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Synthesis and solid state structures of Chalcogenide compounds of Imidazolin-2-ylidene-1,1-Diphenyl-phosphinamine

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Abstract. We report the synthesis and solid state structures of 1,3-di-aryl-imidazolin-2-ylidine-1,1-diphenyl-phosphinamine [(aryl = mesityl (**1a**) and aryl = 2,6-diisopripyl (**1b**)] and their chalcogenide compounds 1, 3-di-aryl-imidazolin-2-ylidine-*P*, *P*-diphenylphosphinicamide (**2a,b**), 1,3-di-aryl-imidazolin-2-ylidine-*P*,*P*-diphenyl-phosphinothioicamide (**3a,b**) and 1,3-diaryl-imidazolin-2-ylidine-*P*, *P*-diphenyl-phosphinoselenoic-amide (**4a,b**). The compounds **1a,b** were prepared in good yield by the reaction of 1,3-di-aryl-imidazolin-2-imine and chlorodiphenylphosphine in the presence of triethylamine in toluene. The reactions of **1a,b** with elemental sulphur and selenium afforded the corresponding chalcogenide compounds **3a,b** and **4a,b** respectively. The corresponding oxo- derivative (**2a,b**) was obtained by reacting compound **1a,b** with 30% aqueous hydrogen peroxide in THF. The molecular structures of **1a, 2a, 3a** and **4a,b** have been established by single crystal X-ray diffraction analyses. The molecular structures reveal that even C1–N1–P1 angle (124.62°) in compound **1a** is less obtuse compared to the corresponding C1–N1–Si1 angles (157.8°) observed in related *N*-silylated 2-iminoimidazolines and trimethylsilyl iminophosphoranes. C1–N1–P1 angles are further widened in compounds **2a, 3a**, and **4a,b** due to the attachment of chalcogen atoms onto phosphorus atom.

Keywords. Imidazol-2-imine; imidazolin-2-ylidene-1,1-diphenyl-phosphinamine; sulfide; selenide.

1. Introduction

N-heterocyclic carbenes (NHCs) of the imidazolin-2-ylidene type[1] are nowadays ubiquitous and essential in research areas such as homogeneous catalysis,[2] materials science[3] and medicinal chemistry[4] and they play very important roles in organotransition metal and coordination chemistry. Imidazolin-2-imines which can be achieved by the reaction of N-heterocyclic carbenes of the imidazolin-2-ylidene-type with organic azides such as trimethylsilyl azide followed by desilylation, are attractive precursors for the generation of mono-anionic imidazolin-2- iminato ligands, used as ancillary ligands to stabilize the early transition metals and metals in a higher oxidation state. Imidazoline-2-iminato complexes are widely used in a number of homogeneous catalysts, in particular for olefin polymerization and alkyne metathesis. Tamm *et al.*, have shown that these ligands are efficient for the synthesis of transition metal and lanthanide complexes,[5] as imidazolin-2-imine ligands can act as $2\sigma, 4\pi$-electron donors analogous to related phosphoraneimides, R_3PN^-,[6] cyclopentadienides, $C_5R_5^-$. Imidazolin-2-imines can also be used as building blocks for a number of multidentate ligands by linking the imidazolin-2-imines fragment to each other or to other functional moieties.[7] Recently, we had reported our preliminary results of extending the imidazolin-2-imine ligand by phosphine group to get related imidazolin-2-ylidene-1,1-diphenylphosphinamine and its chalcogenide derivatives (O, S, Se, Te).[8] In continuation to our study, we were interested to expand our studies with various imidazolin-2-imines. With this contribution, we now wish to give a full account of the synthesis and structural characterization of Im^RNPPh_2 [R = Mes (**1a**), Dipp (**1b**)] and their respective chalcogenide compounds $Im^RNP(=E)Ph_2$ [E = O, R = Mes, (**2a**), Dipp (**2b**); E = S, R = Mes, (**3a**), Dipp (**3b**); E = Se, R = Mes, (**4a**), Dipp (**4b**)].

2. Experimental

2.1 *General Information*

All manipulations were performed in an atmosphere of dry nitrogen by using Schlenk-type glassware on a

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This work is dedicated to Prof. Dr. Peter W. Roesky on the occasion of his 49th Birthday

dual manifold Schlenk line, interfaced to a high vacuum (10^{-4} torr) line. THF was pre-dried over Na wire and distilled under nitrogen from sodium and benzophenone ketyl prior to use. Toluene was distilled under nitrogen from sodium. ^{1}H NMR (400 MHz), ^{13}C{^{1}H} (100 MHz) and ^{31}P{^{1}H} NMR (161.9 MHz) spectra were recorded on a BRUKER AVANCE III-400 spectrometer. BRUKER ALPHA FT-IR was used for FT-IR measurement. Elemental analyses were performed on a BRUKER EURO EA at the Indian Institute of Technology Hyderabad. 1, 3-di-aryl-imidazolin-2-imine (aryl = Mes or Dipp) was prepared according to literature procedure.[9] The NMR solvent $CDCl_3$ was purchased from Sigma Aldrich.

2.2 *Synthesis of $Im^{R}NPPh_2$ [R =Mes (**1a**), Dipp (**1b**)]*

Chlorodiphenylphosphine (0.393 g, 1.79 mmol) was added dropwise over a period of 20 min to a stirred solution of 1,3-di-aryl imidazole-2-imine (1.79 mmol) and triethylamine (0.181 g, 1.79 mmol) in dry toluene (5 mL). The reaction mixture was stirred at room temperature for another 6 h. The white precipitate of triethylammonium hydrochloride was filtered through a frit in an inert atmosphere. In the filtrate, the solvent was removed under vacuum to leave an orange solid. Compound **1a** was re-crystallized from toluene at –35°C. Orange crystals appeared after 2–3 days.

