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Redox Reactions between Phosphines (R_3P; R = ^nBu, Ph) or Carbene ($^iPr_2IM$) and Chalcogen Tetrahalides ChX_4 ($^iPr_2IM$ = 2,5-diisopropylimidazole-2-ylidene; Ch = Se, Te; X = Cl, Br)

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The reactions between chalcogen tetrahalides (ChX_4; Ch = Se, Te; X = Cl, Br) and the neutral donors $^nBu_3P$, Ph_3P, or the N-heterocyclic carbene, 2,5-diisopropylimidazole-2-ylidene ($^iPr_2IM$), have been investigated. In cases involving a phosphine, the chemistry can be understood in terms of a succession of two-electron redox reactions, resulting in reduction of the chalcogen center (e.g., Se(IV) → Se(II)) and the oxidation of phosphorus to the [R_3P–X] cation (P(III) → P(V)). The stepwise reduction of Se(IV) → Se(II) → Se(0) → Se(–II) occurs upon the successive addition of stoichiometric equivalents of Ph_3P to $SeCl_4$, which can readily be monitored by $^{31}P\{^1H\}$ NMR spectroscopy. In the case of reacting SeX_4 with $^iPr_2IM$, a similar two-electron reduction of the chalcogen is observed and there is the concomitant production of a haloimidazolium hexahaloselenate salt. The products have been comprehensively characterized, and the solid-state structures of [R_3PX][SeX_3] (**9**), [Ph_3PCl]$_2$[$TeCl_6$] (**10**), $^iPr_2IM$–SeX_2 (**11**), and [$^iPr_2IM$–Cl]$_2$[$SeCl_6$] (**12**) have been determined by X-ray diffraction analysis. These data all support two electron redox reactions and can be considered in terms of the formal reductive elimination of X_2, which is sequestered by the Lewis base.

Introduction

The chemistry of the heavier main group elements ($n \geq 4$) is often dominated by their propensity for reduction to the metallic state, hampering the discovery of novel transformations involving these members of the p block. However, the tendency for p-block halides (EX_3; E = P, As; X = I, Cl; $SeCl_4$; TeI_4) to undergo reduction in the presence of diphosphine or diimine ligands has been exploited as a facile route for the formation of low-oxidation-state or low-coordinate, cationic compounds. The redox process can occur spontaneously between either neutral bifunctional donors (e.g., **1**, **2**; for P, As, Se, Te)[1−7] or *N*-heterocyclic carbenes (**3**; P, Te).[8,9] The chemistry is considered to proceed via the formal reductive elimination of X_2 (X = Cl, I), where the main group element center is reduced and the formal oxidation byproduct is the elemental halogen (e.g., in the production of **4**−**6**; Figure 1).

Analogous studies on the direct reaction between chalcogen halides and neutral, monodentate donors have largely remained unexplored. Nevertheless, one report on the reac-

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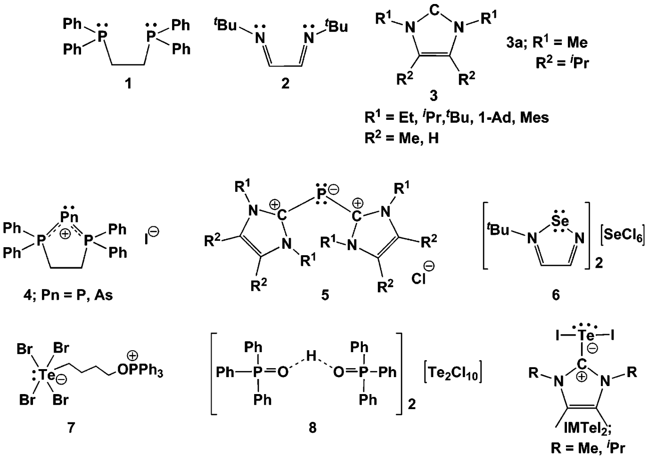
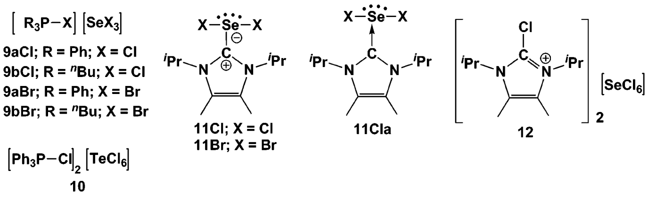


Figure 1. Compounds **1**−**3**.

tion of Ph_3P with $TeBr_4$ yielded an unusual zwitterionic square pyramidal Te center, that was bound to a ring-opened molecule of THF (**7**). In a related investigation, the reaction between TeX_4 and Ph_3P gave products indicative of $Ph_3P{=}O$ formation, which were a result of the reaction conditions (**8**). In both cases, there was no evidence for reduction at Te.[10,11] A report on the reaction between a NHC and TeI_4 alluded to the spontaneous reduction of Te(IV) to Te(II) forming a carbene−TeI_2 complex (IM−TeI_2), with the concomitant formation of I_2 as the oxidation product; however, no information on the fate of the proposed dihalide was provided.[9]

In this context, we have performed a comprehensive study on the outcome of the reaction between ChX_4 (Ch = Se; Ch = Te; X = Cl, Br) with the neutral, mondentate donors R_3P (R = ^{n}Bu, Ph) and the *N*-heterocyclic carbene 2,5-diisopropylimidazole-2-ylidene (**3a**). We report the isolation and comprehensive characterization of a variety of phosphonium halochalcogenate salts (**9**, **10**), carbene adducts of SeX_2 (**11**; ^{i}Pr$_2$IM−SeX_2), and a chloro-imidazolium hexachloroselenate salt (**12**; [^{i}Pr$_2$IM−Cl]$_2$[$SeCl_6$]). This investigation highlights the propensity of the chalcogen tetrahalides to undergo spontaneous redox reactions with neutral Lewis bases. Furthermore, the isolation of **11** and **12** strongly supports the suggestion of the reductive elimination of X_2 as the corresponding oxidation byproduct and is complementary to the already established oxidative addition chemistry of X_2 (X = Br, I) or the interhalogens ICl and IBr to phosphine selenides ($R_3P{=}Se$; R = Me_2N, Et_2N, C_6H_{11}) and thio-, seleno-, or telluroureas.[12−18]



Experimental Section

General Procedures. All manipulations were performed in an N_2-filled MBraun Labmaster 130 glove box, and all reactions were carried out in 4 dram vials affixed with Teflon-lined screw caps. Dichloromethane, THF, MeCN, C_6H_6, and toluene were obtained from Caledon Laboratories and dried using an Innovative Technology, Inc. Controlled Atmospheres solvent purification system, which utilizes dual-alumina columns. The dried solvents were stored in Strauss flasks under an N_2 atmosphere or over 4 Å molecular sieves in the glove box. Solvents for NMR spectroscopy ($CDCl_3$, C_6D_6, CD_3CN) were purchased from Cambridge Isotope Laboratories and dried by stirring for 3 days over CaH_2, distilled prior to use, and stored in the glove box over 4 Å molecular sieves.

