

Nickel and palladium phosphinimine-imine ligand complexes

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The imine ($C_6H_3i-Pr_2$)NCMe₂ **1** was prepared and used to make the phosphine ($C_6H_3i-Pr_2$)NC(Me)CH₂PPh₂ **2**. Oxidation with the substituted arylazide resulted in the isolation of the phosphinimine-imine species ($C_6H_3i-Pr_2$)NC(Me)CH₂PPh₂(NC₆H_{3i-Pr_2}) **3**. The ligand **3** forms the neutral Ni-complex NiBr₂(($C_6H_3i-Pr_2$)NC(Me)CH₂PPh₂(NC₆H_{3i-Pr_2})) **4** while attempts to prepare the analogous Pd species were unsuccessful. Reaction of **3** with *n*-BuLi produced the Li-salt Li(thf)(($C_6H_3i-Pr_2$)NC(Me)CHPPPh₂(NC₆H_{3i-Pr_2})) **5**. Subsequent reaction with NiBr₂(dme) afforded [Ni(($C_6H_3i-Pr_2$)NC(Me)CHPPPh₂(NC₆H_{3i-Pr_2}))(μ-Br)₂Li(thf)₂] **6**. In related syntheses **5** reacted with NiBr₂(dme) or (PhCN)₂PdCl₂ and PPh₃ to give the complexes of formulation MX(($C_6H_3i-Pr_2$)NC(Me)CHPPPh₂(NC₆H_{3i-Pr_2}))(PPh₃) (X = Br, M = Ni **7**; X = Cl, M = Pd **8**). The latter complexes **7** and **8** are phosphinimine-N-C bound. Structural studies of **2** and **4-8** are reported. The implications of these studies for the utility of this phosphinimine-imine ligand in olefin polymerization catalysts are considered.

Introduction

A variety of late transition metal complexes containing chelating ligands have been shown to act as catalysts for the polymerization and oligomerization of olefins. Early work on the Shell Higher Olefin Process (SHOP)¹ utilized neutral Ni catalysts containing P-O chelates. Subsequent work by Keim *et al.* resulted in the development of a Ni-iminophosphorane amidato ligand complex which effected the polymerization of olefins.² More recently, Ni- and Pd-diimine complexes³⁻⁷ and bis(imino)pyridine complexes of Fe and Co^{8,6} have been shown to be effective polymerization catalysts upon activation with methylalumoxane (MAO). Very recent Ni(II) complexes of N-O salicylaldimines, a Ni complex of 2-(2,6-diisopropylanilino)tropone⁹ and a cationic Ni(II)-allyl complex of a P-O chelate¹⁰ act as very active single-component catalysts producing highly linear polyethylene.

In seeking alternative systems, we and others have focused attention on the phosphinimine-based ligand complexes. While a number of bis-phosphinimine complexes¹¹⁻¹⁴ have been prepared, few have been examined for the potential in catalysis. Bochmann and coworkers have shown that Fe complexes of bis(aryliminophosphoranyl)pyridine ligands, which are structurally reminiscent to the bis(imino)pyridine ligand complexes, exhibited only modest activity.¹⁵ The complex ($C_6H_4(NPPH_3)_2$)-NiCl₂ has been recently reported to effect ethylene oligomerisation.¹⁶ In our own work we have shown that Ni and Fe complexes of pyridinephosphinimine chelates act as ethylene dimerization catalysts. Pd-β-diketimininate complexes have been shown to afford dimetallic derivatives upon metallation of the central C atom,¹⁷ whereas Ni-β-diketiminates have been recently shown to stabilize the rather unusual three-coordinate Ni(II) and Ni(I) complexes.^{18,19} In this paper, we consider a hybrid phosphinimine-imine ligand, which is structurally similar to β-diketimininate ligands, with the replacement of one of the imine-groups by a phosphinimine fragment. Ni and Pd complexes of this ligand are prepared and the implications of the structural information with respect to suitability for use in olefin-polymerization catalysts are considered.

Experimental

General data

All preparations were done under an atmosphere of dry, O₂-free N₂ employing both Schlenk-line techniques and a Vacuum Atmospheres inert atmosphere glove box. Solvents were

purified employing a Grubb's type solvent purification system manufactured by Innovative Technology. All organic reagents were purified by conventional methods. ¹H, ³¹P{¹H} and ¹³C{¹H} NMR spectra were recorded on Bruker Avance-300 and 500 spectrometers. All spectra were recorded in C₆D₆ at 25 °C unless otherwise noted. Trace amounts of protonated solvents were used as references and chemical shifts are reported relative to SiMe₄. ³¹P{¹H} NMR spectra were referenced to external 85% H₃PO₄. Combustion analyses were done in-house employing a Perkin Elmer CHN Analyzer. Magnetic susceptibility measurements were performed using the Evans method.

