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Pyridine, Thiophosphine and Selenophosphine Complexes of the Phenylphosphine Dication

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Draft

Abstract

Compounds of the generic formula $[\text{PhPL}][\text{OTf}]_2$ with $\text{L} =$ bipyridine (bipy) and 4,4'-di(*tert*-butyl)-2,2'-bipyridine (Bbipy), and $[\text{PhPL}_2][\text{OTf}]_2$ with $\text{L} =$ 4-dimethylaminopyridine (dmap), tricyclohexyl-thiophosphine and tricyclohexyl-selenophosphine have been prepared by the reaction of dichlorophenylphosphine with two equivalents of trimethylsilyl triflate and the respective ligand. The new complexes of the phenylphosphine dication with this variety of ligands expands the scope of coordination complexes involving phosphorus as an acceptor.

Key words: phosphorus, cations, coordination complexes, synthesis, molecular structure

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Introduction

Much of the chemistry of phosphorus in a formal oxidation state of III involves the phosphorus centre behaving as a Lewis base or ligand. Imposition of a cationic charge on a molecule containing a phosphine centre enables Lewis acid behavior that diversifies the chemistry of phosphorus. Complexes of RNP^+ (**1**)^[1], R_2P^+ (**2**)^[2], RP^{2+} (**3**)^[2a, 2b, 3], $\text{R}_3\text{P-PR}_3^{2+}$ (**4**)^[4] and P^{3+} (**5**)^[5] have been reported with a variety of ligands.^[6] In addition, bipyridine complexes of P^{3+} (**6**)^[7] illustrate the potentially versatile coordination chemistry of phosphorus. We have now expanded the ligand scope for derivatives of **3** for $\text{R} = \text{Ph}$. Complexes of $[\text{PhP}]^{2+}$ as trifluoromethanesulfonate (triflate) salts with 2,2'-bipyridine $\{[\text{PhP}(\text{bipy})][\text{OTf}]_2\}$, 4,4'-di(*tert*-butyl)-2,2'-bipyridine $\{[\text{PhP}(\text{Bbipy})][\text{OTf}]_2\}$, 4-dimethylaminopyridine $\{[\text{PhP}(\text{dmap})_2][\text{OTf}]_2\}$, thiophosphine $\{[\text{PhP}(\text{SPCy}_3)_2][\text{OTf}]_2\}$ and selenophosphine $\{[\text{PhP}(\text{SePCy}_3)_2][\text{OTf}]_2\}$ have been prepared and comprehensively characterized. The compounds represent new derivatives of chelate complexes of phosphorus and the first examples of pyridine, thio- and seleno- complexes of phosphine dication.

Results and Discussion

PhPCl₂ reacts with TMSOTf in the presence of bipy or Bbipy, yielding one new signal in the ³¹P{¹H} NMR spectra of the reaction mixtures (δ = 136.8 ppm for bipy and 133.8 ppm for Bbipy). Clean products and optimal reaction conditions are obtained with a small excess of TMSOTf (2.5 equivalents), which can be removed by precipitating the product from either DCM or acetonitrile, and washing the solid with diethyl ether. Analogous complexes have been formed following a similar synthetic procedures; [PhP(dmap)₂][OTf]₂ (δ = 121.0 ppm), [PhP(SPCy₃)₂][OTf]₂ (δ = 61.5 ppm) or [PhP(SePCy₃)₂][OTf]₂ (δ = 48.9 ppm).^[8] After stirring the reaction mixtures at room temperature for at least one hour, the volatiles were removed under reduced pressure to provide colourless solids. Derivatives of [PhPL_x][OTf]₂ have been crystallized from acetonitrile or DCM solutions layered with diethyl ether and the solid state structures have been determined by X-ray crystallography. The ³¹P{¹H} NMR spectrum for derivatives of [PhP(XPCy₃)₂]²⁺ exhibit a doublet and triplet resonance consistent with a R₃P-X-PR-X-PR₃ chain (Table 1). The ²J_{P,P} values are typical, and the doublet of doublets resonance in the ⁷⁷Se{¹H} NMR spectrum (δ = 119.2, *dd*, *J*_{SeP} = 416.5, 133.5 Hz) for [PhP(SePCy₃)₂]²⁺ are consistent with the observed solid state structure. The PhP centres of [PhP(XPCy₃)₂]²⁺ resonate at significantly lower frequency than those involving pyridine ligands. The tricyclohexylphosphine units on the other hand resonate at higher frequency compared to [HPCy₃][OTf] (δ = 29.5 ppm)^[9] or the free ligand (SPCy₃ δ = 62.4 ppm).^[10] The ¹⁹F chemical NMR shift for the triflate anions is between -78.8 and 79.2 ppm and indicates free triflate in solution with weak to no interaction with the phosphorus dication.