Selenium tetrachloride $SeBr_4$, $TeCl_4$, and $TeBr_4$ were purchased from Alfa Aesar and used as received. Triphenylphosphine was purchased from Aldrich Chemical Co. and dried in vacuo for 12 h prior to use. Tri-*n*-butylphosphine was obtained from Cytec Corp. and distilled prior to use. The 2,5-diisopropylimidazole-2-ylidene (**3a**) was prepared according to literature procedures.[19]

Nuclear magnetic resonance spectra were recorded on an INOVA 400 MHz instrument unless otherwise noted (^{31}P = 161.83 MHz; ^{77}Se = 76.26 MHz; ^{125}Te = 126.12 MHz; ^{13}C = 100.52 MHz). ^{31}P NMR spectra were externally referenced to 85% H_3PO_4 ($\delta = 0.00$). Selenium-77 spectra were referenced relative to Me_2Se ($\delta = 0.00$) and $^{125}Te\{^1H\}$ NMR spectra relative to Me_2Te, using SeO_2 ($\delta = -1302$) and H_6TeO_6 ($\delta = 712$) as external reference standards, respectively.[20,21] Proton and $^{13}C\{^1H\}$ NMR spectra were referenced relative to Me_4Si using residual protons or ^{13}C nuclei in the NMR solvent (^1H: $CHCl_3$, $\delta = 7.26$; C_6HD_5, $\delta = 7.15$; CHD_2CN, $\delta = 1.96$; $^{13}C\{^1H\}$: $CDCl_3$ = 77.2). Elemental analyses were performed by Guelph Chemical Laboratories, Ltd., Guelph, Ontario, Canada.

Samples for FT-Raman spectroscopy were packed in capillary tubes and flame-sealed. Data were collected using a Bruker RFS 100/S instrument, with a resolution of 4 cm^{-1}, unless otherwise noted. FT-IR spectra were collected on samples as nujol mulls on CsI plates using a Bruker Tensor 27 instrument, with a resolution of 4 cm^{-1}. Decomposition/melting points were recorded in flame-sealed capillary tubes using a Gallenkamp Variable Heater. X-ray diffraction data (Table 1) were collected on a Bruker Nonius KappaCCD X-ray diffractometer using graphite-monochromated Mo K_α radiation ($\lambda = 0.71073$ Å). Images from scanning electron

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Table 1. Crystal Data for Compounds **9−12**

compound	**9aBr**	**9aCl**	**9bCl**	**9bBr**	**10**	**11Br**	**11Cl**	**12**
empirical formula	$C_{18}H_{15}Br_4P_1Se_1$	$C_{18}H_{15}Cl_4P_1Se_1$	$C_{12}H_{27}Cl_4PSe_1$	$C_{12}H_{27}Br_4PSe_1$	$C_{36}H_{30}Cl_8P_2Te_1$	$C_{11}H_{20}Br_2N_2Se_1$	$C_{11}H_{20}Cl_2N_2Se_1$	$C_{11}H_{20}Cl_4N_2Se_{0.5}$
fw	660.97	483.03	423.07	600.91	935.74	419.07	330.15	361.57
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	rhombohedral	monoclinic	monoclinic	monoclinic
space group	*P*2(1)/*n*	*P*2(1)/*n*	*P*2(1)/*c*	*P*2(1)/*c*	$R\bar{3}$	*C*2/*c*	*C*2/*c*	*P*2(1)/*n*
a (Å)	13.240(3)	12.882(2)	7.858(1)	8.072(2)	13.166(2)	11.043(2)	10.629(2)	9.375(2)
b (Å)	11.822(2)	11.591(2)	17.965(4)	18.365(4)	13.166(2)	12.112(1)	12.104(2)	9.678(2)
c (Å)	13.376(3)	13.140(2)	13.872(3)	14.090(3)	18.864(4)	12.120(2)	11.764(2)	18.330(4)
α (deg)	90	90	90	90	90	90	90	90
β (deg)	91.49(3)	92.445(1)	101.15(3)	100.57(3)	90	111.473(5)	108.25(3)	102.93(3)
γ (deg)	90	90	90	90	120	90	90	90
V (Å^3)	2092.8(7)	1960.2(5)	1921.4(7)	2053.3(7)	2831.6(8)	1508.6(4)	1437.4(5)	1620.8(6)
D_{calcd} (mg m^{-3})	2.098	1.637	1.462	1.944	1.646	1.845	1.526	1.482
radiation, *λ* (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
temp (K)	150(2)	183(2)	150(2)	150(2)	150(2)	150(1)	183(2)	150(2)
diffractometer	Nonius Kappa CCD							
R1[$I > 2\sigma I$]^a	0.0468	0.0604	0.0415	0.0501	0.0500	0.0627	.0261	.0484
wR2(F^2)^a	0.1045	0.1622	0.1105	0.1389	0.1203	0.1726	0.0733	0.1190
GOF (*S*)^a	1.006	1.161	1.045	0.977	1.006	0.997	1.061	1.024

[a] $R1(F[I > 2\sigma(I)]) = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2(F^2 \text{ [all data]}) = [\sum w(F_o^2 - F_c^2)^2]^{1/2}$; $S(\text{all data}) = [\sum w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = no. of data; p = no. of parameters varied; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$ and a and b are constants suggested by the refinement program.

microscopy (SEM) experiments and EDX analysis were obtained using a Hitachi S-5200, with a 30 kV, 5.5 mA beam current.

Preparation of [Ph$_3$PBr][SeBr$_3$] (9aBr). A solution of PPh$_3$ (0.066 g, 0.251 mmol; THF 5 mL) was added dropwise to a stirred suspension of SeBr$_4$ (0.100 g, 0.251 mmol; THF 5 mL), which resulted in the immediate production of a brown slurry. Further stirring at room temperature (30 min) rendered a shimmering brown precipitate. The reaction mixture was centrifuged, the supernatant decanted and the precipitate washed with THF (3 × 5 mL). The washed solids were dried in vacuo, giving **9aBr** as an iridescent brown powder; 0.101 g, 61%; d.p. = 183 °C; ^{31}P{^{1}H} NMR (CD$_3$CN; δ) 52.8; ^{77}Se{^{1}H} NMR (CD$_3$CN; δ) 1052; Anal. Calcd (Found): C, 32.70 (32.79); H 2.27 (2.20); FT-IR (cm^{-1}(ranked intensity)) 456(7), 507(1), 542(2), 613(12), 684(5), 726(4), 745(6), 853(13), 928(11), 993(8), 1103(3), 1163(9), 1581(10); FT-Raman (cm^{-1}(ranked intensity)) 89(4), 119(5), 148(6), 165(8), 210(1), 232(2), 249(3), 438(14), 541(13), 614(16), 998(9), 1027(11), 1093(12), 1165(15), 1583(10), 3055(7).

Preparation of [Ph$_3$PCl][SeCl$_3$] (9aCl). A solution of PPh$_3$ (0.059 g, 0.226 mmol; CH$_2$Cl$_2$ 2 mL) was added dropwise to a stirred slurry of SeCl$_4$ (0.050 g, 0.226 mmol; CH$_2$Cl$_2$ 2 mL), resulting in a clear orange solution. After 30 min the volatiles were removed in vacuo, giving **9aCl** as an orange powder; 0.107 g, 98%; d.p. = 197 °C; ^{31}P{^{1}H} NMR (CD$_3$CN; δ) 66.9; ^{77}Se{^{1}H} NMR (CD$_3$CN; δ) 1401; Anal. Calcd (Found): C, 44.74 (45.21); H 3.11 (3.46); FT-IR (cm^{-1}(ranked intensity)) 185(3), 294(10), 428(14), 456(12), 511(1), 590(4), 617(9), 682(5), 700(8), 726(2), 748(7), 801(16), 993(11), 1107(6), 1164(13), 1580(15); FT-Raman (cm^{-1}(ranked intensity)) 91(1), 113(2), 152(7), 180(10), 261(9), 293(4), 335(3), 464(15), 591(13), 614(14), 701(20), 998(5), 1027(11), 1098(12), 1111(17), 1167(15), 1194(18) 1584(8), 3060(6), 3083(19).

