Bulky iminophosphonamines for N–P–N coordination: Synthesis and structural characterization of lithium iminophosphonamides and homoleptic *bis*-chelates of Co(II), Ni(II) and Cu(II)

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Abstract. Two new sterically demanding iminophosphonamine ligands (2,4,6-Me₃C₆H₂NH)P(Ph₂)=N(C₆H₂-2,4,6-Me₃) (**1**) and (2,6-*i*Pr₂C₆H₃NH)P(Ph₂)=N(C₆H₂-2,4,6-Me₃) (**2**) and their lithium derivatives as tmeda adducts (Li·tmeda)[(2,4,6-Me₃C₆H₂)NP(Ph₂)=N(C₆H₂-2,4,6-Me₃)] (**3**) and (Li·tmeda)[(2,6-*i*Pr₂C₆H₃)NP(Ph₂)=N(C₆H₂-2,4,6-Me₃)] (**4**), respectively are reported here. Compounds **1–4** have been investigated by ¹H, ¹³C and ¹³P{¹H} NMR spectroscopy. The ⁷Li NMR for complexes **3** and **4** has also been reported. Utility of the ligands and their lithium derivatives have been shown in the synthesis of *bis*-homoleptic metal complexes M[Ph₂P(NC₆H₂-2,4,6-Me₃)₂]₂ (M = Co (**5**), Cu (**6**) and Ni (**7**)). Metal-*bis*-silylamide generated *in situ* was reacted with the ligand (for **5** and **6**) or the lithium derivative of the ligand was reacted with the metal chloride (for **7**). Molecular structure of compounds **1–7** has been elucidated by single crystal X-ray diffraction analyses. The complexes are formed in good yields and are highly lipophilic in a wide range of solvents.

Keywords. Metallacycles; monoanion; homoleptic complexes; iminophosphonamides.

1. Introduction

The NXN ligands have commonly been employed in the synthesis of four-membered metallacycles containing main group, transition as well as inner transition elements (X = CR, N, SR, PR₂).^{1–16} Among this class of ligands, the iminophosphonamides offer the longest X–N bond length (1.60 Å), which in turn allows a wider N–M–N bite angle (usually 70–76°). The sulphinamidinate resembles (1.60–1.62 Å and 70–75°) the iminophosphonamides closely but the former has gained attention recently.^{10–12} Another important feature of iminophosphonamides is that most of the N₂PM metallacycles are nearly planar. The N–P–N coordination of iminophosphonamides has been realized in the form of homoleptic and heteroleptic four-membered chelates. The range of metal ions spans over *s*, *p*, *d* blocks and recently a few lanthanide complexes were also reported.^{17–32} Some of these metal complexes are useful as catalysts and promise a wide scope for future research.^{26–32}

In our ongoing research interest to fine tune the steric and electronic factors of the ligands³³, we have attempted to synthesize sterically bulky iminophosphonamides and to use them in the synthesis

of metallacycles. Consequently, we report here the synthesis and characterization of two new iminophosphonamine ligands (2,4,6-Me₃C₆H₂NH)P(Ph₂)=N(C₆H₂-2,4,6-Me₃) (**1**) and (2,6-*i*Pr₂C₆H₃NH)P(Ph₂)=N(C₆H₂-2,4,6-Me₃) (**2**) and their corresponding lithium derivatives as tmeda adducts (Li·tmeda)[(2,4,6-Me₃C₆H₂)NP(Ph₂)=N(C₆H₂-2,4,6-Me₃)] (**3**) and (Li·tmeda)[(2,6-*i*Pr₂C₆H₃)NP(Ph₂)=N(C₆H₂-2,4,6-Me₃)] (**4**). Application of the ligands and their lithium derivatives are shown in the synthesis of *bis*-homoleptic metal complexes of Co(II) (**5**), Cu(II) (**6**) and Ni(II) (**7**). All these complexes have shown good lipophilicity in a wide range of solvents and have been isolated in good yields.

Iminophosphonamides of lithium reported in the literature comprise of *trans*-1,2-diaminocyclohexane-bridged *bis*-iminophosphonamide,²¹ [{R₂P(NSiMe₃)₂}Li(X)₂] (R = *t*Bu or Ph and X = THF or Py)^{17–19} and (Ph₂P-N)₂PPh₂Li·2THF. The latter compound was isolated as an unprecedented product from the reaction between the phosphinohydrazine (Ph₂P)₂N-N(PPh₂)H and LiN(SiMe₃)₂.²³ Treatment of Py₂P(NSiMe₃)(NHSiMe₃) with lithium reagents LiN(SiMe₂)₂ or MeLi/BuLi leads to the cleavage of P–N bond to yield [Py₂PNLi(SiMe₃)₂] or Py₂PLi(THF)₂, respectively.²⁰

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The only structurally characterized iminophosphonamide of Co(II) reported in the literature is [Co{Ph₂P(N-*p-t*BuC₆H₄)₂}₂].³⁴ No complex of Cu(II) with iminophosphonamides has been reported and only Cu(I) iminophosphonamide derivatives with a series of olefins as co-ligands have been reported.^{35,36} The discrete (π -allyl)nickel(II) iminophosphonamides Ph₂P(NR)₂Ni(η^3 -C₃H₅) (R = SiMe₃ or *p*-Me-C₆H₄),³⁷ [Ni{Ph₂P(NPh)₂}₂]³⁸ and {Ph₂P(NSiMe₃)₂}NiPh(PPh₃)³⁷ are among the structurally characterized heteroleptic iminophosphonamides of Ni(II). The structurally characterized homoleptic iminophosphonamides of Ni(II) are Ni{*i*Pr₂P(NMe)₂}₂ and [Ni{Ph₂P(NSiMe₃)₂}₂].³⁹

2. Experimental

2.1 General remarks

All reactions were performed using standard Schlenk and drybox techniques with appropriately dried solvents. All other chemicals used in this study were purchased from commercial sources and used without further purification. The starting arylaminodiphenylphosphine **1b**,^{40,41} mesitylazide^{42,43} and the metal silylamides^{44–46} were prepared as previously described. The ¹H, ¹³C, ³¹P and ⁷Li NMR spectra were recorded with Bruker 400 MHz spectrometer, respectively, using TMS, H₃PO₄ (85%) and LiCl as the external reference and chemical shift values are reported in ppm.