Table 1: ³¹P{¹H}-NMR data for the dicationic species [PPhL_x]²⁺

	³¹ P{ ¹ H} [δ ppm]	² J _{PP} [Hz]
[PhP(bipy)] ²⁺	136.8 (s)	-
[PhP(Bbipy)] ²⁺	133.8 (s)	-
[PhP(dmap) ₂] ²⁺	121.0 (s)	-
[PhP(SPCy ₃) ₂] ²⁺	73.7 (d), 61.5 (t)	21
[PhP(SePCy ₃) ₂] ²⁺	72.3 (d), 48.9 (t)	26

Table 2: Crystallographic data for [PhP(bipy)][OTf]₂, [PhP(Bbipy)][OTf]₂, [PhP(dmap)₂][OTf]₂, [PhP(SPCy₃)₂][OTf]₂, [PhP(SePCy₃)₂][OTf]₂.

	[PhP(bipy)] [OTf] ₂	[PhP(Bbipy)] [OTf] ₂	[PhP(dmap) ₂] [OTf] ₂	[PhP(SPCy ₃) ₂] [OTf] ₂	[PhP(SePCy ₃) ₂] [OTf] ₂
Empirical formula	C ₁₈ H ₁₃ N ₂ O ₆ F ₆ PS ₂	C ₂₆ H ₂₉ N ₂ O ₆ F ₆ PS ₂	C ₂₉ H ₃₅ N ₆ O ₆ F ₆ PS ₂	C ₄₄ H ₇₁ F ₆ O ₆ P ₃ S ₄	C ₄₄ H ₇₁ O ₆ F ₆ P ₃ S ₂ Se ₂
Formula weight	562.39	674.60	772.72	1031.15	1124.95
Temperature/K	173.15	173.15	173.15	173.15	193.15
Crystal system	triclinic	triclinic	orthorhombic	orthorhombic	orthorhombic
Space group	P-1	P-1	Fdd2	Pca2 ₁	Pca2 ₁
a/Å	7.3772(2)	10.3407(7)	20.5652(4)	19.3394(6)	19.1271(10)
b/Å	11.0469(3)	10.9356(7)	34.7966(7)	10.6524(4)	21.3744(11)
c/Å	14.8136(5)	14.1649(9)	16.2609(3)	24.1489(8)	24.5753(12)
α/°	74.9952(18)	109.229(3)	90	90	90
β/°	77.2568(15)	97.623(3)	90	90	90
γ/°	85.2235(14)	93.345(2)	90	90	90
Volume/Å ³	1136.91(6)	1490.12(17)	11636.3(4)	4974.9(3)	10047.1(9)
Z	2	2	16	4	8
ρ _{calc} /cm ³	1.643	1.504	1.764	1.377	1.487
μ/mm ⁻¹	3.625	2.863	3.066	3.243	1.717
F(000)	568.0	696.0	6400.0	2184.0	4656.0
Reflections collected	7962	10609	19943	174874	82438
Independent reflections	4427	5791	5724	9890	23072
R _{int}	0.0409	0.0260	0.0167	0.0431	0.0554
R _{sigma}	0.0490	0.0334	0.0165	0.0185	0.0578
Data/restraints/parameters	4427/0/316	5791/0/388	5724/1/374	9890/1/568	23072/1/1136
GOF	1.084	1.052	1.078	0.998	1.006