Preparation of [^{n}Bu$_3$PCl][SeCl$_3$] (9bCl). Neat ^{n}Bu$_3$P (0.091 g, 0.455 mmol) was added to a stirred slurry of SeCl$_4$ (0.100 g, 0.455 mmol; CH$_2$Cl$_2$ 5 mL), resulting in a red precipitate. After 30 min the mixture changed to a clear orange solution; the volatiles were then removed in vacuo, giving **9bCl** as a bright orange powder; 0.173 g, 90%; ^{1}H NMR (CDCl$_3$; δ) 3.05 (m, 2H), 1.74 (m, 2H), 1.62 (m, 2H), 0.99 (t, $^3J_{H-H}$ 8.4 3H); ^{13}C{^{1}H} NMR (CDCl$_3$; δ) 27.1 (d, $^1J_{C-P}$ 40.2), 23.8 (d, $^2J_{C-P}$ 6.9), 23.4 (d, $^3J_{C-P}$ 17.2), 13.6 (s); m.p. = 84−85 °C; ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$; δ) 105; ^{77}Se{^{1}H} NMR (CH$_2$Cl$_2$; δ) 1342; FT-IR (cm^{-1}(ranked intensity)) 117(3), 127(4), 135(2), 163(1), 313(5), 382(14), 457(16), 528(6), 780(13), 819(9), 913(7), 1018(11), 1090(8), 1207(12) 1261(10), 1309(15), 3281(17); FT-Raman (cm^{-1}(ranked intensity)) 82(4), 179(5), 246(10) 298(2), 333(1), 528(6), 899(9), 1050(8), 1104(11), 1315(12), 1447(7), 2869(3), 2900(14), 2915(13).

Preparation of [^{n}Bu$_3$PBr][SeBr$_3$] (9bBr). Neat ^{n}Bu$_3$P (0.162 g, 0.804 mmol) was added to a stirred slurry of SeBr$_4$ (0.320 g, 0.804 mmol; THF 3 mL), resulting in a dark brown solution. After 60 min pentane (10 mL) was added, resulting in an orange precipitate. The mixture was cooled to −30 °C for 30 min after which time the supernatant was decanted. The solids were washed with pentane (2 × 5 mL) and the volatiles removed in vacuo, giving **9bBr** as a bright orange powder; 0.340 g, 71%; ^{1}H NMR (CDCl$_3$; δ) 3.15 (m, 2H), 1.70 (m, 4H), 1.01 (t, $^3J_{H-H}$ 7.2 3H); ^{13}C{^{1}H} NMR (CDCl$_3$; δ) 26.5 (d, $^1J_{C-P}$ 36.8), 23.6 (d, $^2J_{C-P}$ 5.9), 22.3 (d, $^3J_{C-P}$ 17.3), 12.27 (s); d.p. = 79 °C; ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$; δ) 97; ^{77}Se{^{1}H} NMR (CH$_2$Cl$_2$; δ) 1073; FT-IR (cm^{-1}(ranked intensity)) 120(2), 126(14), 161(1), 203(15), 229(5), 378(19), 396(8), 448(6), 463(18), 770(17), 814(4), 914(3), 966(12), 1002(20), 1079(7), 1153(16), 1204(13), 1306(10), 2725(11); FT-Raman (cm^{-1}(ranked intensity)) 126(5), 189(2), 228(1), 380(14), 398(11), 420(16), 448(13), 896(9), 1051(7), 1102(12), 1314(10), 1389(18), 1446(6), 2060(15), 2076(17), 2865(3), 2909(4), 2957(8).

Preparation of [Ph$_3$PCl]$_2$[TeCl$_6$] (10). A solution of PPh$_3$ (0.049 g, 0.186 mmol; CH$_2$Cl$_2$ 2 mL) was added dropwise to a stirred suspension of TeCl$_4$ (0.050 g, 0.186 mmol; CH$_2$Cl$_2$ 2 mL) at RT. The reaction mixture immediately changed to a clear, orange solution, and after a further 5 min, a black precipitate formed and a metallic mirror was deposited on the reaction vessel wall. After 30 min the mixture was centrifuged, giving a green solution over a black solid. The solution was decanted and the volatiles were removed in vacuo, yielding **10** as a light green solid; 0.134 g, 77%; d.p. = 250 °C; ^{31}P{^{1}H} NMR (CD$_3$CN; δ) 66.3; ^{125}Te{^{1}H} NMR (CD$_3$CN; δ) 1438; Anal. Calcd. (Found); C, 46.19 (45.92); H 3.21 (3.47); FT-IR (cm^{-1}(ranked intensity)) 448(10), 512(2), 537(9), 578(5), 614(15), 685(3), 727(1), 756(6), 857(17), 932(12), 994(11), 1096(7), 1109(4), 1164(13), 1181(16), 1309(8), 1579(14), 1688(18); FT-Raman (cm^{-1}(ranked intensity)) 138(1), 236(3), 275(2), 318(11), 471(13), 578(10), 615(13), 998(4), 1026(8), 1094(9), 1164(12), 1581(6), 3055(5), 3072(7).

Preparation of ^{i}Pr$_2$IM−SeCl$_2$ (11Cl). A solution of ^{i}Pr$_2$IM (2,5-diisopropylimidazole-2-ylidene; 0.025 g, 0.139 mmol; THF 5 mL) was added dropwise to a stirred solution of SeCl$_4$ (0.023 g, 0.104 mmol; THF 5 mL), resulting in a yellow suspension. After the mixture was stirred at RT for 45 min, the THF was removed in vacuo to give a waxy yellow solid. Benzene (10 mL) was added to the solids, resulting in a yellow solution over a yellow residue, which was centrifuged and the supernatant decanted. The solids were washed with benzene (3 × 5 mL) and the washings were added to the 10 mL of supernatant. The benzene was removed in vacuo, giving **11Cl** as a pale yellow powder; 0.021 g; 59%; d.p. = 119 °C; ^{1}H NMR (CDCl$_3$; δ) 5.75 (sept., $^{3}J_{\mathrm{H-H}}$ 7.20, 2H), 2.40 (s, 6H), 1.69 (d, $^{3}J_{\mathrm{H-H}}$ 7.20, 12H). ^{13}C{^{1}H} NMR (CDCl$_3$; δ) 145.1, 127.9, 55.7, 15.4, 10.6; ^{77}Se{^{1}H} NMR (CDCl$_3$; δ) −266; Anal. Calcd (Found): C, 40.02 (39.82); H 6.06 (5.89); N 8.49 (8.36); FT-IR (cm^{-1}(ranked intensity)) 457(19), 543(13), 578(18), 692(15), 723(7), 752(8), 805(12), 907(6), 940(17), 971(14), 1023(9), 1114(1), 1137(4), 1154(11), 1173(10), 1215(2), 1261(5), 1616(3), 1682(16); FT-Raman (cm^{-1}(ranked intensity)) 86(2), 116(3), 252(1), 460(14), 544(17), 579(18), 789(15), 888(13), 1155(16), 1282(5), 1366(10), 1407(8), 1450(11), 1618(9), 2935(4), 2968(7), 2984(6).