2.2 X-ray crystallography for compounds **1**–**7**

Single crystal X-ray diffraction data were collected on a Bruker AXS KAPPA APEX-II CCD diffractometer (Monochromatic MoK α radiation) equipped with Oxford Cryosystem 700 Plus at 100 K. Data collection and unit cell refinement for the data sets were done using the Bruker APEX-II suite; data reduction and integration were performed by SAINTV 7.685A (Bruker AXS, 2009) and absorption corrections and scaling were done using SADABS 2008/1 (Bruker AXS, 2009). The crystal structures were solved with either OLEX2 or WINGX package using SHELXS-97 and the structure was refined with SHELXL-97 2008.⁴⁷ Single crystal data and refinement results are listed in table 1. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed at geometrically calculated positions and refined using riding model except the NH hydrogens of **1** and **2** that were located from difference Fourier map and refined isotropically. Diamond

version 2.1d was used to generate graphics for the X-ray structures.

2.3 General synthetic method for ligands (**1** and **2**)

2.3a Synthesis of P(Ph₂)NH(C₆H₂-2,4,6-Me₃) (1a**):** A solution of mesitylamine (6.7 g, 50 mmol) in Et₂O (80 mL) was cooled to –78°C followed by addition of *n*BuLi (32 mL, 51 mmol, 1.6 M). The mixture was allowed to cool to room temperature and stirred for 3 h. A solution of Ph₂PCl (11.0 g, 50 mmol) in Et₂O (60 mL) was added drop-wise to this solution at –78°C. The mixture was stirred at room temperature overnight followed by filtration through Celite and removal of all volatiles under vacuum. The viscous oil thus obtained was washed with pentane to afford a light brown solid that was recrystallized from Et₂O, yield: 13.5 g (75%); m.p. 112–114°C; ¹H NMR (C₆D₆, 400 MHz): δ = 2.10 (s, 6 H, *o*-Me), 2.15 (s, 3 H, *p*-Me), 3.55 (d, 1 H, *J*_{H-P} = 8.5 Hz, NH), 6.75 (s, 2 H, Ar-H), 7.06–7.10 (m, 6 H, Ar-H), 7.47–7.50 (m, 4 H, Ar-H); ¹³C NMR (C₆D₆, 100 MHz): δ = 19.32 (d, *J*_{C-P} = 6.3 Hz), 20.77, 128.72 (d, *J*_{C-P} = 6.4 Hz), 128.99, 129.9 (d, *J*_{C-P} = 1.02 Hz), 130.96 (d, *J*_{C-P} = 3.6 Hz), 131.70, 131.90, 140.83 (d, *J*_{C-P} = 14.2 Hz), 143.25 (d, *J*_{C-P} = 15.8 Hz); ³¹P{¹H} NMR (C₆D₆, 162 MHz): δ = 36; IR (ν cm^{–1}, nujol mull): 3362, 3279, 1303, 1260, 1221, 1149, 1091, 1020, 851, 801, 738, 722, 696.

2.3b General method for the Synthesis of ligands (1** and **2**):** A solution of mesitylazide (40.0 mmol, 6.44 g) in THF (20 mL) was added drop-wise to a THF solution (40 mL) of the appropriate (N-diphenylphosphino)-amine (**1a** or **1b**) (36.0 mmol) at 0°C under nitrogen atmosphere. The reaction mixture was stirred for 12 h at room temperature. Removal of all volatiles gave viscous oil which was washed with hexane to give white solid that was recrystallized from THF to afford colourless crystalline solid.

2.3c Synthesis of (2,4,6-Me₃C₆H₂NH)P(Ph₂) = N(C₆H₂-2,4,6-Me₃) (1**):** Colourless crystalline solid; yield: 13.4 g (74%); m.p. 166°C; ¹H NMR (CDCl₃, 400 MHz): δ = 1.92 (s, 12 H, *o*-Me), 2.05 (s, 6 H, *p*-Me), 4.10 (broad, 1 H, NH), 6.59 (s, 4 H, *m*-H), 7.05–7.10 (m, 4 H, Ar-H), 7.12–7.14 (m, 2 H, Ar-H), 7.62–7.67 (m, 4 H, Ar-H); ¹³C NMR (CDCl₃, 100 MHz): δ = 20.44 (br), 20.54, 127.62 (d, *J*_{C-P} = 24.3 Hz), 127.85, 128, 128.85 (br), 130.80 (d, *J*_{C-P} = 2.8 Hz), 131.76 (d, *J*_{C-P} = 9.8 Hz), 134.15, 135.41; ³¹P{¹H} NMR (CDCl₃, 162 MHz): δ = –13.04; EI-MS: *m/z*: 453 [*M*⁺]; IR (ν cm^{–1}, nujol mull): 3340, 1435, 1306, 1279, 1245, 1214, 1182, 1161, 1118, 1058, 1024, 997, 946, 883, 853, 769, 750, 711, 697, 600. Anal. Calcd. in (%) for C₃₀H₃₃N₂P;

Table 1. Crystallographic data and refinement parameters for compounds **1–7**.