$R_1 [I > 2\sigma(I)]$	0.0503,	0.0378,	0.0513,	0.0230,	0.0399,
$wR_2 [I > 2\sigma(I)]$	0.1404	0.1057	0.1527	0.0616	0.0822
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.75/-0.56	0.49/-0.41	1.64/-0.46	0.22/-0.32	1.30/-0.93

As shown in Figure 1, each of the solid state structures contains a PhP unit in which the phosphorus centre is attached to two nitrogen, sulfur or selenium atoms. The pyridine derivatives show long interactions with oxygen atoms from the triflate anions (Table 3). The structure of $[\text{PhP}(\text{bipy})][\text{OTf}]_2$ involves a dimeric arrangement with two triflate anions linking phosphorus centres. All P---O interactions are outside the sum of the P-O covalent radii ($\Sigma_{r,\text{cov}} = 1.74 \text{ \AA}$),^[11] but some are inside the sum of the van der Waals radii ($\Sigma_{r,\text{vdW}} = 3.32 \text{ \AA}$).^[12] The N-P bond lengths in $[\text{PPh}(\text{dmap})_2]^{2+}$ are indistinguishable and are significantly shorter than the N-P bond lengths in $[\text{PhP}(\text{bipy})][\text{OTf}]_2$ and $[\text{PhP}(\text{Bbipy})][\text{OTf}]_2$, consistent with the greater basicity of dmap.

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Figure 1: Solid state structures of the cations in (a) $[\{\text{PhP}(\text{Bbipy})\}_2][\text{OTf}]_4$, (b) $[\text{PhP}(\text{dmap})_2][\text{OTf}]_2$, (c) $[\text{PhP}(\text{bipy})][\text{OTf}]_2$, (d) $[\text{PhP}(\text{SPCy}_3)_2][\text{OTf}]_2$, (e) $[\text{PhP}(\text{SePCy}_3)_2][\text{OTf}]_2$. Hydrogen atoms are omitted for clarity, if not required for understanding only the coordinating oxygen atoms for the triflate anions are shown. Thermal ellipsoids are shown at the 50% probability level, interatomic distances in Å.

Complexes of PhP^{2+} with phosphine chalcogenide ligands represent $\text{R}_3\text{P-X-PR-X-PR}_3$ chains ($\text{X} = \text{S}$ or Se). In the solid state structure of $[\text{PhP}(\text{SPCy}_3)_2][\text{OTf}]_2$ the closest interactions with the triflate anion are outside the sum of the van der Waals radii for sulfur or phosphorus. The terminal P-S bonds (S1-P2 2.0815(7) Å and S2-P3 2.0785(7) Å, respectively) are significantly longer than in SPCy_3 (1.966(5) Å),^[13] but are shorter than the central bonds (S1-P1 2.1638(7) Å and S2-P1 2.1586(7) Å). Interestingly, the S-P bond distances in the neutral carbon analogue $\text{Ph}_3\text{C-S-PPh-S-CPh}_3$ (2.122(1) and 2.120(1) Å, respectively) are only slightly shorter.^[14] The solid state structure of $[\text{PhP}(\text{SePCy}_3)_2][\text{OTf}]_2$ reveals P-Se bond lengths (P2-Se1 2.2350(13) and P3-Se2 2.2342(12) Å) that are consistent with the trends in the sulfur analogue in comparison with SePCy_3 (P-Se 2.108(1) Å),^[15] although the differences are smaller. In comparison, $[\text{Ph}_3\text{P-SePh}]\text{Br}$ exhibits a Se-P bond distance of 2.2260(16) Å,^[16] which is significantly shorter than those in $[\text{PhP}(\text{SePCy}_3)_2][\text{OTf}]_2$.