Synthesis of ($C_6H_3i-Pr_2$)NCMe₂ **1**

100 mL toluene, 20.0 g (112.8 mmol) ($C_6H_3i-Pr_2$)NH₂, 65.5 mL acetone and 100 mL molecular sieves were added to a flask. The mixture was brought to reflux for 6 days, after which heating was stopped and the solution was allowed to cool. The molecular sieves were filtered off and washed with 2 × 50 mL hexanes. A brown oil remained after removal of the solvent *in vacuo*. Distillation (98–103 °C, 0.5 mm) gave 21.48 g (98.8 mmol) of a pale yellow oil. Yield: 88%. ¹H NMR (CDCl₃): δ 7.02–7.13 (m, 3H, *m,p*-Ar), 2.77 (sept, 2H, [³J_{H-H}] = 7 Hz, CH), 2.26 (3H, s, *cis*-CH₃), 1.69 (3H, s, *trans*-CH₃), 1.16 (6H, d, [³J_{H-H}] = 7 Hz, Me), 1.15 (6H, d, [³J_{H-H}] = 7 Hz, Me). ¹³C NMR (CDCl₃): δ 168.9 (s, NC), 146.3 (s, *ipso*-Ph), 136.8 (s, *o*-Ph), 123.5 (s, *p*-Ph), 123.1 (s, *m*-Ph), 28.1 (s, CH), 27.9 (s, Me), 23.6 (s, Me), 23.3 (s, Me), 21.7 (s, Me).

Synthesis of ($C_6H_3i-Pr_2$)NC(Me)CH₂PPh₂ **2**

To a solution of 250 mL *n*-pentane, **1** (10.00 g, 46.0 mmol) and tmen (7.6 mL 5.85 g, 50.4 mmol), cooled to –78 °C, was added *n*-BuLi (20.25 mL of 2.5 M solution (hexanes), 50.6 mmol). The solution immediately turned yellow and a white precipitate formed. The mixture was allowed to warm to 25 °C and stirred for 2 h, whereupon the flask was cooled again to –78 °C and ClPPh₂ (10.10 g, 46.0 mmol) of was added dropwise. After refluxing overnight, the solution containing an off-white precipitate (LiCl) was filtered through Celite, and the solids washed with 2 × 20 mL *n*-pentane. Upon removal of *n*-pentane *in vacuo*, an off-white solid remained. Dissolving the solid in a minimum of boiling EtOH and cooling to 25 °C gave 7.60 g of colorless crystals. Multiple crops offered an additional 6.35 g of material. Yield: 76%. X-Ray quality crystals were obtained by a second recrystallization from EtOH. ¹H NMR (CDCl₃, major

isomer): δ 7.55–7.61 (m, 4H, *o*-PPh₂), 7.35–7.41 (m, 6H, *m,p*-PPh₂), 7.01–7.07 (m, 3H, *m,p*-Ar), 3.43 (d, 2H, CH₂, $^2J_{\text{P-H}}$ = 2 Hz), 2.49 (sept, 2H, CH, $|J_{\text{H-H}}|$ = 7 Hz), 1.77 (s, 3H, Me), 1.00 (d, 6H, Me, $|J_{\text{H-H}}|$ = 7 Hz), 0.99 (d, 6H, Me, $|J_{\text{H-H}}|$ = 7 Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl₃): δ -18.0 (95%, major isomer), -17.5 (5%, minor isomer). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl₃, major isomer): δ 168.5 (s, NC), 146.2 (s, *ipso*-Ar), 138.4 (d, *ipso*-PPh₂, $|J_{\text{P-C}}|$ = 14 Hz), 136.7 (s, *m*-Ar), 133.1 (d, *o*-PPh₂, $^2J_{\text{P-C}}$ = 19 Hz), 129.1 (s, *p*-PPh₂), 128.7 (d, *m*-PPh₂, $^3J_{\text{P-C}}$ = 7 Hz), 123.5 (s, *p*-Ar), 123.0 (s, *m*-Ar), 42.8 (d, CH₂P, $|J_{\text{P-C}}|$ = 16 Hz), 28.0 (s, CH), 23.6 (s, Me), 23.4 (s, Me), 21.6 (d, $|J_{\text{P-C}}|$ = 7 Hz, Me). Anal. Calc. for C₂₇H₃₂NP: C, 80.76; H, 8.03; N, 3.49. Found: C, 80.43; H, 8.27; N, 3.16%.