Compound ^[a]	1	2·0.5(C ₄ H ₈ O)	3	4	5	6·0.5C ₇ H ₈	7·0.5C ₇ H ₈
Formula	C ₃₀ H ₃₃ N ₂ P	C ₃₃ H ₃₉ N ₂ P·0.5 (C ₄ H ₈ O)	C ₃₀ H ₃₂ N ₂ PLi· tmeda	C ₃₃ H ₃₈ N ₂ PLi· tmeda	C ₆₀ H ₆₄ N ₄ P ₂ Co	C ₆₀ H ₆₄ N ₄ P ₂ Cu· 0.5C ₇ H ₈	C ₆₀ H ₆₄ N ₄ P ₂ Ni· 0.5C ₇ H ₈
fw, g mol ^{−1}	452.6	530.7	574.7	616.8	962.1	1050.8	1045.9
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1
<i>T</i> /K	100	100	100	100	100	100	100
<i>a</i> /Å	12.014(2)	12.818(1)	9.575(1)	10.060(1)	12.088(1)	9.906(1)	11.182(1)
<i>b</i> /Å	15.537(2)	18.166(2)	18.389(1)	14.962(1)	13.185(2)	12.054(2)	11.225(2)
<i>c</i> /Å	18.174(2)	25.979(2)	18.839(1)	23.912(2)	17.062(2)	12.615(2)	11.573(2)
α /°	90	90	90	90	87.50(1)	82.02(1)	76.26(1)
β /°	132.97(1)	90.26(1)	90.43(1)	92.57(1)	69.48(2)	80.76(2)	86.14(2)
γ /°	90	90	90	90	88.15(2)	66.87(2)	89.85(2)
<i>V</i> /Å ³	2482.27(2)	6049.14(6)	3317.01(1)	3595.68(2)	2544.03(1)	1362.60(2)	1407.75(4)
<i>Z</i>	4	8	4	4	2	1	1
ρ_c / g·cm ^{−3}	1.21	1.17	1.15	1.14	1.26	1.28	1.23
μ (Mo- <i>K</i> α) / mm ^{−1}	0.131	0.118	0.113	0.108	0.443	0.506	0.446
reflections collected	15384	32165	19787	25973	20123	9308	11480
independent reflections	4373	10633	5867	6353	8959	4768	4881
data/restraints/parameters	4373/0/308	10633/0/714	5867/0/389	6353/0/417	8959/0/616	4768/0/343	4881/0/355
<i>R</i> 1, <i>wR</i> 2 [<i>I</i> > 2 σ (<i>I</i>)] ^[a]	0.036, 0.084	0.061, 0.156	0.035, 0.082	0.036, 0.084	0.066, 0.101	0.066, 0.137	0.039, 0.088
<i>R</i> 1, <i>wR</i> 2 (all data)[a]	0.049, 0.089	0.076, 0.169	0.046, 0.087	0.054, 0.090	0.162, 0.127	0.123, 0.162	0.062, 0.096
GOF	1.031	1.055	1.026	0.968	0.952	1.022	1.01

[a] $R1 = \Sigma \|F_o| - |F_c|\| / \Sigma |F_o|$. $wR2 = [\Sigma w(|F_o|^2 - |F_c|^2)^2 / \Sigma w|F_o|^2]^{1/2}$

C, 79.62; H, 7.35; N, 6.19. Found: C, 79.67; H, 7.32; N, 6.25.

2.3d Synthesis of (2,6-*i*Pr₂C₆H₃NH)P(Ph₂)=N(C₆H₂-2,4,6-Me₃) (2): Colourless crystalline solid; yield: 14.24 g (72%); m.p. 135°C. ¹H NMR (C₆D₆, 400 MHz): δ = 1.14 (d, 12 H, $J_{\text{H-H}}$ = 6.7 Hz, CHMe₂), 2.21 (s, 3 H, *p*-Me), 2.26 (s, 6 H, *o*-Me), 3.43 (broad, 2 H, CHMe₂), 4.13 (broad, 1 H, NH), 6.80 (s, 2 H, Ar-H), 7.07–7.26 (m, 9 H, Ar-H), 7.80–7.86 (m, 4 H, Ar-H); ¹³C NMR (C₆D₆, 100 MHz): δ = 20.60, 20.72, 23.94 (d, $J_{\text{C-P}}$ = 13.7 Hz), 28.94 (d $J_{\text{C-P}}$ = 15 Hz), 119.79 (br d $J_{\text{C-P}}$ = 13 Hz), 123.13 (d $J_{\text{C-P}}$ = 24 Hz), 127.7–128.2 (complex multiplets partially hidden by the solvent resonance), 129.68 (d $J_{\text{C-P}}$ = 14 Hz), 131 (br), 132.18 (vtr, $J_{\text{C-P}}$ = 23 Hz), 134.5 (br), 135.29 (br), 141.55 (br), 143.84 (br); ³¹P{¹H} NMR (C₆D₆, 162 MHz): δ = –15.34; EI-MS: m/z : 495 [M^+], 378 [M^+ –Me₃C₆H₂], 336 [M^+ –*i*Pr₂C₆H₃]; IR (ν cm^{–1}, nujol mull): 3362, 1303, 1254, 1217, 1147, 1105, 1068, 1026, 956, 936, 904, 849, 792, 744, 722, 695. Anal. Calcd. in (%) for C₃₃H₃₉N₂P; C, 80.13; H, 7.95; N, 5.66. Found: C, 79.15; H, 7.90; N, 5.51.