Table 3: Selected structural parameters for $[\text{PPh}(\text{dmap})_2][\text{OTf}]_2$, $[\text{PPh}(\text{Bbipy})][\text{OTf}]_2$, and $[\text{PPh}(\text{bipy})][\text{OTf}]_2$ compared to the chalcogen derivatives $[\text{PhP}(\text{SPCy}_3)_2][\text{OTf}]_2$ and $[\text{PhP}(\text{SePCy}_3)_2][\text{OTf}]_2$. Bond distances in Å and sum of angles around the phosphorus dication (Σ_p) in °. $\text{X} = \text{S}$ or Se , respectively.

ligand	dmap	Bbipy	bipy		SPCy ₃	SePCy ₃
P1-N1	1.761(4)	1.7962(13)	1.8087(19)	P1-X1	2.1638(7)	2.3066(13)
P1-N2	1.764(4)	1.8069(14)	1.805(2)	P1-X2	2.1586(7)	2.2903(13)
P1-C1	1.813(5)	1.8182(17)	1.805(2)	P1-C1	1.814(2)	1.181(5)
				P2-X1	2.0815(7)	2.2350(13)
				P3-X2	2.0785(7)	2.2342(12)
P-OTf	3.847	2.755	2.761	P-OTf	-	3.612
	3.164	3.264	3.045	X-OTf	-	3.219
		3.802	3.564			
			3.724			
Σ_p	300.7	280.3	283.7		290.7	289.6

Conclusion:

We have expanded the scope of ligands that engage the phenylphosphine dication, to include dmap, bipy, Bbipy, SPCy₃ and SePCy₃ and showed the potential of PhP^{2+} being a Lewis acceptor. Such cationic complexes may be further applied as ligands for transition metals or as active species in Lewis acid catalysed organic transformations.

Acknowledgements

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Experimental

All reagents were handled in an Innovative Technology, inc. System One Glovebox under an atmosphere of dry N₂. Solvents were dried over Na (Et₂O) or CaH₂ (CH₂Cl₂) and then distilled. Anhydrous grade MeCN was obtained from Sigma-Aldrich and used without purification. Prior to use, all solvents were stored for at least 48 hr over 3 Å molecular sieves (MeCN) or 4 Å molecular sieves (Et₂O and CH₂Cl₂), which had been activated at 300 °C under dynamic vacuum for 48 hr. Deuterated solvents were dried over their corresponding size molecular sieves and were stored for at least 48 hr. TMSOTf (99 %) was distilled before use. 4-Dimethylaminopyridine (dmap) was purified by sublimation under vacuum. SPCy₃ and SePCy₃ were synthesized according to literature procedures.¹⁷ Bipy and Bbipy were obtained from Sigma-Aldrich and used without further purification.

Reactions were carried out inside the glovebox in screw-cap glass vials that had been dried at 250 °C for at least 1 hr and placed under dynamic vacuum (glovebox antechamber) while still hot. NMR spectra were obtained on a Bruker AVANCE 300 MHz or 360 MHz NMR Spectrometer, field strength is given explicitly with the characterization data for the compounds. ¹H, ³¹P{¹H}, and ¹⁹F{¹H} NMR chemical shifts were referenced to SiMe₄, 85 % H₃PO₄, and CFC₃, respectively. Infrared spectra were collected on samples prepared as nujol mulls between NaCl plates using a Perkin-Elmer Frontier FT-IR spectrometer. Peaks are reported in wavenumbers (cm⁻¹) with intensities (strong, medium, weak) in parentheses, relative to the most intense peak. Melting points were obtained on samples grease-sealed in glass capillaries under dry nitrogen using an electrothermal apparatus. Unless otherwise stated, crystals for single crystal X-ray diffraction studies were obtained from slow diffusion of a layered non-solvent into a saturated solution of the compound. Single crystal X-ray diffraction data were collected on a Bruker D8/APEX II CCD diffractometer at 173 K. All structures were solved by direct methods and refined by full-matrix least squares on *F*² (SHELXL-97 or SHELXL-2013).^[17] All non-hydrogen atoms were refined anisotropically while hydrogen atoms were assigned positions based on the sp² or sp³ hybridization geometries of their attached carbons, and were given thermal parameters 20% greater than those of their parent atoms.