1a: Yield: 1.2 g, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22–7.13 (m, 6H, Ph), 7.03–6.95 (m, 4H, Ph), 6.77 (s, 4H, Ar), 6.59 (s, 2H, NC*H*C*H*N), 2.31 (s, 6H, CH_3), 2.18 (s, 12H, CH_3) ppm. ^{31}P{^{1}H} NMR (161.9 MHz, $CDCl_3$): δ 35.8 ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 141.2 (*ipso*-Ar), 140.1 (N*C*N), 138.92 (*ipso*-Ph), 136.6 (*o*-Ar), 132.2 (*p*-Ar), 130.6 (*o*-Ph), 130.5 (*o*-Ph), 128.9 (*m*-Ar), 128.7 (*p*-Ph), 126.9 (*m*-Ph), 126.8 (*m*-Ph), 115.5 (N*C*H), 21.0 (*C*H3), 18.4 (*C*H_3) ppm. FT-IR selected peak (cm^{-1}): 924 (P-N), 1128 (P-Ph), 1653 (C=N), 3050 (aromatic C-H). Elemental analysis: $C_{33}H_{34}N_3P$ (503.64): Calcd. (%) C 78.70, H 6.80, N 8.34; Found (%) C 78.44, H 6.57, N 8.04.

1b: Yield: 1.6 g (92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21-7.46 (m, 2H, Ar), 7.25-7.21 (m, 4H, Ar), 6.98-6.93 (m, 10H, Ph), 6.39 (s, 2H, NC*H*C*H*N), 2.99 (sept, 4H, $^{3}J_{HH}$ = 6.36 Hz, C*H*(CH_3)$_2$), 1.18 (d, 12H, 3J_{HH} = 6.84 Hz, CH(CH_3)$_2$), 1.04 (d, 12H, $^{3}J_{HH}$ = 6.84 Hz, CH(CH_3)$_2$) ppm. ^{31}P{^{1}H}NMR (161.9 MHz, $CDCl_3$): δ 27.8 ppm. ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ 148.5 (N*C*N), 147.8 (*ipso*-Ar), 134.1 (*ipso*-Ph), 130.4 (*o*-Ar), 130.2 (*p*-Ar), 129.2 (*o*-Ph), 127.0 (*m*-Ar), 126.7 (*p*-Ph), 123.5 (*m*-Ar), 115.1 (N*C*H), 28.8 (*C*H(CH_3)$_2$), 24.6 (CH(*C*H_3)$_2$), 24.6 (CH(*C*H_3)$_2$) ppm. Elemental analysis: $C_{39}H_{46}N_3P$ (587.78): Calcd. (%) C 79.69, H 7.89, N 7.15; Found (%) C 79.39, H 7.42, N 6.88.

2.3 *Synthesis of $Im^{R}NP(=E)Ph_2$[E=O, R =Mes, (**2a**), Dipp (**2b**)*

In a 50 mL of dry Schlenk flask 1 mmol of compound **1a** or **1b** was dissolved in 4 mL of THF. To this solution, H_2O_2 (1.5 equiv.) was added and kept for stirring at ambient temperature. After four hours of stirring the solvent was evaporated white solid was obtained; purified by column chromatography (EtOAc/Hexane). The compound was re-crystallized from dichloromethane at room temperature.

2a: Yield: 1.4 g, 93%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19–7.13 (m, 6H, Ph), 7.06–6.98 (m, 4H, Ph), 6.89 (s, 4H, Ar), 6.47 (s, 2H, NC*H*C*H*N), 2.37 (s, 6H, CH_3), 2.05 (s, 12H, CH_3) ppm. ^{31}P{^{1}H}NMR (161.9 MHz, $CDCl_3$): δ 5.0 ppm. ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ 139.6 (*ipso*-Ar), 138.9 (*ipso*-Ph), 138.2 (N*C*N), 136.9 (*o*-Ar), 132.2 (*p*-Ar), 131.1 (*o*-Ph), 131.0 (*o*-Ph), 129.2 (*m*-Ar), 128.8 (*p*-Ph), 127.1 (*m*-Ph), 127.0 (*m*-Ph), 114.7 (N*C*H), 21.0 (*C*H_3), 17.8 (*C*H_3) ppm. FT-IR selected peak (cm^{-1}): 915 (P-N), 1109 (P-Ph), 1260 (P=O), 1623 (C=N), 2962 (aromatic C-H). Elemental analysis: $C_{33}H_{34}N_3OP$ (519.62): Calcd. (%) C 76.28, H 6.60, N 8.09; Found (%) C 75.91, H 6.31, N 7.88.

2b: Yield: 1.2 g, 90%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (t, 2H, $^{3}J_{HH}$ = 7.84 Hz, p-Ar), 7.24 (d, 4H, $^{3}J_{HH}$ = 7.84 Hz, m-Ar), 7.14-7.01 (m, 6H, Ph), 7.00-6.93 (m, 4H, Ph), 6.57 (s, 2H, NC*H*C*H*N), 2.86 (sept, 4H, $^{3}J_{HH}$ = 6.84 Hz, C*H*(CH_3)$_2$), 1.15 (d, 12H, $^{3}J_{HH}$ = 6.84 Hz, CH(CH_3)$_2$), 1.04 (d, 12H, $^{3}J_{HH}$ = 6.84 Hz, CH(CH_3)$_2$) ppm. ^{31}P{^{1}H}NMR (161.9 MHz, $CDCl_3$): δ 4.4 ppm. ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ 147.4 (*ipso*-Ar), 145.5 (N*C*N), 140.2 (*ipso*-Ph), 138.9 (*ipso*-Ph), 133.0 (*o*-Ar), 131.2 (*o*-Ph), 131.1 (*o*-Ph), 129.8 (*p*-Ar), 129.0 (*p*-Ph), 127.2 (*m*-Ph), 127.0 (*m*-Ph), 123.8 (*m*-Ar)116.0 (N*C*H), 28.9 (*C*H(CH_3)$_2$), 24.9 (CH(*C*H_3)$_2$), 22.3 (CH(*C*H_3)$_2$) ppm. FT-IR selected peak (cm^{-1}): 950 (P-N), 1110 (P-Ph), 1264 (P=O), 1625 (C=N), 2963 (aromatic C-H). Elemental analysis: $C_{39}H_{46}N_3OP$ (603.78): Calcd. (%) C 77.58, H 7.68, N 6.96; Found (%) C 77.15, H 7.37, N 6.64.