2.4 General synthetic method for lithium derivatives (3 and 4)

A solution of ligand (**1** or **2**) (1.0 mmol) and tmeda (0.5 mL) in toluene (20 mL) was cooled to –78°C. To it was added *n*BuLi (0.7 mL, 1.1 mmol, 1.6 M) and allowed to cool to room temperature and stirring was continued for 6 h. Concentration of the mother liquor to 5 mL gave the lithium derivative as colourless crystals at –30°C in 2 days.

2.4a Synthesis of (Li-tmeda)[(2,4,6-Me₃C₆H₂)NP(Ph₂)=N(C₆H₂-2,4,6-Me₃)] (3): Colourless crystalline solid; yield 0.38 g (66%); m.p. 145°C (decomposition); ¹H NMR (400 MHz, C₆D₆): δ = 1.81 (s, 4 H, N-CH₂), 1.92 (s, 12 H, N-Me), 2.24–2.26 (overlapped singlet, 18 H, *o*- & *p*-Me), 6.91 (s, 4 H, Ar-H), 6.99–7.04 (m, 6 H, Ar-H), 7.67–7.72 (m, 4 H, Ar-H); ¹³C NMR (100 MHz, C₆D₆): δ = 20.99 (d, $J_{\text{C-P}}$ = 4.3 Hz), 22.06 (d, $J_{\text{C-P}}$ = 4.1 Hz), 45.39, 56.51, 126.93 (br), 127.32 (overlapped doublets), 128.96 (br), 129.32 (br), 131.66 (vtr, $J_{\text{C-P}}$ = 12.7 Hz), 133.37 (vtr, $J_{\text{C-P}}$ = 11.6 Hz), 142.15 (dd, $J_{\text{C-P}}$ = 92 & 4.9 Hz), 147.73 (d, $J_{\text{C-P}}$ = 3.6 Hz); ³¹P{¹H} NMR (162 MHz, C₆D₆): δ = –8.34; ⁷Li NMR (155 MHz, C₆D₆): δ = 1.18; IR (ν cm^{–1}, nujol mull): 1434, 1375, 1309, 1267, 1158, 1111, 1099, 1032, 943, 852, 794, 760, 726, 704, 656, 584, 535, 525, 497, 455.

2.4b Synthesis of (Li-tmeda)[(2,6-*i*Pr₂C₆H₃)NP(Ph₂)=N(C₆H₂-2,4,6-Me₃)] (4): Colourless crystal-

line solid; yield: 0.38 g (62%); m.p. 182°C; ¹H NMR (400 MHz, C₆D₆): δ = 1.07 (d, $J_{\text{H-H}}$ = 6.8 Hz, 12 H, CHMe₂), 1.70 (broad, 4 H, N-CH₂), 1.92 (s, 12 H, N-Me), 2.16 (s, 6 H, *o*-Me), 2.20 (s, 3 H, *p*-Me), 4.10 (sept, 6.8 Hz, 2 H, CHMe₂), 6.94 (s, 2 H, Ar-H), 6.95–7.04 (m, 7 H, Ar-H), 7.20–7.22 (m, 2H, Ar-H), 7.53–7.57 (m, 4 H, Ar-H); ¹³C NMR (100 MHz, C₆D₆): δ = 21.04 (d, $J_{\text{C-P}}$ = 3 Hz), 21.70 (d, $J_{\text{C-P}}$ = 3 Hz), 24.76 (d, $J_{\text{C-P}}$ = 3.5 Hz), 28.40 (br), 45.50 (br), 56.72 (br), 120.04, 123.53, 127.19–127.34 (overlapped doublets), 128.95, 129.40, 131.57 (br), 133.95 (vtr, $J_{\text{C-P}}$ = 10.3 Hz), 142.30 (dd, $J_{\text{C-P}}$ = 92.2 & 4.6 Hz), 144.06 (vtr, $J_{\text{C-P}}$ = 9.2 Hz), 147.09 (d, $J_{\text{C-P}}$ = 2.2 Hz), 147.82 (br); ³¹P{¹H} NMR (162 MHz, C₆D₆): δ = –11.01; ⁷Li NMR (155 MHz, C₆D₆): δ = 0.92; IR (ν , cm^{–1}, nujol mull): = 1376, 1307, 1261, 1219, 1151, 1097, 1025, 945, 851, 796, 747, 697, 584, 520, 454.

2.5 General synthetic method for metal complexes 5 and 6

M[N(SiMe₃)₂]₂ was generated *in situ* by MCl₂ (0.4 mmol) and LiN(SiMe₃)₂ (0.8 mmol) 10 mL dry THF in a 50 mL Schlenk flask. To it was added a solution of **1** (0.34 g, 0.75 mmol) in 10 mL THF at –78°C. The mixture was stirred overnight at ambient temperature. All volatiles were removed under vacuum and the product was extracted in dry toluene (20 mL). The filtrate was concentrated to about 8 mL and stored at –30°C to give crystals of the metal complexes.

2.5a Co[Ph₂P(NC₆H₂-2,4,6-Me₃)₂]₂ (5): Blue crystalline solid; yield: 0.54 g (74%); m.p. 186°C. EI-MS (m/z): 961 [M^+], 843 [M^+ –Me₃C₆H₂], 776 [M^+ –C₆H₅], 591 [M^+ –2 P(C₆H₅)₂], 511 [M^+ –C₃₀H₃₁N₂P]; IR (ν cm^{–1}, nujol mull): 1307, 1256, 1215, 1162, 1075, 853, 802, 751, 722, 697, 659, 578, 539.

