosphadiazonium cation (Figure 1). In this context, complexes of the ureas are considered to involve σ-electrons (i.e., lone pair), while the thio- and seleno-ureas use π-electrons to interact with phosphorus, consistent with the established coordination chemistry of the chalcogen-based ligands.[54]

Conclusions

Mes*NPOTf readily forms Lewis acid−base complexes with chalcogeno-ureas to effect displacement of the OTf anion, but only minor distortion of the C−N−P iminophosphine framework. The resulting cations $[Mes^*NP{\bullet}L]^+$ are best described as complexes of a neutral ligand on a phosphadiazonium acceptor and represent a new synthetic approach to the formation of P−Ch bonds. The complexes 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.

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Supporting Information Available: Thermal ellipsoid diagrams of [Mes*NP•ChIm]OTf (Ch = O, S, Se) and [Mes*NP•OU]OTf, and crystallographic information files (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(44) 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.

(45) Baker, M. J.; Harrison, K. N.; Orpen, A. G.; Pringle, P. G.; Shaw, G. *J. Chem. Soc., Dalton Trans.* **1992**, 2607−2614.

(46) Keder, N. L.; Shibao, R. K.; Eckert, H. *Acta Crystallogr.* **1992**, *C48*, 1670−1671.

(47) Burford, N.; Royan, B. W.; White, P. S. *Acta Crystallogr.* **1990**, *C46*, 274−276.

(48) Chernega, A. N.; Ruban, A. V.; Romanenko, V. D. *Zh. Strukt. Khim* **1991**, *32*, 158−160.

(49) Markovskii, L. N.; Romanenko, V. D.; Ruban, A. V.; Drapailo, A. B.; Chernega, A. N.; Antipin, M. Y.; Struchkov, Y. T. *Zh. Obshch. Khim.* **1988**, *58*, 291−295.

(50) Pötschke, N.; Nieger, M.; Niecke, E. *Acta Chem. Scand.* **1997**, *51*, 337−339.

(51) Pötschke, N.; Barion, D.; Nieger, M.; Niecke, E. *Tetrahedron* **1995**, *51*, 8993−8996.

(52) Chernega, A. I.; Antipin, M. Y.; Struchkov, Y. T.; Ruban, A. V.; Romanenko, V. D. *Zh. Strukt. Khim* **1990**, *31*, 134−140.

(53) Chernega, A. N.; Antipin, M. Y.; Struchkov, Y. T.; Ruban, A. V.; Romanenko, V. D.; Markovskii, L. N. *Dokl. Akad. Nauk SSSR* **1989**, *307*, 610−612.

(54) Burford, N. *Coord. Chem. Rev.* **1992**, *112*, 1−18.