2.4 *Synthesis of [$Im^{R}NP(=E)Ph_2$] [E =S, R =Mes, (**3a**), Dipp (**3b**)]*

In a 50 mL of dry Schlenk flask 1 mmol of compound **1a** or **1b** was dissolved in 10 mL of toluene. To this solution, elemental sulphur (1mmol) was added and the solution was kept at 90°C for 12 h under stirring. The solvent was evaporated under vacuum and the crude product obtained was purified by column chromatography (EtOAc/hexane). The title compound was re-crystallized from CH_2Cl_2/hexane at room temperature.

3a: Yield: 0.62 g, 97%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21-7.12 (m, 6H, Ph), 7.03-6.96 (m, 4H, Ph), 6.77 (s, 4H, Ar), 6.59 (s, 2H, NC*H*C*H*N), 2.31 (s, 6H, CH_3), 2.18 (s, 12H, CH_3) ppm. ^{31}P{^{1}H}NMR (161.9 MHz, $CDCl_3$): δ 35.8 ppm. ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ 139.6 (*ipso*-Ar), 138.9 (*ipso*-Ph), 138.2 (N*C*N), 136.6 (*o*-Ar), 132.2 (*p*-Ar), 130.6 (*o*-Ph), 130.5 (*o*-Ph), 128.9 (*m*-Ar), 128.7 (*p*-Ph), 126.9 (*m*-Ph), 126.8 (*m*-Ph), 115.5 (N*C*H), 21.0 (*C*H_3), 18.4 (*C*H_3) ppm. FT-IR selected peak (cm^{-1}): 732 (P=S), 911 (P-N), 1434 (P-Ph), 1561 (C=N), 3052 (aromatic C-H). Elemental analysis: $C_{33}H_{34}N_3PS$ (535.68): Calcd. (%) C 73.99, H 6.40, N 7.84; Found (%): C 73.56, H 6.12, N 7.36.

3b: Yield: 0.83 g, 96%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (t, 2H, $^{3}J_{HH}$ = 7.84 Hz, p-Ar), 7.17 (d, 4H, $^{3}J_{HH}$ = 7.84 Hz, m-Ar), 7.13-7.04 (m, 6H, Ph), 7.00-6.90 (m, 4H, Ph), 6.68 (s, 2H, NC*H*C*H*N), 3.00 (sept, 4H, $^{3}J_{HH}$ = 6.84 Hz, CH(CH_3)2), 1.14 (d, 12H, $^{3}J_{HH}$ = 6.84 Hz, CH(CH_3)$_2$), 1.13 (d, 12H, $^{3}J_{HH}$ = 6.84 Hz, CH(CH_3)$_2$) ppm. ^{31}P{^{1}H}NMR (161.9 MHz, $CDCl_3$): δ 36.1 ppm. ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ 147.5 (NCN), 147.2 (*ipso*-Ar), 141.8 (*ipso*-Ph), 140.6 (*ipso*-Ph), 133.0 (*o*-Ar), 130.6 (*o*-Ph), 130.5 (*o*-Ph), 129.8 (*p*-Ar), 128.7 (*p*-Ph), 127.0 (*m*-Ph), 126.9 (*m*-Ph), 123.9 (*m*-Ar)116.9 (N*C*H), 28.7 (*C*H(CH$_3$)$_2$), 25.3 (CH(*C*H$_3$)$_2$), 22.6 (CH(*C*H$_3$)$_2$ ppm. FT-IR selected peak (cm^{-1}): 728 (P=S), 907 (P-N), 1467 (P-Ph), 1561 (C=N), 3055 (aromatic C-H). Anal Calc. for $C_{39}H_{46}N_3PS$ (619.84): Calcd. (%) C 75.57, H 7.48, N 6.78; Found (%) C 75.09, H 7.21, N 6.59.

2.5 *Synthesis of [Im^{R}NP(=E)Ph$_2$] [E =Se, R =Mes, (**4a**), Dipp (**4b**)]*

In a 50 mL of dry Schlenk flask 1equiv. of compound **1a** or **1b** was dissolved in 10 mL of toluene and to this solution elemental selenium (1.8 equiv.) was added and kept for stirring at 90°C for 12 h. The solvent was evaporated under vacuum and a white solid residue was obtained which was purified by column chromatography (EtOAc/hexane). The title compound was re-crystallized from CH_2Cl_2/hexane at room temperature.