Preparation of ^{i}Pr$_2$IM−SeBr$_2$ (11Br). A solution of 2,5-diisopropylimidazole-2-ylidene (0.120 g, 0.669 mmol; THF 5 mL) was added dropwise to a stirred solution of SeBr$_4$ (0.200 g, 0.502 mmol; THF 5 mL), resulting in a brown suspension. After the mixture was stirred at RT for 90 min, the THF was removed in vacuo, leaving a brown solid. Toluene (10 mL) was added to the solids to give a yellow solution over a brown residue, which was centrifuged and the supernatant decanted. The solids were washed with toluene (2 × 5 mL) and the washings were added to the 10 mL of supernatant. The toluene was removed in vacuo, giving **11Br** as a yellow powder; 0.068 g; 51%; d.p. = 235−242 °C; ^{1}H NMR (CDCl$_3$; δ) 5.72 (sept, $^{3}J_{\mathrm{H-H}}$ 6.00, 2H), 2.39 (s, 6H), 1.69 (d, $^{3}J_{\mathrm{H-H}}$ 6.00, 12H). ^{13}C{^{1}H} NMR (CDCl$_3$; δ) 141.5, 128.2, 55.7, 20.8, 10.5; ^{77}Se{^{1}H} NMR (CDCl$_3$; δ) 66; Anal. Calcd (Found): C, 31.54 (31.67); H, 6.68 (6.42); N, 4.77 (5.00)FT-IR (cm^{-1}(ranked intensity)) 226(11), 248(12), 279(13), 543(15), 722(2), 753(5), 910(6), 974(12), 1018(7), 1115(3), 1138(8), 1206(1), 1541(14), 1558(13), 1617(4); FT-Raman (cm^{-1}(ranked intensity)) 154(1), 271(5), 302(8), 431(16), 459(14), 546(17), 579(18), 673(19), 790(13), 892(12), 1155(15), 1283(2), 1366(10), 1408(6), 1451(11), 1618(9), 2939(3), 2965(7), 2983(4).

Preparation of [^{i}Pr$_2$IM−Cl]$_2$[SeCl$_6$] (12). The solids obtained and separated from the production of **11Cl** were dried in vacuo, giving **12** as a white powder; 0.025 g 33%; ^{1}H NMR (CDCl$_3$; δ) 4.89 (sept., $^{3}J_{\mathrm{H-H}}$ 4.00, 2H), 2.42 (s, 6H), 1.68 (d, $^{3}J_{\mathrm{H-H}}$ 4.00, 12H); ^{77}Se{^{1}H} NMR (CDCl$_3$; δ) 873; FT-IR (cm^{-1}(ranked intensity)) 245(1), 382(14), 465(13), 537(12), 723(6), 897(10), 1027(8), 1124(3), 1191(7), 1289(5), 1411(4), 1503(2), 1550(11), 1634(9); FT-Raman (cm^{-1}(ranked intensity)) 147(3), 244(1), 286(2), 499(6), 887(9), 1289(10), 1396(8), 1443(7), 2924(4), 2985(5). Elemental analysis consistently returned elevated values for C and H.

Monitoring the Reaction of Ph$_3$P with SeCl$_4$ by ^{31}P{^{1}H} NMR Spectroscopy. A solution of Ph$_3$P (0.036 g; 0.138 mmol; CH$_2$Cl$_2$ 1 mL) was added to a solution of SeCl$_4$ (0.031 g; 0.138 mmol; CH$_2$Cl$_2$ 1 mL) and stirred for 30 min. A 0.7 mL aliquot was transferred by pipet into an NMR tube, and the ^{31}P{^{1}H} NMR spectrum was recorded. The aliquot was returned to the reaction vial, whereupon a second stoichiometric equivalent of PPh$_3$ (0.036 g; 0.138 mmol; CH$_2$Cl$_2$ 1 mL) was added and the resulting reaction mixture stirred for an additional 45 min. The solids in the reaction mixture were allowed to settle, a 0.7 mL aliquot of the supernatant was transferred by pipet into an NMR tube, and the ^{31}P{^{1}H} NMR spectrum was obtained. This was repeated an additional two times so that a total of 4 molar equiv of Ph$_3$P was added.

Results and Discussion

Phosphines and carbenes are some of the most exploited ligands in transition metal and coordination chemistry. Both are strong two electron neutral donors that readily bind to transition metals, coordinatively unsaturated or Lewis acidic centers.[22−25] Although NHCs are known to have an established redox chemistry, phosphines are rarely considered to be effective reducing agents toward other p-block elements. The identification of the reductive ability of P(III) toward other main group acceptors such as P, As, and now Se and Te, indicates that this may be a widespread phenomenon across the p block ($n \geq 4$).

The addition of an equimolar amount of R$_3$P (R = ^{n}Bu; Ph) to SeCl$_4$ in CH$_2$Cl$_2$ at room temperature immediately results in the formation of a deep yellow-orange solution. Phosphorus-31 NMR spectra obtained from samples of the reaction mixtures reveal sharp singlets significantly downfield relative to the free phosphine and are consistent with the generation of a chlorophosphonium cation (R = ^{n}Bu, δ = 106; R = Ph, δ = 67).[26] The volatiles were removed in vacuo, leaving bright orange powders, and the ^{31}P{^{1}H} NMR spectra of the redissolved solids gave chemical shifts identical to those observed from the reaction mixtures and only one selenium signal was observed for each sample in the ^{77}Se{^{1}H} NMR spectrum (R = ^{n}Bu, δ = 1342; R = Ph, δ = 1401). Orange, single crystals were grown for each compound from a concentrated MeCN solution of the bulk powder at −30 °C (for Ph$_3$P) or from the vapor diffusion of

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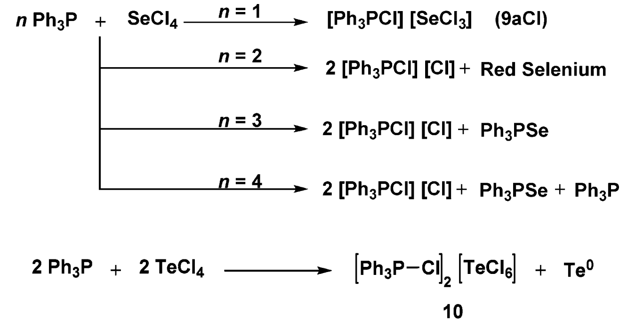
Scheme 1



Et_2O into a CH_2Cl_2 solution (for ${}^nBu_3P$). X-ray diffraction analysis confirmed the compounds to be the salts **9aCl** and **9bCl**, which are obtained in quantitative yields.

Similar reactivity is observed between an equimolar amount of Ph_3P and $SeBr_4$, in that a single ${}^{31}P\{{}^1H\}$ and ${}^{77}Se\{{}^1H\}$ NMR signal at $\delta = 53$ and 1052, respectively, are detected from redissolved solids acetonitrile-d_3 that precipitate during the reaction. Single crystals suitable for X-ray diffraction studies were grown from a concentrated MeCN solution of the redissolved precipitate at −30 °C and confirmed the identity of the compound as **9aBr**.

Samples of the 1:1 stoichiometric reaction mixture of ${}^nBu_3P$ and $SeBr_4$ were analyzed by ${}^{31}P\{{}^1H\}$ NMR spectroscopy and indicated the production of two phosphorus-containing compounds ($\delta = 50, 97$) in an approximate 1:9 ratio. The major product was easily separated from the reaction mixture via precipitation with *n*-pentane. Filtration and drying of the solids in vacuo yielded a shiny orange powder that, when redissolved, gave rise to the signal at $\delta = 97$, consistent with a $[{}^nBu_3PBr]$ cation.[27] Single crystals grown from a concentrated THF solution of the bulk powder at −30 °C confirmed the identity of the product as the salt $[{}^nBu_3PBr][SeBr_3]$ **(9bBr)**.