2.5b Cu[Ph₂P(NC₆H₂-2,4,6-Me₃)₂]₂ (6): Reddish brown crystalline solid; yield: 0.58 g (83 %); m.p. 157°C; EI-MS (m/z): 967 [M^+], 951 [M^+ –Me], 727 [M^+ –2 Me₃C₆H₂], 693 [M^+ –Me₃C₆H₂ & 2 C₆H₅], 514 [M^+ –C₃₀H₃₁N₂P]; IR (ν cm^{–1}, nujol mull): 1307, 1259, 1159, 1102, 1019, 848, 799, 746, 720, 710, 696, 660, 582, 525.

2.5c Ni[Ph₂P(NC₆H₂-2,4,6-Me₃)₂]₂ (7): A solution of **1** (0.45 g, 1.0 mmol) in dry toluene (10 mL) was cooled to –78°C; to this solution *n*BuLi (0.75 mL, 1.2 mmol, 1.6 M) was added and the solution was allowed to cool to room temperature with further stirring for 2 h. This solution was added via a cannula to a suspension of (PPh₃)₂NiCl₂ (0.33 g, 0.5 mmol) in 15 mL toluene. The

colour slowly changed to greenish yellow. It was stirred overnight at ambient temperature followed by filtration through Celite and concentration to 10 mL. Storage of this solution at -30°C gave reddish brown crystals after one week, yield: 0.73 g (76%); m.p. 240°C ; ^1H NMR (400 MHz, $\{d_8\}$ THF): δ = 1.67 (s, 12 H, *p*-Me), 2.03–2.09 (merged singlets, 24 H, *o*-Me), 6.48 (s, 4 H, Ar-H), 6.61 (s, 4 H, Ar-H), 7.28–7.32 (m, 8 H, Ar-H), 7.35–7.39 (m, 4 H, Ar-H), 7.76–7.81 (m, 8 H, Ar-H); $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, C_6D_6): δ = -16.83 ; EI-MS (m/z): 962 [M^+], 948 [$M^+ - \text{Me}$], 723 [$M^+ - 2 \text{ Me}_3\text{C}_6\text{H}_2$], 652 [$M^+ - 4 (\text{C}_6\text{H}_5)_2$], 590 [$M^+ - 2 \text{ P}(\text{C}_6\text{H}_5)_2$], 509 [$M^+ - \text{C}_{30}\text{H}_{31}\text{N}_2\text{P}$]; IR ($\nu \text{ cm}^{-1}$, nujol mull): 1307, 1258, 1214, 1150, 996, 887, 852, 782, 747, 722, 696, 537.

3. Results and Discussion

Arylaminediphenylphosphines Ph_2PNHAr (Ar = 2,4,6- $\text{Me}_3\text{C}_6\text{H}_2$ **1a**; Ar = 2,6-*i*- $\text{Pr}_2\text{C}_6\text{H}_3$ **1b**) were synthesized from ArNHLi and ClPPh_2 in Et_2O and purified by recrystallization from Et_2O .^{40,41} The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **1a** shows a single resonance at 36 ppm and the corresponding signal for **1b** appears at 45.5 ppm. Ligands **1** and **2** have been prepared by Staudinger type reaction using mesitylazide following the synthetic route outlined in scheme 1. These iminophosphonamine ligands have been characterized by ^1H , ^{13}C and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, EI mass spectrometry, and single crystal X-ray structural analysis. The ^1H NMR spectrum of **1** reveals NH at 4.10 ppm and two singlets that appear at 1.92 and 2.05 ppm correspond to *o*- and *p*-Me of the mesityl group. The aromatic *m*-H appears as a singlet at 6.59 ppm. Other aromatic hydrogen atoms of **1** appear as multiplets between 7.05–7.10 and 7.12–7.14 ppm. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum for this compound shows a single resonance at -13.04 ppm, an up-field shift compared

to the precursor **1a**. The base peak in the EI mass spectrum of **1** appeared at m/z 453 that also corresponds to the molecular ion. The NH stretch in **1** was observed at 3340 cm^{-1} . Single crystals of **1** suitable for X-ray structure analysis were grown from toluene at -30°C after several days. Compound **1** crystallizes in monoclinic system with $P2_1/c$ space group (table 1). In solid state structure of **1**, the central P atom shows distorted tetrahedron geometry (figure 1). The NPN backbone of **1** is arranged in a plane and the phenyl rings on central P atom are arranged above and below this plane. The two aryl substituents on the N atoms are mutually transoid. The amine N(1)–P(1) bond length is 1.675(1) Å, whereas the imine bond N(2)–P(1) (1.538(1) Å) is shorter than N(1)–P(1) and these bond lengths are similar to that reported for $[\text{Py}_2\text{P}(\text{NSiMe}_3)(\text{NHSiMe}_3)]$.²⁰

The ^1H NMR features of compound **2** are as expected, showing the NH at 4.13 ppm and a broad septet at 3.43 ppm for CHMe_2 . The CHMe_2 appear as a doublet at 1.14 ppm and the respective *o*- and *p*-Me of mesityl groups are seen at 2.26 and 2.21 ppm. The aromatic *m*-H appears as a singlet at 6.80 ppm. Other aromatic hydrogen atoms of **2** appear as complex multiplets between 7.07–7.26 and 7.80–7.86 ppm. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2** shows a single resonance at -15.34 ppm, which is shifted up-field compared to its precursor **1b** (45.5 ppm). The most abundant ion as well as the molecular ion in the EI mass spectrum of **2** appeared at m/z 495. The FT-IR spectrum of **2** showed the NH stretch at 3362 cm^{-1} .