Synthesis of [PhP(bipy)][OTf]₂: To a rapidly stirring solution of PhPCl₂ (1.00 mmol, 0.179 g) and TMSOTf (2.00 mmol, 0.445 g) in 5 mL DCM, bipy (1.00 mmol, 0.268 g) was added, producing a pale-yellow solution. The solution was stirred for 1 hr and the solvent was removed under reduced pressure. The resulting white powder was washed with Et₂O three times and was crystallized from MeCN layered with diethyl ether at -26 °C. Yield: 0.427 g (76 %); mp: 218 °C dec.; ¹H NMR (CD₃CN, 298 K, 300 MHz, δ [ppm]): 9.38 – 9.35 (*m*, 2H, CH_{arom}), 9.20 (*dt*, 1.1 Hz, 8.3 Hz, 2H, CH_{arom}), 9.00 (*td*, 1.2 Hz, 8.2 Hz, 2H, CH_{arom}), 8.41 – 8.37 (*m*, 2H, CH_{arom}), 7.87 – 7.58 (*m*, 5H, CH_{arom}); ¹³C{¹H} NMR (CD₃CN, 298 K, 75.4 MHz, δ [ppm]): 151.1 (*s*), 146.3 (*d*, ²J_{CP} = 16.2 Hz), 138.8 (*s*), 136.3 (*d*, J_{CP} = 31.3 Hz), 132.9 (*d*, ³J_{CP} = 2.1 Hz), 131.8 (*d*, ²J_{CP} = 11.6 Hz), 129.7 (*s*), 129.3 (*s*), 127.8 (*d*, ²J_{CP} = 7 Hz); ³¹P{¹H} NMR (CD₃CN, 298 K, 121.4 MHz, δ [ppm]): 136.8 (*s*); ¹⁹F{¹H} NMR (CD₃CN, 298 K, 282.2 Hz, δ [ppm]): -79.2 (*s*); IR (Nujol mull, NaCl plates, cm⁻¹): 1622 (*m*), 1480 (*m*),

Synthesis of [PhP(Bbipy)][OTf]₂: To a rapidly stirring solution of PhPCl₂ (1.00 mmol, 0.179 g) and TMSOTf (2.00 mmol, 0.445 g) in 5 mL DCM, Bbipy (1.00 mmol, 0.268 g) was added, producing a pale-yellow solution. The solution was stirred for 1 hr and the solvent was removed under reduced pressure and washed with Et₂O three times. The colourless powder was crystallized from MeCN layered with diethyl ether at -26 °C. Yield: 0.594 g (88 %); mp: 230 - 231 °C; ¹H NMR (CD₃CN, 298 K, 300 MHz, δ [ppm]): 9.20 – 9.17 (*m*, 4H, CH_{arom}), 8.33 (*dt*, 6.7 Hz, 1.9 Hz, 2H, CH_{arom}), 7.85 – 7.58 (*m*, 5H, CH_{arom}), 1.55 (*s*, 18H, CH₃); ¹³C{¹H} NMR (CD₃CN, 298 K, 75.4 MHz, δ [ppm]): 177.4 (*s*), 146.2 (*d*, ³J_{CP} = 4.2 Hz), 145.0 (*d*, ²J_{CP} = 16.3 Hz), 138.4 (*s*), 135.9 (*d*, J_{CP} = 31.4 Hz), 131.6 (*d*, ²J_{CP} = 10.1 Hz), 130.4 (*s*), 129.9 (*d*, ³J_{CP} = 2.1 Hz), 125.4 (*d*, ³J_{CP} = 4.3 Hz), 39.1 (*s*), 30.4 (*s*); ³¹P{¹H} NMR (CD₃CN, 298 K, 121.4 MHz, δ [ppm]): 133.8 (*s*); ¹⁹F{¹H} NMR (CD₃CN, 298 K, 282.2 Hz, δ [ppm]): -79.2 (*s*); IR (Nujol mull, NaCl plates, cm⁻¹): 1963 (*w*), 1703 (*w*), 1629 (*s*), 1542 (*s*),