Upon further examination of the $Ph_3P/SeCl_4$ system, it was ascertained that the outcome of the reaction could be varied on the basis of the stoichiometric ratio of Ph_3P to $SeCl_4$ (Scheme 1a). Two stoichiometric equivalents of Ph_3P in CH_2Cl_2 produce a flocculent red precipitate over the course of 30 min, within a pale yellow supernatant. Phosphorus-31 NMR spectra obtained from a sample of the filtered reaction mixture revealed a broad singlet at $\delta = 59$, which is consistent with the $[Ph_3PCl]$ cation in the presence of a chloride anion.[28] The volatiles were removed from the supernatant, leaving a white crystalline powder. Single crystals were grown by the vapor diffusion of Et_2O into CH_2Cl_2 solutions of the bulk powder, and a unit cell analysis of the crystals confirmed the product to be $[Ph_3PCl][Cl]$.[28] The remaining red precipitate proved to be insoluble in all common organic solvents and turned gray upon heating to 180 °C in a flame-sealed N_2-filled melting point tube, and upon further heating, the gray solids melted at 220 °C. The red powder was then subjected to EDX analysis (Figure 2), which indicated that the only element present was selenium. An FT-Raman spectrum of the same sample revealed characteristic vibrational bands for red, monoclinic α-Se (252 (E_2), 246 (A_1), 236 (E_3), 124 (E_3), 111 (A_1), and 83 cm^{-1} (E_2); Figure 2). Most notably, there was no vibration at 138 cm^{-1}, indicating the production of amorphous red selenium. The triclinic form can also be ruled out, as this morphology has only two characteristic Raman-active vibrations at 237 cm^{-1} and 143 cm^{-1}.[29]

These data clearly indicate that a redox process is occurring, where P(III) is being oxidized to P(V) and selenium is reduced from Se(IV) to Se(II) upon reaction with the first equivalent of Ph_3P, then further reduced to Se(0) when a second stoichiometric equivalent of Ph_3P is added. Concomitant with the redox process is the chlorine transfer to phosphorus, forming the $[Ph_3PCl][Cl]$ salt.

Further reduction to Se(−II) is observed if a third stoichiometric equivalent of Ph_3P is added to the reaction mixture, where the red selenium is consumed, and a new signal appears in the ${}^{31}P\{{}^1H\}$ NMR spectrum corresponding to the production of Ph_3PSe ($\delta = 36$; ${}^1J_{P-Se} = 725$ Hz; Figure 3).[30] Further addition of Ph_3P does not impose additional changes in the NMR spectrum, other than the emergence of a corresponding signal for unreacted Ph_3P ($\delta = -5$).[30]

A similar redox phenomenon is observed in an equimolar reaction of Ph_3P with $TeCl_4$, which immediately results in the formation of a black precipitate and the deposition of a metallic mirror within a lime green supernatant. The reaction mixture was centrifuged and ${}^{31}P\{{}^1H\}$ and ${}^{125}Te\{{}^1H\}$ NMR spectra of the supernatant revealed single resonances at $\delta = 66$ and 1438, respectively, indicative of the formation of **10**.[31] Lime green single crystals suitable for X-ray diffraction analysis were grown from a concentrated MeCN solution of the bulk powder via the vapor diffusion of Et_2O and confirmed the identity of **10**. These products are indicative of a redox process, where phosphorus is oxidized from P(III) to P(V) and tellurium is reduced from Te(IV) to Te(0). Unlike the $SeCl_4$ system, the outcome of this reaction showed no dependence on the stoichiometric ratios of the reagents (Scheme 1b).

Identical reactions using ${}^nBu_3P$ resulted in varied reaction outcomes depending on the tellurium tetrahalide used.

In an equimolar reaction with $TeCl_4$ in CH_2Cl_2, the reaction mixture turns black almost immediately and a metallic mirror is deposited on the reaction vial, indicative of the production of Te metal. Phosphorus-31 NMR spectroscopy of the yellow supernatant revealed two phosphorus containing products at $\delta = 24$ and 106 in a 1:1 ratio, where the downfield signal is consistent with the $[{}^nBu_3PCl]$ cation and the upfield signal shows coupling to ${}^{125}Te$ ($J_{P-Te} = 1361$ Hz). The ${}^{125}Te\{{}^1H\}$ NMR spectrum also displays two signals: a singlet indicative of a chloro-tellurium species ($\delta = 1330$) and doublet at $\delta = -145$ with a *J*-value identical to the one observed in the

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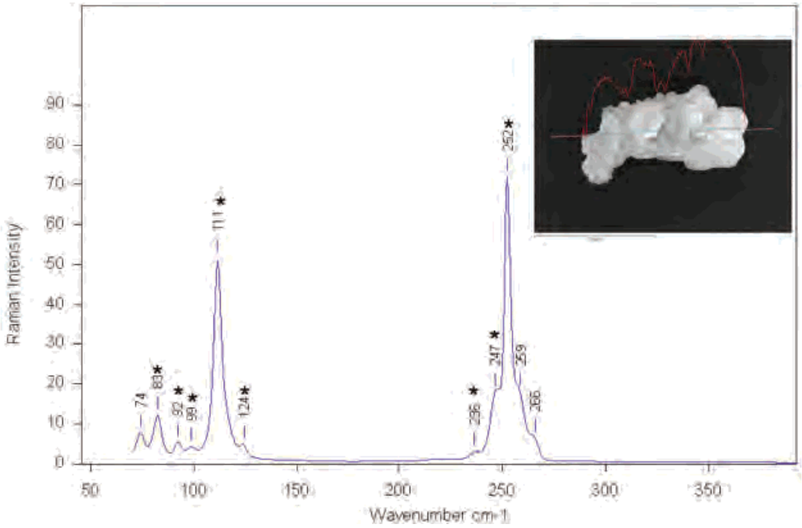

Figure 2. FT-Raman spectrum of red insoluble powder from the 2:1 reaction of Ph_3P and $SeCl_4$. (*) are diagnostic for monoclinic α-Se. The spectrum was collected using a 1 cm^{-1} resolution. Observed [Literature value] (cm^{-1}): 83[84]; 92[92]; 111[114]; 124[128]; 236[239]; 247[249]; 252[254].