Compound **2** crystallizes in monoclinic system with $P2_1/c$ space group (table 1). The central P atom in compound **2** resides in tetrahedral environment similar to that of **1** (figure 2). The N(1)–P(1) and N(2)–P(1) bond lengths are 1.657(1) and 1.536(1) Å, respectively, similar to that of **1**. The N(1)–P(1)–N(2), N(1)–P(1)–C(28), C(28)–P(1)–C(22) and C(28)–P(1)–N(2) bond

Scheme 1. Synthesis of sterically congested iminophosphonamine ligands **1** and **2**.

Figure 1. Single crystal X-ray structure of **1**. All hydrogen atoms, except that on N(1) are omitted for clarity. Thermal ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and bond angles (°): N(1)–P(1) 1.675(1), N(2)–P(1) 1.538(1), N(1)–C(1) 1.444(1), N(2)–C(10) 1.393(1); N(1)–P(1)–N(2) 120.90(1), C(1)–N(1)–P(1) 126.31(2), C(10)–N(2)–P(1) 142.51(1).

angle, respectively, 109.60(1), 110.13(2), 104.93(2), 114.20(1)° are close to tetrahedral bond angles; whereas the other angles {C(22)–P(1)–N(2) 118.10(1)° and N(1)–P(1)–C(22) 98.69(1)°} deviate slightly from the regular tetrahedral angle.

Treatment of **1** and **2** with *n*BuLi in toluene in the presence of tmeda (tetramethylethylenediamine)

Figure 2. Molecular structure of **2**. All hydrogen atoms, except that on N(1), and THF molecule in the lattice are omitted for clarity. Thermal ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and bond angles (°): N(1)–P(1) 1.657(1), N(2)–P(1) 1.536(1), N(1)–C(13) 1.441(1), N(2)–C(1) 1.396(1); N(1)–P(1)–N(2) 109.60(1), N(1)–P(1)–C(28) 110.13(2), C(22)–P(1)–N(2) 118.10(1), C(13)–N(1)–P(1) 127.64(2), C(1)–N(2)–P(1) 143.85(1), C(28)–P(1)–C(22) 104.93(2), C(28)–P(1)–N(2) 114.20(1).

afforded the corresponding tmeda adduct of highly moisture sensitive lithium derivatives **3** and **4** (scheme 2); and as observed in ^7Li NMR, the chelates are highly stable and no loss of tmeda was observed even after drying under vacuum for several hours. Complexes **3** and **4** are the first examples of NPnLi moiety with tmeda chelate, the evidence for tmeda chelate was observed in the ^1H and ^{13}C NMR and was confirmed by single crystal X-ray structure of **3** and **4**.

The ^1H NMR spectra of **3** and **4** show the absence of NH signals, tmeda NCH_2 appears as a singlet at 1.81 and NCH_3 of the same is observed as a singlet at 1.92 for **3** (the corresponding signals of tmeda for **4** appear at 1.70 and 1.92 ppm, respectively). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **3** and **4** exhibit resonances at –8.34 and –11.01 ppm; nearly 4.7 and 4.3 ppm downfield shift compared to the corresponding parent molecules **1** and **2**. The Li resonance in ^7Li NMR of **3** and **4** are observed, respectively, at 1.18 and 0.92 ppm. Crystals of **3** and **4** suitable for single crystal X-ray analysis were grown from toluene and C_6D_6 , respectively. Compounds **3** and **4** crystallize in monoclinic systems ($P2_1/n$ and $P2_1/c$) (table 1 and figures 3 and 4).

Both **3** and **4** in the solid state exist as discrete N_2PLi nearly planar four-membered rings with Li having four as coordination number including two N atoms from a molecule of tmeda. The uniform P–N distances in compounds **3** and **4** (1.574(1)–1.594(2) Å) within the N_2PLi heterocycle indicate that the anionic charge is delocalized over the N–P–N framework. The N_2PLi ring in complexes **3** and **4** is nearly planar and the two endocyclic angles subtended at the lithium atom, being bite angles are acute 75.18(1) and 84.83(1)° for N(1)–Li(1)–N(2) and N(3)–Li(1)–N(4), respectively, for compound **3**. The corresponding values for **4** are 73.95(2)° and 83.63(1)°. The two aryl substituents on the terminal N atoms are mutually transoid. The four Li–N bond lengths fall in the range from 2.010(1) to 2.196(1) Å, consistent with values

Scheme 2. Preparation of the tmeda adducts of lithium derivatives **3** and **4**.

Figure 3. Single crystal X-ray structure of **3**. All hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and bond angles (°): Li(1)–N(1) 2.085(3), Li(1)–N(2) 2.010(3), Li(1)–N(3) 2.196(3), Li(1)–N(4) 2.104(3), P(1)–N(1) 1.591(1), P(1)–N(2) 1.591(1); N(1)–P(1)–N(2) 103.47(1), N(1)–Li(1)–N(2) 75.18(2), N(3)–Li(1)–N(4) 84.83(1), N(1)–Li(1)–N(4) 111.33(1), N(2)–Li(1)–N(4) 128.37(2).