Synthesis of [PhP(dmap)₂][OTf]₂: To a rapidly stirring solution of PhPCl₂ (1.00 mmol, 0.179 g) and TMSOTf (2.00 mmol, 0.445 g) in 5 mL DCM, dmap (4.00 mmol, 0.489 g) was added, producing a pale pink solution. The solution was stirred for 1 hr and then checked by ³¹P{¹H} NMR spectroscopy. The solvent was removed under reduced pressure and washed with diethyl ether three times. The colourless powder was crystallized from MeCN layered with diethyl ether at -26 °C for 48 hr, yielding pale peach crystals. Yield: 0.442 g (68 %); mp: 159 – 161 °C; EA [calc.]: C, 46.29; H, 4.33, N, 4.15 EA [found.]: C, 45.97; H, 4.42; N 4.05, ¹H NMR (CD₂Cl₂, 298 K, 300 MHz, δ [ppm]): 8.32 – 8.29 (*m*, 4H, CH_{arom}), 7.77 – 7.63 (*m*, 5H, CH_{arom}), 7.05 – 7.01 (*m*, 4H, CH_{arom}), 3.30

(*broad s*, 12H, CH₃); ¹³C{¹H} NMR (CD₂Cl₂, 298 K, 75.4 MHz, δ [ppm]): 158.4 (*s*), 143.6 (*s*), 134.4 (*s*), 131.1 (*s*), 119.3 (*s*), 110.1 (*s*), 66.2 (*s*), 41.3 (*s*); ³¹P{¹H} NMR (CD₂Cl₂, 298 K, 121.4 MHz, δ [ppm]): 121.03 (*s*); ¹⁹F{¹H} NMR (CD₂Cl₂, 298 K, 282.2 Hz, δ [ppm]): -78.8 (*s*); IR (Nujol mull, NaCl plates, cm⁻¹): 1645 (*s*), 1579 (*s*), 1533 (*s*), 1507 (*s*),

Synthesis of [PhP(SPCy₃)₂][OTf]₂: To a rapidly stirring solution of PhPCl₂ (0.408 mmol, 0.073 g) and TMSOTf (0.816 mmol, 0.181 g) in 5 mL DCM, SPCy₃ (0.816 mmol, 0.255 g) was added, producing a colourless solution. The solution was stirred for 1 hr and the solvent was removed under reduced pressure and washed with Et₂O three times. The colourless powder product was crystallized from DCM layered with Et₂O at room temperature. Yield: 0.240 g (57 %); mp: 188 - 190 °C; EA [calc.]: C, 51.25; H, 6.94, N, 4.15 EA [found.]: C, 50.92; H, 7.16; N <0.3, ¹H NMR (CD₃CN, 298 K, 300 MHz, δ [ppm]): 8.13 – 7.62 (*m*, 5H, CH_{arom}), 2.76 – 1.20 (*m*, 60H, CH₂); ¹³C{¹H} NMR (CD₃CN, 298 K, 75.4 MHz, δ [ppm]): 136.0 (*s*), 134.5 (*s*), 134.13 (*s*), 131.8 (*d*, *J*_{CP} = 10.3 Hz), 36.0 (*d*, *J*_{CP} = 29.5 Hz), 28.6 (*broad s*), 27.3 (*d*, *J*_{CP} = 13.1 Hz), 26.1 (*s*); ³¹P{¹H} NMR (CD₃CN, 298 K, 121.4 MHz, δ [ppm]): 73.7 (*d*, ²*J*_{PP} = 21 Hz), 61.5 (*t*, ²*J*_{PP} = 21 Hz); ¹⁹F{¹H} NMR (CD₃CN, 298 K, 282.2 Hz, δ [ppm]): -79.2 (*s*); IR (Nujol mull, NaCl plates, cm⁻¹): 1580 (*w*),.