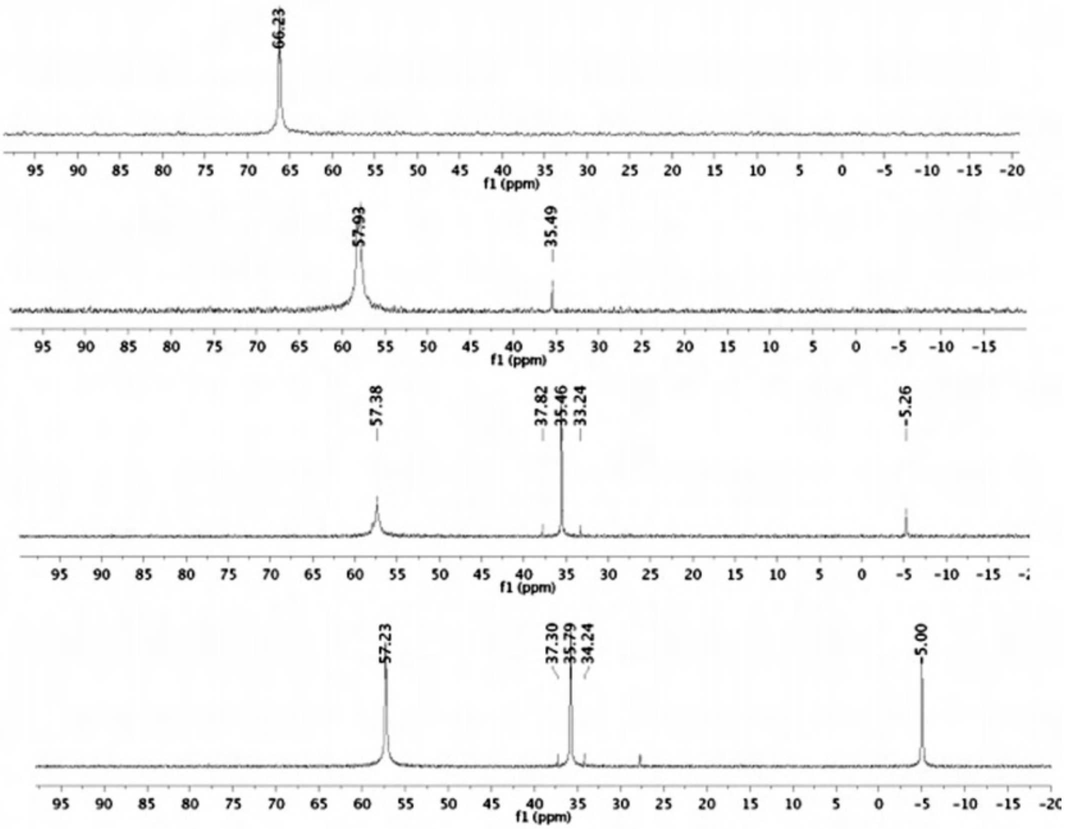

Figure 3. Sequential $^{31}P\{^1H\}$ NMR spectra of the stepwise equimolar addition of Ph_3P to the $Ph_3P + SeCl_4$ reaction mixture. (A) 1:1 stoichiometry; (B) total of 2 equiv of Ph_3P; (C) 3 equiv of Ph_3P; (D) 4 equiv of Ph_3P.

$^{31}P\{^1H\}$ NMR spectrum. These chemical shifts do not match either $^nBu_3PTe$ or R_3PTeCl_2, and unfortunately, all efforts to isolate and comprehensively characterize either species resulted in the decomposition of the reaction mixture.[32,33]

The 1:1 stoichiometric reaction of $TeBr_4$ and $^nBu_3P$ in THF initially gives a clear orange solution and shows only one peak in the $^{31}P\{^1H\}$ NMR spectrum at $\delta = 97$ ($[^nBu_3PBr]$ cation). However the reaction mixture decomposes rapidly, producing a number of phosphorus-containing compounds that could not be separated along with the concomitant deposition of Te metal on the reaction vessel.

While no compounds could be isolated and fully characterized from the $TeX_4/^nBu_3P$ system, it is clear from the ^{31}P-

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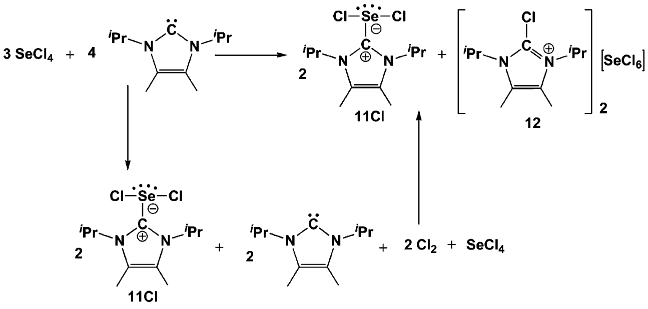
(32) Note: $^nBu_3PTeCl_2$ is not a known compound; however, Et_3PTeCl_2 is, and one would expect a similar chemical shift in the multinuclear NMR spectra. Konu, J.; Chivers, T. *Dalton Trans.* **2006**, *2006*, 3941−3946.

(33) Jones, C. H. W.; Sharma, R. D. *Organometallics* **1987**, *6*, 1419−1423.

Scheme 2



{^{1}H} NMR and deposition of metallic tellurium that a redox process is dominant in both cases.

Reactions Between Carbene and SeX$_4$. The 4:3 reaction between ^{i}Pr$_2$IM and SeCl$_4$ in THF results in the formation of a cloudy yellow reaction mixture, where upon removing the volatiles in vacuo, a waxy yellow solid remained. Proton NMR spectra of the redissolved solids in CDCl$_3$ revealed a mixture of two carbene-containing compounds in an approximate 1:1 ratio. Washing the bulk material with C_6H_6 afforded the facile separation of the two species. Selenium-77 NMR spectra from the benzene soluble portion revealed a single resonance at $\delta = -266$, which is indicative of a low-valent selenium center. The benzene-insoluble fraction was separated and redissolved in MeCN, which gave a single resonance in the ^{77}Se{^{1}H} NMR spectrum at $\delta = 873$, suggesting the presence of an [SeCl$_6$] dianion.[34] Single crystals of the two compounds were grown via the vapor diffusion of Et$_2$O into concentrated CH$_2$Cl$_2$ solutions of the bulk powders. X-ray diffraction studies revealed the identity of the two compounds as being the carbene adduct of SeCl$_2$ (**11Cl**) and the chloroimidazolium heaxcholorselenate salt (**12**).

The generation of **11Cl** and the imidazolium salt **12** can be considered in the context of the formal reductive elimination of Cl$_2$ (Cl(−I) to Cl(0)) from SeCl$_4$ (Se(IV) to Se(II)) along with the consumption of half the carbene ligand. The highly reactive "Cl$_2$" byproduct would immediately be sequestered by the remaining carbene, with concomitant addition of two chloride ions to SeCl$_4$ giving the [SeCl$_6$] dianion (Scheme 2). A similar phenomenon has been reported for phosphorus, where a carbene-stabilized P(I) cation was produced and the resulting Cl$_2$ was trapped by an excess of carbene.[8] Analogous reactivity was observed for SeBr$_4$ resulting in the formation of **11Br**, nonetheless there are side reactions, which produce a multitude of other products. These can be readily separated from **11Br**; however, their separation from each other and subsequent characterization was not pursued.

X-ray Crystallography. Compounds **9Cl**, **9Br**, **10**, **11Cl**, **11Br**, and **12** have all been characterized by single-crystal X-ray diffraction (Table 1), and views of the formula units are shown in Figures 4−11. The [R$_3$PCl] cations in compounds **9Cl** and **10** all exhibit a distorted tetrahedral geometry with the expected P−C and P−Cl bond distances (P−C, 1.774−1.780 Å; P−Cl, **9aCl**, 1.972(2) Å; **9bCl** 2.001(1) Å; **10**, 1.995(2) Å).[28] The cations in **9Br** are isostructural, with little notable difference in the P−C bond lengths and exhibits P−Br bond lengths of 2.151(2) Å and 2.165(2) Å.

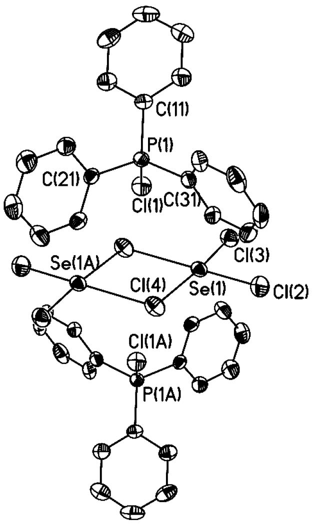


Figure 4. Solid-state structure of **9aCl**. Ellipsoids are drawn to 50% probability, and hydrogen atoms are removed for clarity. Bond lengths (Å) and angles (deg): P(1)−Cl(1) 1.979(2), P(1)−C(11) 1.774(6), P(1)−C(21) 1.779(4), P(1)−C(31) 1.780(6), Se(1)−Cl(2) 2.241(2), Se(1)−Cl(3) 2.2900(18), Se(1)−Cl(4) 2.6288(18), Se(1)−Cl(4A) 2.817(2), Cl(2)−Se(1)−Cl(3) 93.59(8), Cl(3)−Se(1)−Cl(4) 174.31(7).