Figure 4. Molecular structure of **4**. All hydrogen atoms and disordered toluene molecule in the crystal lattice are deleted for clarity. Thermal ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and bond angles (°): Li(1)–N(1) 2.107(3), Li(1)–N(2) 2.063(3), Li(1)–N(3) 2.199(3), Li(1)–N(4) 2.139(3), P(1)–N(1) 1.574(1), P(1)–N(2) 1.594(1); N(1)–P(1)–N(2) 104.73(1), N(1)–Li(1)–N(2) 73.95(2), N(1)–Li(1)–N(3) 100.70(1), N(1)–Li(1)–N(4) 169.95(1), N(2)–Li(1)–N(3) 151.78(1), N(2)–Li(1)–N(4) 106.45(1), N(3)–Li(1)–N(4) 83.63(1).

observed in $\text{Li(Py)}_2[\text{Ph}_2\text{P(NSiMe}_3)_2]$ (2.043–2.123 Å),¹⁹ $\text{Li(THF)}_2[\text{Ph}_2\text{P(NSiMe}_3)_2]$ (2.04–2.08 Å).^{17a}

The moderately air-sensitive *bis*-iminophosphonamide complexes of Co(II) (**5**) and Cu(II) (**6**) with iminophosphonamine **1** were prepared as outlined in scheme 3. The *in situ* generated metal silylamides were reacted with the iminophosphonamine **1**.

Irrespective of the ligand and the metal silylamide stoichiometric ratio, the product formed is always the *bis*-homoleptic complex of iminophosphonamide and the yield can be improved by using 2:1 stoichiometry of ligand and metal silylamide. This probably is an indication that the intermediate heteroleptic monophosphonamides of **5** and **6** are more labile towards the formation of *bis*-homoleptic-chelate of these metal ions.

The molecular ion in the EI mass spectrum of **5** is revealed at m/z 961 and that of **6** at m/z 967, whereas the base peak for both **5** and **6** is observed at m/z 453 corresponding to the free ligand. Complex **5** crystallizes in triclinic system with space group $P\bar{1}$ and two molecules of **5** are present in the unit cell (table 1). The X-ray structure of **5** shows that cobalt atom is

encapsulated in a four-membered non-planar CoN_2P metallacycle as η^2 -chelates with two ligand units (figure 5). The bond angles at cobalt range from 73.57(1) to 143.27(2)° with considerable distortion from tetrahedral geometry and the mesityl groups on the ligand N atoms are placed in such a way that the steric congestion between them is minimized. The Co atom deviates from the plane of N_2P moiety by 0.089 and 0.108 Å for P(1) and P(2) containing ligand scaffolds, respectively, and the dihedral angle between the two planes is ca. 88.01°. The four Co–N bond lengths lie within 2.015(1)–2.045(1) Å, consistent with the only structurally characterized iminophosphonamides of Co(II) $[\text{Co}\{\text{Ph}_2\text{P(N-}p\text{-}t\text{BuC}_6\text{H}_4)_2\}_2]$ (1.999–2.025 Å).³⁴ The anionic charges of both the iminophosphonamide ligands are delocalized over their respective N–P–N backbones (with four similar P–N bond lengths P(1)–N(1) 1.614(2), P(1)–N(2) 1.609(3), P(2)–N(3) 1.607(3), P(2)–N(4) 1.605(2) Å). The bite angles of N(1)–Co(1)–N(2) and N(3)–Co(1)–N(4) are 73.83(1) and 73.57(1)°, respectively.

Scheme 3. Preparation of *bis*-iminophosphonamide of cobalt(II) **5** and copper(II) **6**.

Complex **6** crystallizes in triclinic system with *P*-1 space group and the asymmetric unit contains half a molecule of complex **6** and half a molecule of disordered toluene (table 1). The copper atom in **6** resides in a square planar environment formed by two η^2 -chelates from two iminophosphonamide ions, the mesityl substituents on the ligand N atoms are oriented in such a way to minimize the steric crowding between them (figure 6). The copper atom lies exactly in the plane of four nitrogen atoms and P atoms are 0.097 Å away from this plane. As in complex **5**, four similar N–P bond lengths have also been observed for **6** [P(1)–N(1) 1.608(1) and P(1)–N(2)

1.621(1) Å]. The Cu(1)–N(2) distance (1.988(1) Å) is slightly shorter than that of Cu(1)–N(1) (2.018(1) Å). The bite angles of N(1)–Cu(1)–N(2) and N(1)–P(1)–N(2) are 75.74(1) and 99.20(2)°, respectively.

A nickel(II)-*bis*-iminophosphonamide, [PPh₂{N(2,4,6-Me₃C₆H₂)₂}]Ni (**7**) was prepared in a reaction of Li[(2,4,6-Me₃C₆H₂)NP(Ph₂)=N(C₆H₂-2,4,6-Me₃)] with half equivalent of (PPh₃)₂NiCl₂ in toluene (scheme 4)

Figure 5. Molecular structure *bis*-iminophosphonamide of cobalt(II) **5**. All hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and bond angles (°): Co(1)–N(1) 2.015(1), Co(1)–N(2) 2.038(2), Co(1)–N(3) 2.017(1), Co(1)–N(4) 2.045(1), P(1)–N(1) 1.614(1), P(1)–N(2) 1.609(3), P(2)–N(3) 1.607(1), P(2)–N(4) 1.605(2); N(1)–Co(1)–N(2) 73.83(1), N(3)–Co(1)–N(4) 73.57(2), N(2)–Co(1)–N(3) 121.14(2), N(1)–Co(1)–N(3) 125.29(1), N(2)–Co(1)–N(4) 127.04(2), N(1)–Co(1)–N(4) 143.27(1), N(1)–P(1)–N(2) 98.11(1), N(3)–P(2)–N(4) 98.45(1).