Synthesis of (C₆H₃*i*-Pr₂)NC(Me)CH₂PPh₂(NC₆H₃*i*-Pr₂)**3**

To a solution of **2** (6.83 g, 17.5 mmol) in 125 mL CH₂Cl₂ was added (C₆H₃*i*-Pr₂)N₃ (5.10 g, 25 mmol). N₂ evolution commenced immediately and the mixture was refluxed for 3 h. Removal of CH₂Cl₂ under vacuum left a thick brown oil. The oil was dissolved in 300 mL boiling MeOH, filtered through Celite and cooled overnight. Filtration of solids and washing with 2 × 50 mL cold *n*-pentane gave 6.60 g of a white powder. Additional crops gave an extra 0.54 g of material. Yield of **3**·MeOH: 70%. Analytical crystals were grown from a hot MeOH solution slowly cooled to 25 °C. ^1H NMR (major isomer): δ 7.71–7.75 (m, 10H, PPh₂), 6.99–7.18 (m, 6H, *m,p*-Ar), 3.73 (d, $^2J_{\text{P-H}}$ = 14 Hz, 2H, PCH₂), 3.67 (sept, $|J_{\text{H-H}}|$ = 7 Hz, 2H, CH), 2.57 (sept, $|J_{\text{H-H}}|$ = 7 Hz, 2H, CH), 1.62 (s, 3H, Me), 1.17 (d, $|J_{\text{H-H}}|$ = 7 Hz, 12H, Me), 1.06 (d, $|J_{\text{H-H}}|$ = 7 Hz, 6H, Me), 1.05 (d, $|J_{\text{H-H}}|$ = 7 Hz, 6H, Me). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD₂Cl₂, major isomer): δ 165.3 (d, $^2J_{\text{P-C}}$ = 6 Hz, NC), 146.1 (imine *ipso*-Ar), 144.2 (*ipso*-Ar), 142.5 (d, $^3J_{\text{P-C}}$ = 8 Hz, *o*-Ar), 136.4 (*o*-Ar), 133.8 (d, $|J_{\text{P-C}}|$ = 98 Hz, *ipso*-PPh₂), 131.8 (*p*-PPh₂), 131.6 (*o*-PPh₂), 128.9 (d, $^3J_{\text{P-C}}$ = 12 Hz, *m*-PPh₂), 124.1 (*p*-Ar), 123.2 (*m*-Ar), 123.0 (*m*-Ar), 119.2 (*p*-Ar), 45.7 (d, $|J_{\text{P-C}}|$ = 65 Hz, CH₂) 29.0 (PCH), 28.0 (CH), 24.0 (Me), 23.8 (Me), 23.3 (Me), 22.6 (Me); $^{31}\text{P}\{^1\text{H}\}$ NMR: δ -13.2 (73%, major isomer), 3.6 (27%, minor isomer). Anal. Calc. for C₄₀H₅₃N₂PO: C, 78.91; H, 8.77; N, 4.60. Found: C, 78.76; H, 9.12; N, 4.59%.

Synthesis of NiBr₂((C₆H₃*i*-Pr₂)NC(Me)CH₂PPh₂-(NC₆H₃*i*-Pr₂))**4**

In toluene (8 mL) **3** (132 mg, 0.229 mmol) was combined with NiBr₂(dme) (71 mg, 0.229 mmol) and the mixture was allowed to stir overnight. A blue precipitate formed. The solvent was removed *in vacuo* to give a light blue powder **4**. The solid was dissolved in CH₂Cl₂ (6 mL), filtered through Celite and the blue solution layered with toluene (12 mL). After two days, blue crystals were separated from the solution by decantation. The crystals were washed with *n*-pentane. Yield: 30%, magnetic susceptibility: 4.34 μ_{B} . Anal. Calc. for C₄₆H₅₇N₂PNiBr₂: C, 62.26; H, 6.47; N, 3.16. Found: C, 61.99; H, 6.42; N, 3.03%.