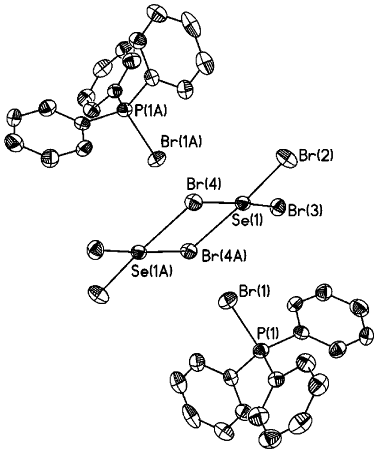


Figure 5. Solid-state structure of **9aBr**. Ellipsoids are drawn to 50% probability, and hydrogen atoms are removed for clarity. P(1)−Br(1) 2.1512(17), P(1)−C(11) 1.802(6), P(1)−C(21) 1.786(6), P(1)−C(31) 1.791(6), Se(1)−Br(2) 2.4114(10), Se(1)−Br(3) 2.4298(10), Se(1)−Br(4) 2.8042(18), Se(1)−Br(4A) 2.900(2), Br(2)−Se(1)−Br(4) 90.96(4), Br(3)−Se(1)−Br(4) 175.10(3).

In the solid state, the [SeCl$_3$] anion in **9Cl** dimerizes to form the dianion [Se$_2$Cl$_6$], where each [SeCl$_3$] fragment exhibits a classic T-shape, indicative of an AX$_3$E$_2$ VSEPR geometry, where selenium can formally be considered to carry two "lone pairs" of electrons. The Se−Cl(ax) bond lengths are shortened with respect to the Se−Cl(eq) bonds ((ax) 2.241(2) Å and 2.2638(1) Å; (eq) 2.688(1) Å and 2.629(2) Å), based on a trigonal bipyramidal electron pair geometry. The dimerization of the two [SeCl$_3$] anions occurs via long Se···Cl contacts (2.817(2) Å; 2.712(1) Å), which is a common phenomenon in anions of this type.[35,36] An isostructural, T-shaped [SeBr$_3$] anion is present in **9Br** with

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(34) Collins, M. J.; Ratcliffe, C. I.; Ripmeester, J. A. *J. Magn. Reson.* **1986**, *68*, 172−179.

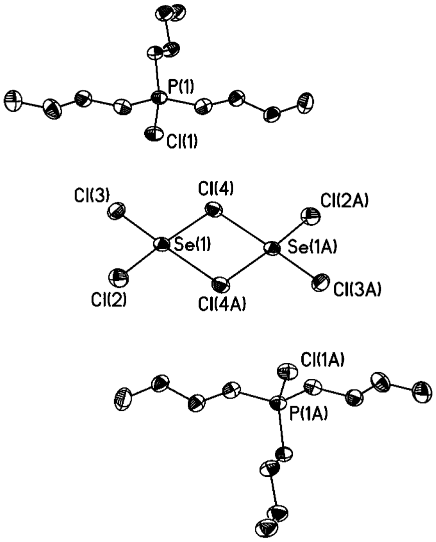

Figure 6. Solid-state structure of **9bCl**. Ellipsoids are drawn to 50% probability, and hydrogen atoms are removed for clarity. Bond lengths (Å) and angles (deg): P(1)−Cl(1) 2.001(1), Se(1)−Cl(2) 2.2621(9), Se(1)−Cl(3) 2.2638(9), Se(1)−Cl(4) 2.688(1), Se(1)−Cl(4A) 2.712(1), Cl(2)−Se(1)−Cl(3) 92.94(4), Cl(2)−Se(1)−Cl(4) 176.39(3).

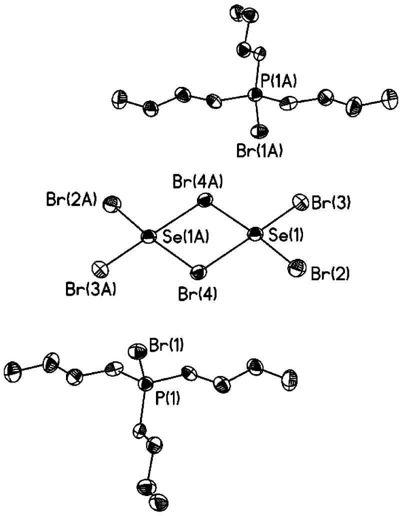

Figure 7. Solid-state structure of **9bBr**. Ellipsoids are drawn to 50% probability and hydrogen atoms are removed for clarity. Bond lengths (Å) and angles (deg): P(1)−Br(1) 2.165(2), Se(1)−Br(2) 2.417(1), Se(1)−Br(3) 2.528(1), Se(1)−Br(4) 2.826(1), Se(1)−Br(4A) 2.826(1), Br(2)−Se(1)−Br(3) 93.56(4), Br(2)−Se(1)−Br(4) 177.25(4).

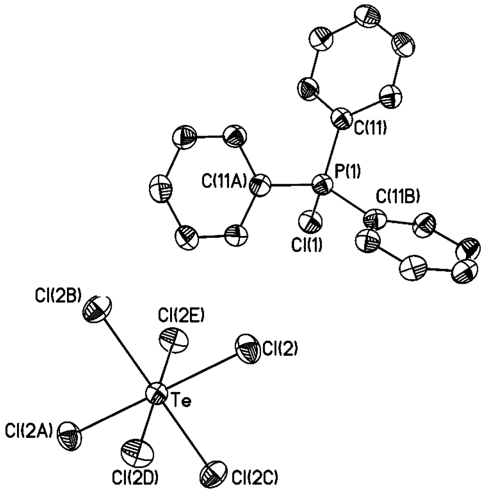

Figure 8. Solid-state structure of **10**. Ellipsoids are drawn to 50% probability and hydrogen atoms are removed for clarity. Bond lengths (Å) and angles (deg): P(1)−Cl(1) 1.995(2), P(1)−C(11) 1.779(4), Te−Cl(2) 2.5339(10).

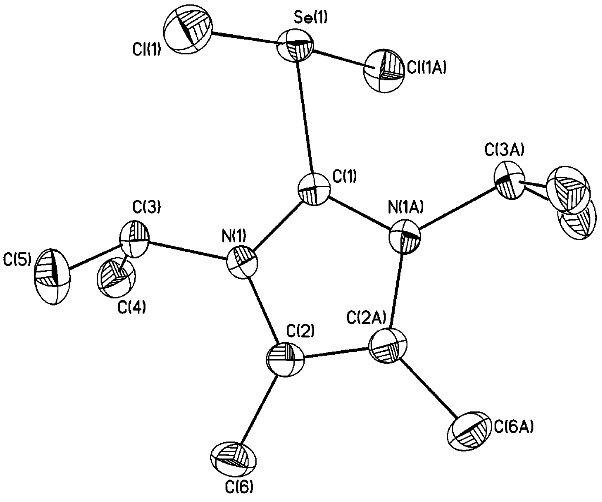

Figure 9. Solid-state structure of **11Cl**. Ellipsoids are drawn to 50% probability, and hydrogen atoms are removed for clarity. Bond lengths (Å) and angles (deg): Se(1)−C(1) 1.884(2), Se(1)−Cl(1) 2.4179(7), C(1)−N(1) 1.3425(19), N(1)−C(2) 1.385(2), C(2)−C(2A) 1.365(3), C(1)−Se(1)−Cl(1) 87.873(13), Cl(1)−Se(1)−Cl(1A) 175.75(3).