Synthesis of [PhP(SePCy₃)₂][OTf]₂: To a rapidly stirring solution of PhPCl₂ (0.380 mmol, 0.068 g) and TMSOTf (1.00 mmol, 0.222 g) in 5 mL DCM, SePCy₃ (0.950 mmol, 0.341 g) was added, producing a deep yellow solution. The solution was stirred for 30 minutes, becoming a pale yellow, and then checked by ³¹P{¹H} NMR spectroscopy. The solvent was removed under reduced pressure and washed with diethyl ether three times. The colourless powder product was crystallized from DCM layered with diethyl ether at -26 °C for 48 hours, producing pale yellow crystals. Yield: 0.402 g (94 %); Melting Point: dec. 198 °C; EA [calc.]: C, 46.98; H, 6.36, N, 0 EA [found.]: C, 47.16; H, 6.52; N <0.3, ¹H NMR (CD₂Cl₂, 298 K, 300 MHz, δ [ppm]): 8.21 – 7.56 (*m*, 5H, , CH_{arom}), 2.75 – 1.11 (*m*, 60H, , CH₂); ¹³C{¹H} NMR (CD₂Cl₂, 298 K, 75.4 MHz, δ [ppm]): 134.4 (*d*, *J*_{CP} = 28.2 Hz), 130.8 (*d*, ²*J*_{CP} = 8.6 Hz), 123.4 (*s*), 119.8 (*s*), 35.7 (*d*, *J*_{CP} = 23.2 Hz), 28.8 (*s*), 26.8 (*d*, *J*_{CP} = 12.3 Hz), 25.7 (*s*); ³¹P{¹H} NMR (CD₂Cl₂, 298 K, 121.4 MHz, δ [ppm]): 72.3 (*d*, ²*J*_{PP} = 26 Hz, ¹*J*_{PSe} = 417 Hz), 48.9 (*t*, ²*J*_{PP} = 26 Hz, broadening for the Se satellites); ¹⁹F{¹H} NMR (CD₂Cl₂, 298 K, 282.2 Hz, δ [ppm]): -79.2 (*s*); ⁷⁷Se{¹H} NMR (CD₂Cl₂, 298 K, 68.2 Hz, δ [ppm]): 119 (*dd*, *J*_{SeP} = 416.5, 133.5 Hz).