Synthesis of [Li(thf)][(C₆H₃*i*-Pr₂)NC(Me)CHPPH₂-(NC₆H₃*i*-Pr₂)]**5**

To a solution of 302 mg (0.524 mmol) **3** in 5 mL of thf was added 0.231 mL of 2.5 M *n*-BuLi in hexanes (10% excess). The solution immediately turned orange–yellow and was allowed to stir for 2 h, after which the solvent was removed under vacuum. The yellow solids were then dissolved in *ca.* 15 mL hot *n*-pentane and filtered through a pad of Celite to remove any insoluble material. The clear yellow solution was then stored at 25 °C, giving 261 mg of large yellow blocks. Yield: 77%, ^1H NMR: δ 7.92–8.00 (m, 4H, *o*-PPh₂, *o*-Ar), 7.01–7.23 (m, 11H, *m,p*-PPh₂, *m,p*-Ar), 3.96 (sept, 2H, $|J_{\text{H-H}}|$ = 7 Hz, CH), 3.96 (d, 1H, $^2J_{\text{P-H}}$ = 27 Hz, CHP), 3.29 (sept, 2H, $|J_{\text{H-H}}|$ = 7 Hz, CH), 2.94–2.98 (m, 2H, thf), 1.89 (d, 3H, $^4J_{\text{P-H}}$ = 2 Hz, Me) 1.33 (d, 6H, $|J_{\text{H-H}}|$ = 7 Hz, Me), 1.28 (br d, 12H, $|J_{\text{H-H}}|$ = 7 Hz, Me), 1.13 (d,

6H, $|J_{\text{H-H}}|$ = 7 Hz, Me), 1.01–1.06 (m, 2H, thf). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 169.5 (NC), 150.2, 146.8 (d, 9 Hz), 145.0 (d, 7 Hz), 142.9, 136.8 (d, $|J_{\text{P-C}}|$ = 94 Hz, *ipso*-PPh₂), 132.6 (d, 7 Hz), 130.1, 127.7–128.3 (m, obscured by C₆D₆), 123.3, 123.1, 122.8, 121.3 (d, 4 Hz), 68.1, 65.8 (d, $|J_{\text{P-C}}|$ = 29 Hz, PCH), 28.8, 27.7, 25.0, 24.9, 24.4, 23.9 (d, $^3J_{\text{P-C}}$ = 18 Hz, Me). $^{31}\text{P}\{^1\text{H}\}$ NMR: δ 11.5. Anal. Calc. for C₄₃H₅₆N₂OPLi: C, 78.87; H, 8.62; N, 4.28. Found: C, 78.63; H, 8.69; N, 4.30%.

Synthesis of [Ni((C₆H₃*i*-Pr₂)NC(Me)CHPPH₂(NC₆H₃*i*-Pr₂))-(μ -Br)₂Li(thf)₂]**6**

To a solution of **3** (159 mg, 0.276 mmol) in thf (4 mL) was added *n*-BuLi in hexanes (0.181 mL, 1.6 M). The resulting yellow solution was allowed to stir for 1 h and NiBr₂(dme) (85 mg, 0.276 mmol) in thf (4 mL) was added. After stirring overnight, the solvent was removed and the dark solids dissolved in hot *n*-pentane. After filtration through Celite, the solution was stored at -35 °C overnight yielding black/red crystals of **6**. Yield: 37%, magnetic susceptibility: 3.93 μ_{B} . Anal. Calc. for C₄₇H₆₄N₂O₂PNiBr₂Li: C, 59.71; H, 6.82; N, 2.96. Found: C, 59.80; H, 6.68; N, 2.92%.

Synthesis of MX((C₆H₃*i*-Pr₂)NC(Me)CHPPH₂(NC₆H₃*i*-Pr₂))-(PPh₃) (X = Br, M = Ni **7**; X = Cl, M = Pd **8**)