4a: Yield: 0.63 g, 98%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21-7.12 (m, 6H, Ph), 7.03-6.96 (m, 4H, Ph), 6.77 (s, 4H, Ar), 6.60 (s, 2H, NCH=CHN), 2.31 (s, 6H, CH_3), 2.21 (s, 12H, CH_3) ppm. ^{31}P{^{1}H}NMR (161.9 MHz, $CDCl_3$): δ 25.7 ppm. ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ 140.3 (*ipso*-Ar), 139.3 (NCN), 137.9 (*ipso*-Ph), 135.5 (*o*-Ar), 131.1 (*p*-Ar), 129.7 (*o*-Ph), 129.5 (*o*-Ph), 127.9 (*m*-Ar), 127.7 (*p*-Ph), 127.7 (*m*-Ph), 114.7 (N*C*H), 20.0 (*C*H_3), 17.7 (*C*H_3) ppm. FT-IR selected peak (cm^{-1}): 965 (P=Se), 917 (P-N), 1615 (C=N), 3049 (aromatic C-H). Elemental analysis: $C_{33}H_{34}N_3PSe$ (582.50): Calcd. (%) C 68.03, H 5.88, N 7.21; Found (%) C 67.79, H 5.55, N 7.07.

4b: Yield: 0.47 g, 96%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (t, 2H, $^{3}J_{HH}$ = 7.84 Hz, p-Ar), 7.16 (d, 4H, $^{3}J_{HH}$ = 7.76 Hz, m-Ar), 7.12-7.04 (m, 6H, Ph), 7.00-6.90 (m, 4H, Ph), 6.71 (s, 2H, NC*H*C*H*N), 3.05 (sept, 4H, $^{3}J_{HH}$ = 6.36 Hz, C*H*(CH$_3$)$_2$), 1.17 (d, 12H, $^{3}J_{HH}$ = 6.84 Hz, CH(CH_3)$_2$), 1.14 (d, 12H, $^{3}J_{HH}$ = 6.84 Hz, CH(CH_3)$_2$) ppm. ^{31}P{^{1}H}NMR (161.9 MHz, $CDCl_3$): δ 36.1 ppm. ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ 148.1 (N*C*N), 147.1 (*ipso*-Ar), 141.4 (*ipso*-Ph), 140.4 (*ipso*-Ph), 132.8 (*o*-Ar), 130.7 (*o*-Ph), 130.6 (*o*-Ph), 129.9 (*p*-Ar), 128.7 (*p*-Ph), 127.0 (*m*-Ph), 126.9 (*m*-Ph), 124.0 (*m*-Ar), 117.2 (N*C*H), 28.7 (*C*H(CH$_3$)$_2$), 25.5 (CH(*C*H$_3$)$_2$), 22.8 (CH(*C*H$_3$)$_2$) ppm. FT-IR selected peak (cm^{-1}): 956 (P=Se), 908 (P-N), 1600 (C=N), 3054 (aromatic C-H). Elemental analysis: $C_{39}H_{46}N_3PSe$ (666.74): Calcd. (%) C 70.26, H 6.95, N 6.30; found (%) C 70.02, H 6.79, N 6.14.

2.6 *Single-Crystal X-Ray Structure Determinations*

2.6a *X-ray Crystallographic Analyses*: Single crystals of compound **1a** were grown from toluene at –35°C whereas crystals of **2a, 3a, 4a,b** were grown from CH_2Cl_2/hexane mixture at room temperature. In each case, a crystal of suitable dimensions was mounted on a CryoLoop (Hampton Research Corp.) with a layer of light mineral oil and placed in a nitrogen stream at 150(2) K. All measurements were made on an Agilent Supernova X-calibur Eos CCD detector with graphite-monochromatic Cu-Kα (1.54184 Å) radiation. Crystal data and structure refinement parameters are summarized in the table 1. The structures were solved by direct methods (SIR2004)[10] and refined on F^2 by full-matrix least-squares methods; using SHELXL-97.[11] Non-hydrogen atoms were anisotropically refined. H-atoms were included in the refinement on calculated positions riding on their carrier atoms. The function minimized was $[\sum w(Fo^2-Fc^2)^2]$ (w = 1 / $[\sigma^2$ (Fo^2) + (aP)^2+ bP]), where P = (Max(Fo^2,0) + 2Fc^2) / 3 with $\sigma^2(Fo^2)$ from counting statistics. The function $R1$ and $wR2$ were ($\Sigma \| Fo| - |Fc\|$) / $\Sigma|Fo|$ and $[\Sigma w(Fo^2 - Fc^2)^2$ / $\Sigma(wFo^4)]^{1/2}$, respectively. The ORTEP-3 program[12] was used to draw the molecule. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as a supplementary publication no. CCDC 1420028-1420032. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK

Table 1. Crystallographic details of **1**, **2a**, **3a**, **4a** and **4b**.