Se−Br(ax) bond distances in the range of 2.4114(1)−2.528(1) Å, and Se−Br(eq) 2.826(1)−2.8042(10) Å. In a similar fashion to the [$SeCl_3$] moiety in **9Cl**, the anion in **9Br** dimerizes through long Se···Br contacts of 2.900(2) Å and 2.826(1) Å. The bonding arrangement about both [SeX_3] monoanionic fragments is indicative of Se(II) and confirms a necessary two-electron reduction of selenium, with the corresponding oxidation of Ph_3P to the [Ph_3PX] cation (P(III) to P(V)).

The [$TeCl_6$] dianion in **10** is almost perfectly octahedral, with a sterochemically inactive "lone pair" of electrons and having Te−Cl bond lengths of 2.533(1) Å, which are consistent with those previously reported for anions of this type.[36] Clearly, a second one-half stoichiometric equivalent of $TeCl_4$ assists in sequestering the transfer of two chloride anions after the redox process between the first one-half equivalent of $TeCl_4$ and Ph_3P occurs.

The solid-state structure of compound **11Cl** reveals the $^{i}Pr_2IM$ bound to a $SeCl_2$ fragment, via the carbenic carbon (C(1)−Se(1) 1.884(2) Å). The Se(1)−Cl bonds are slightly elongated at 2.418(1) Å. The three-coordinate selenium center also exhibits a T-shaped, AX_3E_2 geometry (C(1)−Se(1)−Cl(1) 87.87(1)°; Cl(1)−Se(1)−Cl(1A) 175.74(3)°), indicative of two "lone pairs" of electrons at Se and the required two-electron reduction of Se(IV) to Se(II). This structure is reminiscent of other carbene-ChX_2 species, which have been synthesized from the parent chalcoureas and elemental halogens, X_2 (X = Br, I) or interhalogens via oxidative addition (XY, X = I, Br; Y = Cl). Compound

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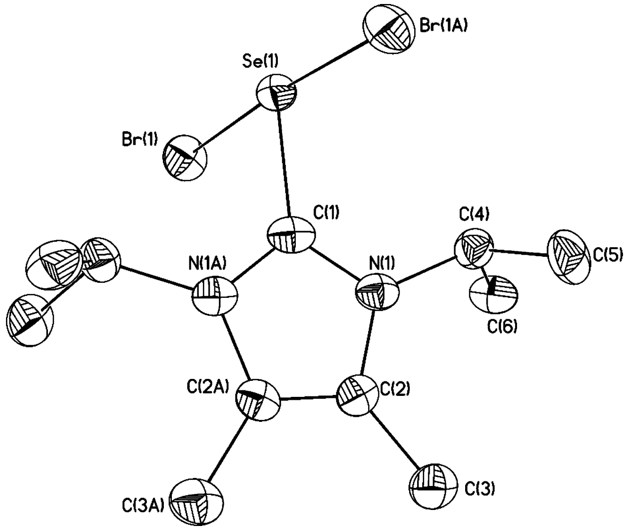

Figure 10. Solid-state structure of **11Br**. Ellipsoids are drawn to 50% probability, and hydrogen atoms are removed for clarity. Bond lengths (Å) and angles (deg): Se(1)−C(1) 1.901(11), Se(1)−Br(1) 2.5870(10), C(1)−N(1) 1.339(9), N(1)−C(2) 1.395(10), C(2)−C(2A) 1.332(16), C(1)−Se(1)−Br(1) 87.87(3), Br(1)−Se(1)−Br(1A) 175.73(6).

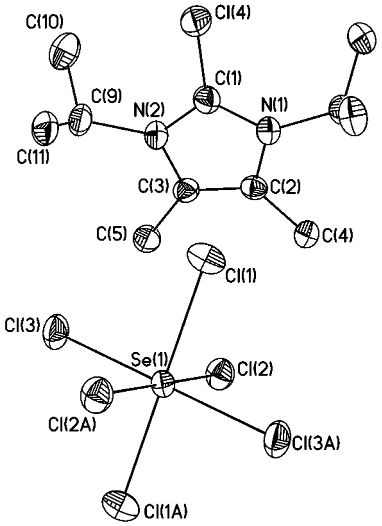

Figure 11. Solid-state structure of **12**. Ellipsoids are drawn to 50% probability, and hydrogen atoms are removed for clarity. Only one of the cations is shown. Bond lengths (Å) and angles (deg): C(1)−Cl(4) 1.685(4), N(1)−C(1) 1.344(5), N(1)−C(2) 1.387(4), C(2)−C(3) 1.353(5), Se(1)−Cl(1) 2.4047(13).

11Cl can be described as an ylide, or as a Lewis base stabilized $SeCl_2$ (**11Cla**).[12−14,16,37,38] Related "base stabilized" compounds have been reported for TeX_2 and SeX_2, where the Lewis base is a phosphine, and the T-shaped geometry is also apparent.[15,17,32] Similar to the previously reported carbene adducts, these were prepared by the oxidative addition of the elemental halogen to the trialkylphosphine chalcogenide.

Compound **11Br** is isostructural having **11Cl** with almost identical bond lengths and angles (Se(1)−C(1) 1.901(1) Å; Se(1)−Br(1) 2.587(1) Å; Se(1)−C(1)−Br(1) 87.87(3)°; Br(1)−Se(1)−Br(1A) 175.73(6)°). The solid-state structure of the chloroimidazolium hexachloroselenate byproduct (**12**) reveals little change in the geometry of the heterocycle as it exhibits the expected endocyclic N−C and C−C bond distances for an imidazolium cation (C(1)−N(1) 1.497(4) Å; C(1)−N(2) 1.331(5) Å; C(2)−C(3) 1.353(5) Å) and has a C(1)−Cl(11) of 1.685(4) Å).[39] The counterion is a rare example of a crystallographically characterized [$SeCl_6$] dianion, which exhibits a slightly distorted octahedral geometry (Se(1)−Cl 2.397(1)−2.405(1) Å). The Se center formally carries a "lone pair" of electrons, which remains stereochemically inactive, similar to the [$TeCl_6$] dianion in **10**.

Conclusions

We have studied the reaction between the Lewis bases $^{n}Bu_3P$, Ph_3P, and $^{i}Pr_2IM$ with the chalcogen tetrahalides $SeCl_4$, $SeBr_4$, $TeCl_4$, and $TeBr_4$. These experiments have yielded a series of phosphonium or imidazolium halochalcogenate salts and strongly support a two-electron redox reaction between the Lewis base and the chalcogen tetrahalide. This can be understood in terms of the formal reductive elimination of Cl_2 or Br_2, where this reactivity is complementary to the already established oxidative addition chemistry of elemental halogens (or interhalogens) to R_3PSe and thio-, seleno-, or telluroureas. The highly reactive dihalide oxidation byproduct is immediately sequestered by the Lewis base and promotes salt formation. These observations are critical as this redox phenomenon may indicate a general behavioral trend for other heavier p-block elements ($n \geq 4$) in the presence of strong Lewis bases.

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Supporting Information Available: Representative NMR spectra for compounds **9**, **10**, **11**, and **12**, FT-RAMAN spectra for the α-Se (red), additional EDX data, and tables of X-ray crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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