These compounds were prepared in a similar fashion and thus only one preparation is detailed. To a solution of **3** (116 mg, 0.201 mmol) in 4 mL thf was added *n*-BuLi in hexanes (0.087 mL, 2.5 M). The yellow solution was allowed to stir for 1 h, after which (PhCN)₂PdCl₂ (76 mg) in 3 mL thf was added, forming a dark brown solution. Then PPh₃ (52 mg) was added and the mixture was stirred overnight. Removal of solvent, addition of toluene and filtration through Celite gave a green–brown solution. After 2 days, 123 mg of light brown crystals of **8** were isolated after washing with *n*-pentane. **7**: Yield: 57%. ^1H NMR (CD₂Cl₂): δ 6.85–7.14 (m, Ph), 4.50 (sept, 1H, CH, $|J_{\text{H-H}}|$ = 7 Hz), 3.87 (sept, 1H, CH, $|J_{\text{H-H}}|$ = 7 Hz), 1.81 (sept, 1H, CH, $|J_{\text{H-H}}|$ = 7 Hz), 1.51 (d, 3H, Me, $|J_{\text{H-H}}|$ = 7 Hz), 1.27 (d, 3H, Me, $|J_{\text{H-H}}|$ = 7 Hz), 1.24 (d, 3H, Me, $|J_{\text{H-H}}|$ = 7 Hz), 1.12 (d, 3H, Me, $|J_{\text{H-H}}|$ = 7 Hz), *ca.* 1.11 (m, obscured by adjacent Me peak, 1H, CH), 1.03 (s, 3H, Me), 0.88 (d, 3H, Me, $|J_{\text{H-H}}|$ = 7 Hz), 0.86 (d, 3H, Me, $|J_{\text{H-H}}|$ = 7 Hz), 0.74 (d, 3H, Me, $|J_{\text{H-H}}|$ = 7 Hz), 0.50 (d, 3H, Me, $|J_{\text{H-H}}|$ = 7 Hz), 0.21 (d, 3H, Me, $|J_{\text{H-H}}|$ = 7 Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (CH₂Cl₂): δ 171.61 (d, NC, $^2J_{\text{P-C}}$ = 6 Hz), 149.2 (d, 5 Hz), 147.6, 146.2, 144.5, 144.0, 138.8, 138.7, 138.3, 137.8, 137.8, 137.0, 136.8, 136.7, 135.4, 135.2, 134.6, 133.0, 132.9, 132.5, 132.0, 130.6, 130.2, 130.1, 128.5, 128.4, 128.4, 128.3, 124.1, 123.4, 123.3, 123.2, 123.0, 122.8, 29.5, 28.2, 27.2, 25.8, 24.4, 24.4, 24.8, 23.7, 23.5, 23.5, 23.3, 6.1 (d of d, $^1J_{\text{P-C}}$ = 76 Hz, $^2J_{\text{P-C}}$ = 17 Hz, CH). $^{31}\text{P}\{^1\text{H}\}$ NMR: δ 24.4 (d, $^3J_{\text{P-P}}$ = 39 Hz), 18.0 (d, $^3J_{\text{P-P}}$ = 39 Hz). Anal. Calc. for C₅₈H₆₅N₂P₂NiCl₂Br: C, 65.62; H, 6.17; N, 2.64. Found: C, 65.43; H, 6.45; N, 2.49%. **8**: Yield 57%. ^1H NMR: δ 7.80–8.05 (m, 10H, *o*-PPh₂), 6.87–7.56 (m, 26H, *m,p*-PPh₂, *m,p*-Ar), 4.43 (sept, 1H, CH, $|J_{\text{H-H}}|$ = 7 Hz), 3.30 (sept, 1H, CH, $|J_{\text{H-H}}|$ = 7 Hz), 3.29 (sept, 1H, CH, $|J_{\text{H-H}}|$ = 7 Hz), 2.35 (s, 3H, Me), 1.91 (d of d, 2H, CH, $^1J_{\text{P-H}}$ = 7 Hz, $^2J_{\text{P-H}}$ = 6 Hz), 1.70 (sept, 1H, CH, $|J_{\text{H-H}}|$ = 7 Hz), 1.35 (d, 3H, Me, $|J_{\text{H-H}}|$ = 7 Hz), 1.21 (d, 6H, Me, $|J_{\text{H-H}}|$ = 7 Hz), 0.96 (d, 3H, Me, $|J_{\text{H-H}}|$ = 7 Hz), 0.95 (d, 3H, Me, $|J_{\text{H-H}}|$ = 7 Hz), 0.93 (s, 3H, Me), 0.69 (d, 3H, Me, $|J_{\text{H-H}}|$ = 7 Hz), 0.47 (d, 3H, Me, $|J_{\text{H-H}}|$ = 7 Hz), 0.19 (d, 3H, Me, $|J_{\text{H-H}}|$ = 7 Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 171.3 (d, NC, $^2J_{\text{P-C}}$ = 6 Hz), 149.0 (d, 7 Hz), 148.2, 146.5, 139.3 (d, 8 Hz), 138.6, 137.7, 137.2, 137.1, 135.4–136.0 (m), 133.4, 133.3, 132.7, 132.5, 132.4, 131.4, 130.7, 130.6, 129.6, 128.8–129.1 (m), 125.8, 124.5, 123.7, 123.6, 123.4, 123.2, 122.7, 29.9, 28.8, 28.4, 27.6, 25.8, 25.0, 24.9, 24.8, 24.2, 24.1, 24.0, 23.7, 23.6, 23.3, 21.7, 15.9 (d, $^1J_{\text{P-C}}$ = 79 Hz, CH). $^{31}\text{P}\{^1\text{H}\}$ NMR: 29.2 (d, $^3J_{\text{P-P}}$ = 15 Hz), 25.5 (d, $^3J_{\text{P-P}}$ = 15 Hz). Anal. Calc. for C₆₄H₇₁N₂P₂-PdCl: C, 71.70; H, 6.68; N, 2.61. Found: C, 71.39; H, 6.59; N, 2.82%.