References

- [1] a) N. Burford, P. Losier, A. D. Phillips, P. J. Ragonna, T. S. Cameron, *Inorg. Chem.* **2003**, *42*, 1087-1091; b) N. Burford, H. A. Spinney, M. J. Ferguson, R. McDonald, *Chem. Commun.* **2004**, 2696-2697; c) N. Burford, A. D. Phillips, H. A. Spinney, M. Lumsden, U. Werner-Zwanziger, M. J. Ferguson, R. McDonald, *J. Am. Chem. Soc.* **2005**, *127*, 3921-3927.
- [2] a) P. A. Gray, Y.-y. Carpenter, N. Burford, R. McDonald, *Dalton Trans.* **2016**, *45*, 2124-2129; b) K. Schwedtmann, S. Schulz, F. Hennersdorf, T. Strassner, E. Dmitrieva, J. J. Weigand, *Angew. Chem. Int. Ed.* **2015**, *54*, 11054-11058; c) J. J. Weigand, K. O. Feldmann, F. D. Henne, *J. Am. Chem. Soc.* **2010**, *132*, 16321-16323; d) M. Azouri, J. Andrieu, M. Picquet, H. Cattey, *Inorg. Chem.* **2009**, *48*, 1236-1242.
- [3] a) Á. Kozma, J. Rust, M. Alcarazo, *Chem. - Eur. J.* **2015**, *21*, 10829-10834; b) L. Gu, G. Gopakumar, P. Gualco, W. Thiel, M. Alcarazo, *Chem. - Eur. J.* **2014**, *20*, 8575-8578; c) K. Schwedtmann, M. H. Holthausen, K. O. Feldmann, J. J. Weigand, *Angew. Chem. Int. Ed.* **2013**, *52*, 14204-14208; d) R. Bashforth, A. J. Boyall, P. K. Coffey (née Monks), K. B. Dillon, A. E. Goeta, J. a. K. Howard, A. M. Kenwright, M. R. Probert, H. J. Shepherd, A. L. Thompson, *Dalton Trans.* **2012**, *41*, 1165-1172; e) K. B. Dillon, A. E. Goeta, J. a. K. Howard, P. K. Monks, H. J. Shepherd, A. L. Thompson, *Dalton Trans.* **2008**, 1144; f) A. Schmidpeter, S. Lochschmidt, K. Karaghiosoff, W. S. Sheldrick, *J. Chem. Soc., Chem. Commun.* **1985**, 1447.
- [4] J. J. Weigand, S. D. Riegel, N. Burford, A. Decken, *J. Am. Chem. Soc.* **2007**, *129*, 7969-7976.
- [5] J. Petušková, M. Patil, S. Holle, C. W. Lehmann, W. Thiel, M. Alcarazo, *J. Am. Chem. Soc.* **2011**, *133*, 20758-20760.
- [6] a) J. L. Dutton, P. J. Ragonna, *Coord. Chem. Rev.* **2011**, *255*, 1414-1425; b) C. A. Dyker, N. Burford, *Chem. Asian J.* **2008**, *3*, 28-36; c) J. J. Weigand, N. Burford, A. Decken, A. Schulz, *Eur. J. Inorg. Chem.* **2007**, *3*, 4868-4872; d) V. G. Nenajdenko, N. E. Shevchenko, E. S. Balenkova, I. V. Alabugin, *Chem. Rev.* **2003**, *103*, 229-282; e) T. A. Engesser, M. R. Lichtenthaler, M. Schleep, I. Krossing, *Chem. Soc. Rev.* **2016**, *45*, 789-899; f) A. P. M. Robertson, P. A. Gray, N. Burford, *Angew. Chem. Int. Ed.* **2014**, *53*, 6050-6069; g) F. D. Henne, A. T. Dickschat, F. Hennersdorf, K. O. Feldmann, J. J. Weigand, *Inorg. Chem.* **2015**, *54*, 6849-6861.
- [7] S. S. Chitnis, A. P. M. Robertson, N. Burford, B. O. Patrick, R. McDonald, M. J. Ferguson, *Chem. Sci.* **2015**, *6*, 6545-6555.
- [8] a) K. L. Bamford, A. P. M. Robertson, H. A. Jenkins, B. O. Patrick, N. Burford, *Can. J. Chem.* **2015**, *93*, 375-379; b) K. Tani, K. Matsuyama, S. Kato, K. Yamada, H. Mifune, *Bull. Chem. Soc. Jpn.* **2000**, *73*, 1243-1252.
- [9] M. H. Stewart, M. J. A. Johnson, J. W. Kampf, *Organometallics* **2007**, *26*, 5102-5110.
- [10] J. E. McDonough, A. Mendiratta, J. J. Curley, G. C. Fortman, S. Fantasia, C. C. Cummins, E. V. Rybak-Akimova, S. P. Nolan, C. D. Hoff, *Inorg. Chem.* **2008**, *47*, 2133-2141.
- [11] P. Pyykkö, M. Atsumi, *Chem. - Eur. J.* **2009**, *15*, 186-197.
- [12] S. Alvarez, *Dalton Trans.* **2013**, *42*, 8617.
- [13] K. A. Kerr, P. M. Boorman, B. S. Misener, J. G. H. v. Roode, *Can. J. Chem.* **1977**, *55*, 3081-3085.
- [14] P. L. Folkins, B. R. Vincent, D. N. Harpp, *Tetrahedron Lett.* **1991**, *32*, 7009-7012.
- [15] J. A. Davies, S. Dutremez, A. A. Pinkerton, *Inorg. Chem.* **1991**, *30*, 2380-2387.
- [16] N. A. Barnes, S. M. Godfrey, R. T. A. Halton, I. Mushtaq, R. G. Pritchard, S. Sarwar, *Dalton Trans.* **2006**, 1517-1523.
- [17] G. M. Sheldrick, *Acta Cryst. Sect. A* **2008**, *64*, 112-122.

Graphical Abstract

Compounds with the generic formula $[\text{PhPL}_2][\text{OTf}]_2$ contain cations that represent complexes of the phenylphosphine dication expanding the scope of coordination complexes involving phosphorus as an acceptor.