Crystal	**1**	**2a**	**3a**
CCDC No.	1420028	1420029	1420030
Empirical formula	$C_{33}H_{34}N_3P$	$C_{33}H_{34}N_3OP$	$C_{33}H_{34}N_3PS$
Formula weight	503.60	519.60	535.66
T(K)	150(2)	293(2)	293(2)
λ (Å)	1.54184	1.54184	1.54184
Crystal system	Triclinic	Monoclinic	Orthorhombic
Space group	$P\bar{1}$	$P2_1/c$	$P2_12_12_1$
a (Å)	8.8079(6)	8.4818(4)	8.7492(4)
b (Å)	10.3470(8)	31.2129(2)	18.4412(1)
c (Å)	16.7289(1)	14.0448(9)	18.4548(8)
α (°)	89.195(6)	90	90
β (°)	80.155(6)	103.174(6)	90
γ (°)	69.595(7)	90	90
V (Å^3)	1406.1(2)	3620.4(4)	2977.6(3)
Z	2	4	4
D_{calc} Mg m^{-3}	1.189	0.953	1.195
μ (mm^{-1})	1.051	0.850	1.660
F (000)	536	1104	1136
Theta range for data collection	4.56 to 70.60°	3.52 to 69.99°	3.39 to 70.79°.
Limiting indices	−10<=h<=10, −12<=k<=12, −20<=l<=15	−10<=h<=10, −37<=k<=37, −12<=l<=17	−10<=h<=6, −20<=k<=20, −22<=l<=20
Reflections collected / unique	9935 / 5287 [R(int) = 0.0220]	16013 / 6827 [R(int) = 0.0314]	6407 / 4510 [R(int) = 0.0208]
Completeness to theta	97.7%	99.0%	88.5%
Absorption correction	Multi-Scan	Multi-Scan	Multi-Scan
Max. and min. transmission	1.0000 and 0.636	1.0000 and 0.537	1.00000 and 0.794
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	5287/ 0 / 340	6793/ 0 / 349	4510 / 0 / 351
Goodness-of-fit on F^2	1.056	1.064	1.039
Final R indices [I> 2sigma(I)]	$R_1 = 0.0633$, $wR_2 = 0.1822$	$R_1 = 0.0764$, $wR_2 = 0.2321$	$R_1 = 0.0368$, $wR_2 = 0.1031$
R indices (all data)	$R_1 = 0.0674$, $wR_2 = 0.1867$	$R_1 = 0.0906$, $wR_2 = 0.2451$	$R_1 = 0.0384$, $wR_2 = 0.1055$

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3. Results and Discussion

3.1.1 *Synthesis of compound **1a,b**:* The phosphinimine (**1a,b**) can be achieved in quantitative yield by the treatment of respective imidazolin-2-imine and chlorodiphenylphoshine in toluene solution at room temperature and in the presence of triethylamine (scheme 1).[8] The conversion of imidazolin-2-imine to (**1a,b**) can easily be detected by ^{1}H and ^{31}P{^{1}H}NMR spectroscopy. In ^{1}H NMR, the gradual disappearance of the singlet resonance for imine proton (*NH*) observed for compound imidazolin-2-imine at δ 4.28 ppm (Mes) 4.21 ppm (Dipp) ensured the formation of related phosphinamine compound **1**. A significant low field shift [δ 6.59 ppm (**1a**) and 6.39 ppm (**1b**)] occurs for the resonances of olefinic *NCH* protons observed, compared to that (δ 5.71 and 5.87 ppm) of free imidazolin-2-imine reported by Tamm *et al.*[9] In ^{31}P{^{1}H}NMR spectra, both the compounds display a singlet resonance at δ 35.8 ppm (**1a**) and 27.8 ppm (**1b**) for the phosphorus atom bound to imine nitrogen in. In addition, a marked low-field shift of the N*C*N carbon atoms in ^{13}C{^{1}H}NMR spectra, observed at δ 141.2 ppm (**1a**) and 148.5 ppm (**1b**) indicate the formation of N-P bond in each case. Re-crystallization of **1a** from toluene furnished colorless crystals, which were used for single crystal X-ray diffraction analysis to establish the molecular structure of **1a**.

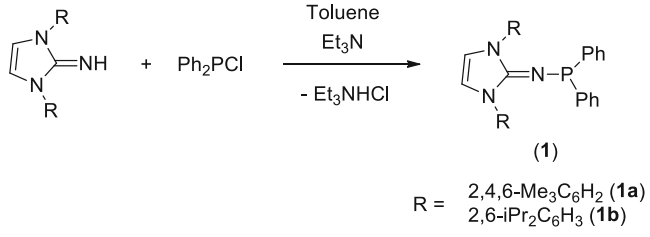
The solid state structure of **1a** confirmed the formation of phosphorus and nitrogen bond through the elimination of triethylamine hydrochloride. The compound **1a** crystallizes in triclinic space group $P\bar{1}$

Table 1. Crystallographic details of **1**, **2a**, **3a**, **4a** and **4b** (contd).

Crystal	**4a**	**4b**
CCDC No.	1420031	1420032
Empirical formula	$C_{33}H_{34}N_3PSe$	$C_{39}H_{46}N_3PSe$
Formula weight	582.56	666.72
T(K)	293(2)	150(2)
λ (Å)	1.54184	1.54184
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$P2_1/c$
a (Å)	8.9524(3)	11.5944(2)
b (Å)	18.2570(8)	15.0183(3)
c (Å)	18.5025(8)	21.3146(5)
α (°)	90	90
β (°)	90	108.205(2)
γ (°)	90	90
V (Å^3)	3024.1(2)	3525.69(12)
Z	4	4
D_{calc} Mg m^{-3}	1.282	1.256
μ (mm^{-1})	2.366	2.092
F (000)	1212	1400
Theta range for data collection	3.40 to 71.11°	3.66 to 70.62°.
Limiting indices	−10<=h<=6, −22<=k<=18, −22<=l<=13	−13<=h<=14, −18<=k<=11, −24<=l<=26
Reflections collected / unique	8084 / 4885 [R(int) = 0.0243]	13913 / 6617[R(int) = 0.0328]
Completeness to theta	97.8%	97.6%
Absorption correction	Multi-Scan	Multi-Scan
Max. and min. transmission	1.000 and 0.552	1.00000 and 0.715
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	4885 / 0 / 350	6617 / 0 / 405
Goodness-of-fit on F^2	1.029	1.084
Final R indices [I>2sigma(I)]	$R_1 = 0.0381$, $wR_2 = 0.0989$	$R_1 = 0.0355$, $wR_2 = 0.0978$
R indices (all data)	$R_1 = 0.0444$, $wR_2 = 0.1059$	$R_1 = 0.0379$, $wR_2 = 0.1000$

having two molecules in the unit cell. The molecular structure of the compound **1a** is shown in figure 1, and selected bond lengths and angles are given in table 2. The detailed structure and refinement parameters are given in table 1.