Table 1 Crystallographic data

	2	4	5	6	7	8
Formula	C ₅₄ H ₆₄ N ₂ P ₂	C ₄₆ H ₅₇ Br ₂ N ₂ NiP	C ₄₃ H ₅₅ LiN ₂ OP	C ₄₇ H ₆₄ Br ₂ LiN ₂ NiO ₂ P	C ₅₉ H ₇₀ BrCl ₄ N ₂ NiP ₂	C ₆₄ H ₇₁ ClN ₂ P ₂ Pd
Formula wght	803.01	887.44	653.80	945.44	1149.53	1072.02
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	<i>P2₁/c</i>	<i>P2₁/c</i>	<i>P2₁/n</i>	<i>P1</i>	<i>P2₁/c</i>	<i>P2₁/n</i>
<i>a</i> /Å	21.355(12)	13.932(7)	10.687(7)	11.284(6)	23.05(3)	10.367(7)
<i>b</i> /Å	17.586(10)	13.976(7)	19.406(12)	13.404(7)	10.399(15)	26.477(17)
<i>c</i> /Å	13.052(7)	23.942(12)	19.757(12)	18.234(10)	24.60(3)	23.410(15)
<i>a</i> °				81.631(10)		
<i>β</i> °	98.315(12)	105.303(9)	98.359(13)	74.457(12)	104.11(3)	96.274(13)
<i>γ</i> °				67.997(9)		
<i>V</i> /Å ³	4850(5)	4497(4)	4054(4)	2460(2)	5719(14)	6387(7)
<i>D_c</i> /g cm ⁻³	1.100	1.311	1.071	1.276	1.335	1.115
<i>Z</i>	4	4	4	2	4	4
<i>μ</i> /cm ⁻¹	0.125	2.276	0.100	2.086	1.319	0.418
Data collected	20418	18638	17063	10205	19576	27188
Data <i>F_o</i> ² > 3σ(<i>F_o</i> ²)	4287	6404	5785	6993	8239	9140
Variables	523	457	433	501	622	631
<i>R</i>	0.0390	0.0369	0.0498	0.0675	0.0684	0.0541
<i>R_w</i>	0.0925	0.0747	0.1085	0.1491	0.1749	0.1416
GOF	0.905	1.000	1.012	0.908	0.862	1.099

X-Ray data collection and reduction

Crystals were manipulated and mounted in capillaries in a glove box, thus maintaining a dry, O₂-free environment for each crystal. Diffraction experiments were performed on a Siemens SMART System CCD diffractometer. The data were collected in a hemisphere of data in 1329 frames with 10 s exposure times. The observed extinctions were consistent with the space groups in each case. The data sets were collected (4.5 < 2θ < 45–50.0°). A measure of decay was obtained by re-collecting the first 50 frames of each data set. The intensities of reflections within these frames showed no statistically significant change over the duration of the data collections. The data were processed using the SAINT and XPREP processing packages.^{20a} An empirical absorption correction based on redundant data was applied to each data set. Subsequent solution and refinement was performed using the SHELXTL^{20b} solution package operating on a Pentium computer.

Structure solution and refinement

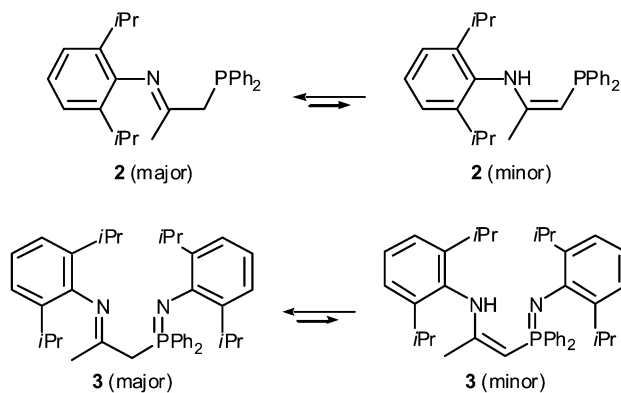
Non-hydrogen atomic scattering factors were taken from the literature tabulations.²¹ The heavy atom positions were determined using direct methods employing the SHELXTL direct methods routine. The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on *F_o*, minimizing the function $w(|F_o| - |F_c|)^2$ where the weight *w* is defined as $4F_o^2/2\sigma(F_o^2)$ and *F_o* and *F_c* are the observed and calculated structure factor amplitudes. In the final cycles of each refinement, all non-hydrogen atoms were assigned anisotropic temperature factors in the absence of disorder or insufficient data. In the latter cases atoms were treated isotropically. C–H atom positions were calculated and allowed to ride on the carbon to which they are bonded assuming a C–H bond length of 0.95 Å. H-Atom temperature factors were fixed at 1.10 times the isotropic temperature factor of the C-atom to which they are bonded. The H-atom contributions were calculated, but not refined. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance. Crystallographic data are provided in Table 1.

CCDC reference numbers 211491–291496.