Figure 6. Molecular structure of *bis*-iminophosphonamide of copper(II) **6**. Disordered toluene molecule and all hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and bond angles (°): Cu(1)–N(1) 2.018(1), Cu(1)–N(2) 1.988(2), P(1)–N(1) 1.608(1), P(1)–N(2) 1.621(1); N(1)–Cu(1)–N(2) 75.74(1), N(1)–P(1)–N(2) 99.20(1), N(2)–Cu(1)–N'(2) 179.99(2), N(1)–Cu(1)–N'(1) 179.99(2), N(2)–Cu(1)–N'(1) 104.26(1), N(1)–Cu(1)–N'(2) 104.26(1).

at -30°C . The initial green solution gradually turned to reddish brown, and **7** was crystallized from the same solvent as reddish-brown crystals (76% isolated yield). The ^1H NMR spectrum of **7** reveals one singlet that appears at 1.67 corresponding to *p*-Me of the mesityl group; this is up-field shifted compared to the free ligand (2.05 ppm). The *o*-Me groups in **7** become magnetically non-equivalent and appear as overlapped singlets between 2.03 and 2.09 ppm; these H atoms in **7** are downfield shifted compared to the free ligand (1.92 ppm). This magnetic non-equivalency can be attributed to weak agostic interaction of these remote *o*-Me hydrogen atoms that interact with Ni(II) to occupy the vacant axial sites of the octahedron geometry in **7** (figure 7).

Other 6 *o*-Me groups that are oriented away from Ni(II) do not participate in any such interaction. The same was also observed in the solid state structure of **7**, vide infra. The *m*-H of mesityl group appears as two singlets at 6.48 and 6.61 ppm. Other aromatic hydrogen atoms of **7** appear as complex multiplets between 7.28–7.32, 7.35–7.39 and 7.76–7.81 ppm. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum for this compound shows a single resonance at -16.83 ppm, an up-field shift compared to **1**. The molecular ion peak in the EI mass spectrum of **7** was observed at m/z 962. Complex **7** crystallizes in triclinic system with *P*-1 space group (table 1) with half a molecule of **7** and half a molecule of disordered toluene in an asymmetric unit. As shown in figure 7, complex **7** is structurally similar to complex **6** with four nitrogen atoms from two ligand units in an essentially square planar arrangement around nickel. However, unlike **6** the P atoms in **7** also lie in this plane thus making the four-membered metallacycles co-planar. The mesityl groups on the nitrogen atoms occupy planes oriented at $127.99(2)$ and $129.72(2)^{\circ}$ to this plane and the average Ni–N bond distance is 1.943 Å. The monoanionic charge is delocalized over the NPN backbone, $[\text{P}(1)\text{--}\text{N}(1) 1.610(2)$ and $\text{P}(1)\text{--}\text{N}(2) 1.599(2)$ Å]. The chelate rings have acute $\text{N}(1)\text{--}\text{Ni}(1)\text{--}\text{N}(2)$ angle as $76.44(2)$ and

Figure 7. Single crystal X-ray structure of **7**. Disordered toluene molecule and all hydrogen atoms, except those involved in $\text{Ni} \cdots \text{H}$ interaction, are omitted for clarity. Thermal ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and bond angles ($^{\circ}$): $\text{Ni}(1)\text{--}\text{N}(1)$ 1.942(2), $\text{Ni}(1)\text{--}\text{N}(2)$ 1.944(2), $\text{P}(1)\text{--}\text{N}(1)$ 1.610(2), $\text{P}(1)\text{--}\text{N}(2)$ 1.599(2), $\text{P}(1)\text{--}\text{C}(25)$ 1.814(1), $\text{P}(1)\text{--}\text{C}(19)$ 1.815(2); $\text{N}(1)\text{--}\text{P}(1)\text{--}\text{N}(2)$ $97.06(2)$, $\text{N}(1)\text{--}\text{Ni}(1)\text{--}\text{N}(2)$ $76.44(2)$, $\text{N}'(1)\text{--}\text{Ni}(1)\text{--}\text{N}(2)$ $103.56(2)$, $\text{N}(1)\text{--}\text{Ni}(1)\text{--}\text{N}'(1)$ $180.00(2)$, $\text{N}(2)\text{--}\text{Ni}(1)\text{--}\text{N}'(2)$ $180.00(2)$.

$\text{N}(1)\text{--}\text{P}(1)\text{--}\text{N}(2)$ angle as $97.06(2)^{\circ}$ consistent with values previously reported for $[\text{Ni}\{\text{Ph}_2\text{P}(\text{NSiMe}_3)_2\}_2]$.³⁹ The very weak $\text{Ni} \cdots \text{H}_{\delta}$ agostic interaction of Ni(1) and H(7B) measures $2.673(1)$ Å and is shorter than that seen in $[\{\text{PPh}_2(\text{NSiMe}_3)_2\} \text{Ni Ph}(\text{PPh}_3)]$ ($\text{Ni} \cdots \text{H}_{\gamma}$ 2.81 Å).³⁷ This interaction is probably responsible for magnetic non-equivalence of *o*-Me groups that interact with Ni to that of those not involved in this interaction (vide supra).

Scheme 4. Synthesis of bis-iminophosphonamide of nickel(II) **7**.

4. Conclusions

We have synthesized and structurally characterized iminophosphonamine ligands containing sterically bulky substituents. The ligands can be easily deprotonated by alkylolithiums or transition metal silylamides. The lithium iminophosphonamides have been isolated as tmeda adducts and a lithium iminophosphonamide has been used to prepare *bis*-homoleptic complex of Ni(II). The neutral iminophosphonamines is also a suitable precursor to prepare metal complexes, for example, *bis*-homoleptic complexes of Co(II) and Cu(II) have been prepared and structurally characterized by using *bis*-silylamide of the respective metals. It is expected that the same synthetic strategy can be adopted for the synthesis of main group metal complexes as well. Such studies are currently underway in our laboratory.

Supplementary Information

CCDC 928556–928562 contains the supplementary crystallographic data for compounds **1–7**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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