The bond distance and bond angles are similar to 1,3-di-*tert*-butyl-imidazolin-2-ylidine-1,1-diphenyl-phosphinamine reported earlier by us.[8] The carbon nitrogen imine bond C1–N1 distance [1.301(3) Å] in **1a** is slightly increased with respect to the corresponding free imidazolin-2-imine [1.289(2) Å] and silyl derivative (1.267(2) Å) reported in literature.[13] This slight elongation in C1–N1 bond length indicates that the phosphinamine **1a** exhibits presumably a stronger ylidic behavior than their imine or silyl congeners. However, C1-N2 [1.376(3) Å] and C1-N3 [1.384(3) Å] bond distances are within a similar range to that of free imines. The phosphorus atom P1 lies 0.591 Å above the plane drawn by the least square fit of the N1, C1, N2, N3, C2 and C3 atoms of the molecule **1a** indicating clear



Scheme 1. Synthesis of phosphinimines **1a,b** from imidazolin-2-imine.

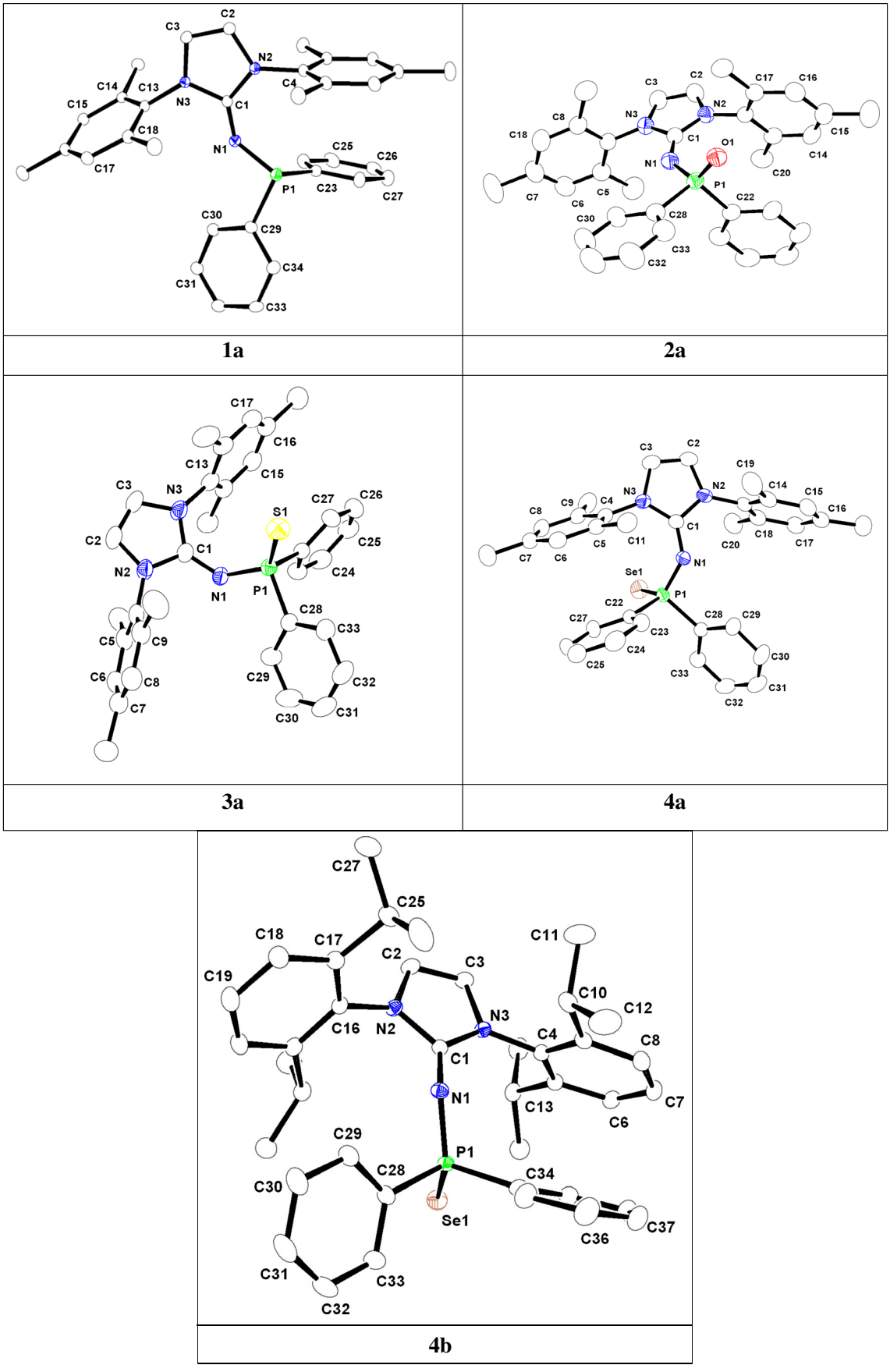


Figure 1. Solid state structures of compounds **1a, 2a, 3a, 4a** and **4b;** ellipsoids are drawn to encompass 30% probability. Selected bond lengths and bond angles are given in table 2.