See <http://www.rsc.org/suppdata/dt/b3/b306110h/> for crystallographic data in CIF or other electronic format.

Results and discussion

The imine (C₆H₃-Pr₂)NCMe₂ **1** was prepared from the condensation of the arylamine and acetone over 6 days. This product was reacted with *n*-BuLi in the presence of tmen and subsequently reacted with ClPPh₂ to give the phosphine (C₆H₃-Pr₂)NC(Me)CH₂PPh₂ **2**. A similar strategy has been reported for related phosphineimines.²² NMR data for this product revealed the presence of two isomers which gave rise to ³¹P{¹H} NMR signals at δ –18.0 and –17.5 in a 95 : 5 ratio. These were attributed to the enolization of the imine (Scheme 1). The major isomer was attributed to the imine form based on the ¹H and ¹³C NMR data. X-Ray data (Fig. 1) also supported this formulation of **2** and were consistent with the major isomer as the imine as the observed N–C bond length was 1.276(3) Å.



Scheme 1

Oxidation of the **2** with the substituted arylazide resulted in the evolution of N₂ and the isolation of the phosphinimine-imine species (C₆H₃-Pr₂)NC(Me)CH₂PPh₂(NC₆H₃-Pr₂) **3** in a yield of 70%. As expected, this species also existed in two forms as indicated by the ³¹P{¹H} NMR signals at δ –13.2 and 3.6 observed in a 73 : 27 intensity ratio. Again the major isomer is assigned to the imine species (Scheme 1). The higher proportion of the amine isomer in the case of **3** compared to **2** may result from some degree of hydrogen bonding of the amine NH to the phosphinimine nitrogen.

The ligand **3** reacts with NiBr₂(dme) to give the blue complex NiBr₂((C₆H₃-Pr₂)NC(Me)CH₂PPh₂(NC₆H₃-Pr₂)) **4** in good yield. This species was paramagnetic with a magnetic moment of 4.34 μ_B. X-Ray quality crystals of **4** were obtained upon

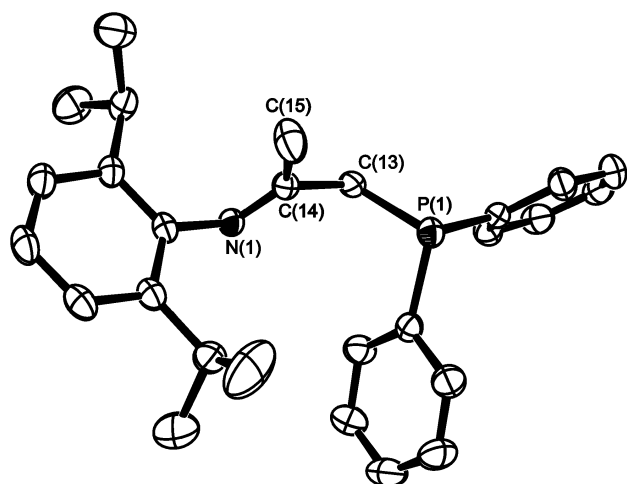


Fig. 1 ORTEP²³ drawing of **2**; 30% thermal ellipsoids are shown. Hydrogen atoms are omitted for clarity. Selected bond distances (Å): P(1)–C(1) 1.834(2), P(1)–C(7) 1.837(2), P(1)–C(13) 1.869(2), N(1)–C(14) 1.276(3), N(1)–C(16) 1.443(2).

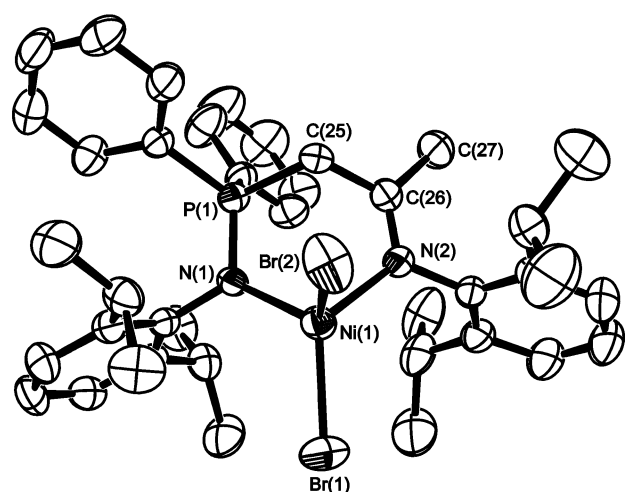
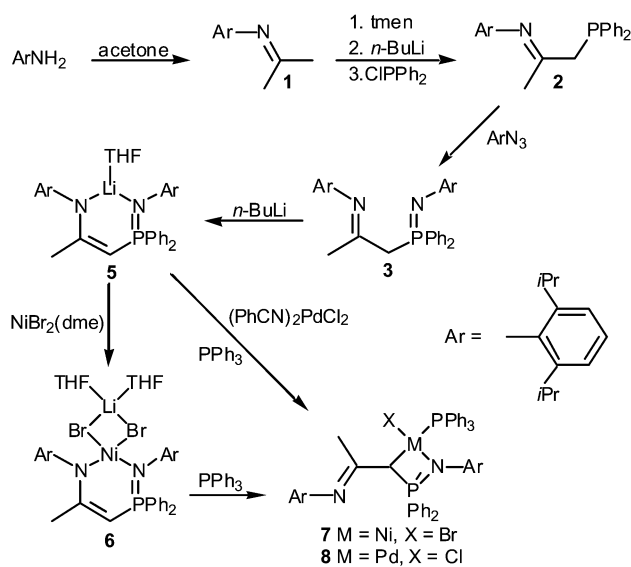