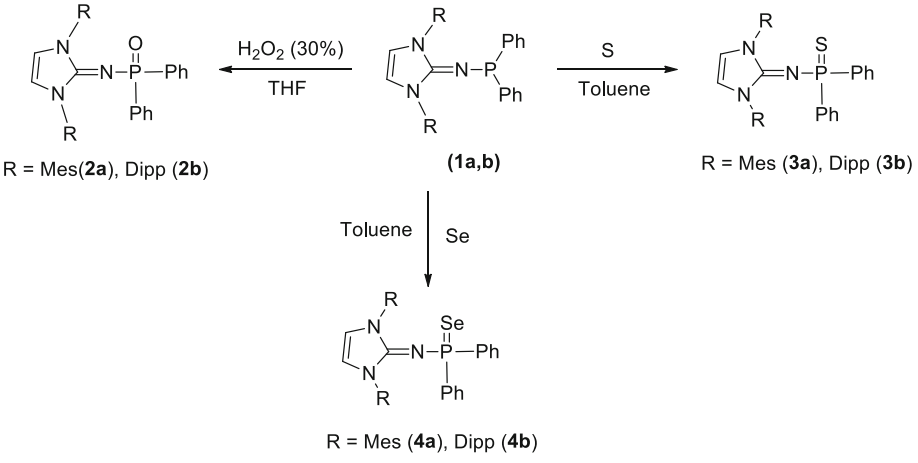
Table 2. Selected bond lengths [Å] and angles [°] of compounds **1a, 2a, 3a, 4a** and **4b**.

	1a	**2a**	**3a**	**4a**	**4b**
Bond Lengths (Å)					
N1–C1	1.301(3)	1.292(4)	1.311(3)	1.306(4)	1.309(2)
N1–P1	1.674(2)	1.597(3)	1.6121(18)	1.609(3)	1.6070(1)
P1–E1	———	1.476(2)	1.9522(8)	2.1081(9)	2.1182(4)
C1–N2	1.376(3)	1.371(4)	1.359(3)	1.365(4)	1.372(2)
C1–N3	1.384(3)	1.368(4)	1.365(3)	1.356(4)	1.373(2)
N2–C2	1.403(3)	1.398(5)	1.390(3)	1.388(2)	1.388(2)
N3–C3	1.395(3)	1.399(5)	1.400(3)	1.396(2)	1.396(2)
C2–C3	1.330(3)	1.350(5)	1.320(4)	1.327(6)	1.345(2)
Bond Angles (°)					
C1–N1–P1	124.58(2)	138.9(3)	130.92(2)	132.2(3)	132.90(1)
N1–P1–E1	———	120.44(2)	119.36(7)	118.08(10)	118.42(5)
Ph–P1–Ph	97.06(1)	105.97(2)	101.82(9)	101.47(13)	103.83(8)
N2–C1–N3	104.65(2)	104.9(3)	131.3(2)	106.2(3)	105.31(1)
N1–C1–N2	132.5(2)	133.2(3)	122.5(2)	122.0(3)	123.57(1)
N1–C1–N3	122.8(2)	121.9(3)	106.08(2)	131.6(3)	130.84(1)

deviation from the co-planarity of P1 atoms from the imidazole ring plane. The angle C1–N1–P1 [124.58(2)°] is considerably smaller than that present one in the corresponding free silyl derivative 147.2(1)°. The sum of the angles around the C1 atom is 359.9°.

3.1.2 *Synthesis of oxo, sulfide and selenide compounds:* The corresponding sulfide (**3a,b**) and selenide (**4a,b**) compounds were isolated in good yield through the reaction of **1a,b** with either elemental sulphur or selenium in toluene under reflux condition (scheme 2). However, the reaction of compound **1a,b** with 30% aqueous hydrogen peroxide in THF afforded the corresponding oxo-compound **2a,b** in good yield (scheme 2). All the new compounds were characterized by spectroscopic and analytical techniques and the solid state structures of compounds **2a, 3a,** and **4a,b** were established by single crystal X-ray diffraction analysis.

In FT-IR spectra, the oxo compounds **2a** and **2b** display a strong absorption band at 1260 and 1224 cm^{-1}, respectively which can be assigned to P=O stretching frequency of the corresponding compounds. Each of the sulfide and selenide compounds **3a,b** and **4a,b** show its characteristic strong absorption band (732 cm^{-1} for **3a**, 728 for **3b**, 965 cm^{-1} for **4a**, 956 cm^{-1} for **4b**) for P=E (E = S, Se) bond stretching. The observed values are in agreement with literature report.[13] In ^{1}H NMR spectra, each compound displays characteristic singlet resonance signals of two olefinic *NCH* protons present in the imidazolium ring, (δ 6.47 ppm for **2a**, 6.57 ppm for **2b**, 6.77 ppm for **3a** and 6.68 ppm for **3b**, 6.60 ppm for **4a** and 6.71 ppm for **4b**) which falls in the same range as compound **1a,b** (δ 6.59 ppm and



Scheme 2. Synthesis of chalcogenide compounds **2a,b**, **3a,b** and **4a,b**.

6.39 ppm, respectively). Two separate sharp singlets (δ 2.37, 2.05 ppm for **2a**, 2.31, 2.18 ppm for **3a** and 2.31, 2.21 ppm for **4a**) with an integration ratio of 3:6 can be assigned to the methyl protons present in the mesityl groups attached in imidazol rings of the compounds **2a**, **3a** and **4a**. The Dipp groups attached to the imidazole rings of the compounds **2b**, **3b** and **4b** also show the characteristic resonance signals as one septet (δ 2.86 ppm for **2b**, 3.0 ppm for **3b** and 3.05 ppm for **4b**) and two doublets (δ 1.15, 1.04 ppm for **2b**, 1.14, 1.13 ppm for **3b** and 1.17, 1.14 ppm for **4b**) with average coupling constant of 6.8 Hz. $^{31}P\{^{1}H\}$NMR spectra are more informative as compounds **2a** and **2b** show sharp peaks at δ 5.0 and 4.4 ppm, respectively, which are slightly downfield shifted to that of similar compound $CH_2(6\text{-}t\text{-Bu-4-Me}C_6H_2O)_2P(O)NMe_2$ (δ 1.6 ppm) reported by Chakravarty *et al.*[14] Compounds **3a** and **3b** display sharp singlets at upfield region δ 35.8 and 36.1 ppm, respectively, compared to that of compound $CH_2(6\text{-}t\text{-Bu-4-Me}C_6H_2O)_2P(S)NMe_2$($\delta$ 73.8 ppm) synthesized by Chakravarty *et al.*[14] In case of compounds **4a** and **4b**, $^{31}P\{^{1}H\}$NMR the resonance peaks were observed at δ 25.7 and 26.2 ppm, respectively, which are in same range to that of reported compound *cis*-{(t-BuNH)P(Se)(μ-N-t-Bu)$_2$P(O)H}.[15] The resonance signals in the $^{13}C\{^{1}H\}$ are in the expected ranges and match with the values reported in literature.[13]

The compound **2a** was crystallized from a solution of CH_2Cl_2 and dioxane (2:1) at ambient temperature. In solid state, the compound **2a** crystallizes in monoclinic space group $P2_1/c$ having 4 molecules in the unit cell. One dioxane molecule is also crystallized in the asymmetric unit as solvate. The compounds **3a** and **4a**, each crystallizes in orthorhombic space group $P2_12_12_1$ having four molecules in the unit cell. However, the compound **4b** crystallizes in monoclinic space group $P2_1/c$ having four molecules in the unit cell. The details of the structural parameters are given in table 1 and the molecular structures of the compounds **2a**, **3a**, **4a** and **4b** are given in figure 1. The P-E (E = O, S, Se) bond distances (1.476(2) Å for **2a** and 1.952(8) Å for **3a**, 2.108(9) Å for **4a**, 2.118(4) Å for **4b**] (table 2) are well in agreement with previously reported values 1.440(2) Å [$CH_2(6\text{-}t\text{-Bu-4-Me}C_2H_2O)_2P(O)NMe_2$],[14] 1.500(3) Å [{$Ph_2P(O)NH(2,6\text{-}Me_2C_6H_3)CaI(THF)_3$} I],[16] 1.910(1) Å [$CH_2(6\text{-}t\text{-Bu-4-Me}C_2H_2O)_2P(O)NMe_2$],[14] 1.947(7) Å for [$Ph_2P(S)NHCPh_3$], 2.059(1) Å [$CH_2(6\text{-}t\text{-Bu-4-Me}C_2H_2O)_2P(O)NMe_2$][14] and 2.102(8) Å for [$Ph_2P(Se)NH(2,6\text{-}Me_2C_6H_3)$], respectively, to consider as phosphorus-chalcogen (O, S, Se) double bond.[16,17] P-N bond distances 1.597(3) Å (**2a**), 1.612(2) Å (**3a**), 1.609(3) Å (**4a**) and 1.607(1) Å (**4b**) are similar and slightly shorter than that of compound **1a** [1.674(2) Å]. Thus the shortening of the phosphorus nitrogen distances can be explained by the formation of pπ-dπ bonding between lone pair of nitrogen and the vacant *d* orbital of the adjacent phosphorus atom. Similar observation was noticed in our previous results as well.[16,17]

The C1-N1-P1 angles [138.9(3)° (**2a**), 130.9(2)° (**3a**), 132.2(3)° (**4a**) and 132.9(12)° (**4b**)] for the compounds are similar but wider than that of compound **1a** [124.58(2)°]. In comparison with reported *N*-silylated imidazolin-2-imines [the C-N-Si angles range from 147(1) to 157.8(1)°],[8b] analogous C1-N1-P1 angles are more acute due to the attachment of the [P(E)Ph$_2$] fragment to the imine nitrogen. The N1-P1-E angles [120.4(2)° (**2a**), 119.4(7)° (**3a**), 118.1(1)° (**4a**) and 118.4(5)° (**4b**)] are also very similar to each other indicating a trigonal pyramidal geometry around the phosphorus center in each compounds. The phosphorus atom P1 lies 0.07 Å (**2a**), 0.755 Å (**3a**), 0.738 Å (**4a**) and 0.912 Å (**4b**) above the plane drawn by the least squares fit of the N3, C3, C2, N2, C1 and N1 atoms of each compound indicating near coplanar geometry of the imidazole moiety with N1 and P1 atoms in compound **2a** and much deviation from co-planarity for other compounds. Even though electronic factors might also be accounted, these deviations in the position of the phosphorus atom with respect to imidazolin-2-imine fragment clearly indicate steric influence of the sulfur and selenium atom attached to the phosphorus atom. Thus, deviation from the C1-N1-P1 angle from linearity and the non-coplanarity of the N1 and P1 atoms with the imidazole ring for compounds **3a**, **4a** and **4b** indicate that the delocalization of electrons from C1 carbon (formation of an imidazolium cation) to phosphorus atom P1 via imine nitrogen N1 to form a zwitter-ionic structure is absent.[8] This is opposite to the observation of the imidazolin-2-iminato metal complexes where imidazolin-2-iminato serves as a six electron donor to the adjacent metal center.[5]

4. Conclusions

In summary, we have successfully demonstrated the synthesis and structural characterization of imidazolin-2-iminophosphine and their oxo, sulfide and selenide compounds. From their molecular structures in the solid state we have observed that unlike imdazolin-2-imines, the delocalization cannot be extended from the imidazole ring to the phosphorus atom through imine nitrogen.

Supplementary Information (SI)

The ^{1}H and $^{31}P\{^{1}H\}$NMR spectra of compounds **1a, 1b, 2a, 2b, 3a, 3b, 4a** and **4b** are given in Supplementary Information, available at www.ias.ac.in/chemsci.

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