Fig. 2 ORTEP²³ drawing of **4**; 30% thermal ellipsoids are shown. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Ni(1)–N(1) 2.019(3), Ni(1)–N(2) 2.036(3), Ni(1)–Br(1) 2.3309(10), Ni(1)–Br(2) 2.4193(11), P(1)–N(1) 1.605(3), P(1)–C(7) 1.803(4), P(1)–C(25) 1.803(4), P(1)–C(1) 1.816(4), N(1)–C(13) 1.473(4), N(2)–C(26) 1.286(4), N(2)–C(28) 1.469(4); N(1)–Ni(1)–N(2) 98.26(12), N(1)–Ni(1)–Br(1) 112.29(9), N(2)–Ni(1)–Br(1) 119.33(9), N(1)–Ni(1)–Br(2) 110.53(8), N(2)–Ni(1)–Br(2) 96.71(9), Br(1)–Ni(1)–Br(2) 117.35(4), C(13)–N(1)–P(1) 119.1(2), C(13)–N(1)–Ni(1) 120.7(2), P(1)–N(1)–Ni(1) 118.39(16), C(26)–N(2)–C(28) 118.2(3), C(26)–N(2)–Ni(1) 120.1(2), C(28)–N(2)–Ni(1) 121.7(2).

recrystallization from CH₂Cl₂ layered with toluene (Fig. 2). The geometry about the Ni center is approximately tetrahedral as expected with the coordination sphere comprised of the two N and two Br atoms. The Ni–N distances were found to be 2.019(3) and 2.036(3) Å for the phosphinimine and imine N atoms, respectively. This is consistent with previous observations that suggest that phosphinimines are in fact stronger σ-donors than imines. The N–Ni–N ligand bite angle is 98.26(12)°. This is larger than the bite-angle of 93.7(2)° seen for the related diketinimine complex NiBr₂((C₆H₃*i*-Pr₂)NCMe)₂-CH₂.¹⁷ The Ni–Br distances were found to be 2.3309(10) and 2.4193(11) Å while the Br–Ni–Br angle is 117.35(4)°. The longer Ni–Br distance is associated with the Br atom that affords the relative small N–Ni–Br angle of 96.71(9)°. Thus it may be that the closer approach of the imine substituent to this Br results in steric congestion and thus the longer Ni–Br distance. The P–N distances along with the remainder of the ligand metric parameters are unexceptional.

In a similar synthetic procedure, attempts to react ligand **3** with (PhCN)₂PdCl₂ did not give the square-planar species PdCl₂((C₆H₃*i*-Pr₂)NC(Me)CH₂PPh₂(NC₆H₃*i*-Pr₂)). The nature of the product(s) remains unclear. In contrast to the related diimine ligands,¹⁷ the presence of the diphenylphosphino-fragments in the backbone of **3** may impact on the in-plane steric congestion and prevent this seemingly straightforward complexation.

Reaction of **3** with *n*-BuLi proceeds rapidly to give a yellow solution and subsequently yellow crystals of Li(thf)((C₆H₃*i*-Pr₂)NC(Me)CHPPh₂(NC₆H₃*i*-Pr₂)) **5** in 77% yield (Scheme 2). Both NMR and an X-ray structure determination confirmed the formulation of **5** (Fig. 3). The geometry about Li is distorted trigonal planar as the sum of the angles about Li exceeds 359°. The N–Li–N angle or the ligand bite angle is 108.5(3)°. The Li–N distances are similar with the phosphinimine N–Li distance of 1.925(6) Å and the imine N–Li distance of 1.914(6) Å. The imine N–C distance is 1.321(3) Å, slightly longer than that



Scheme 2

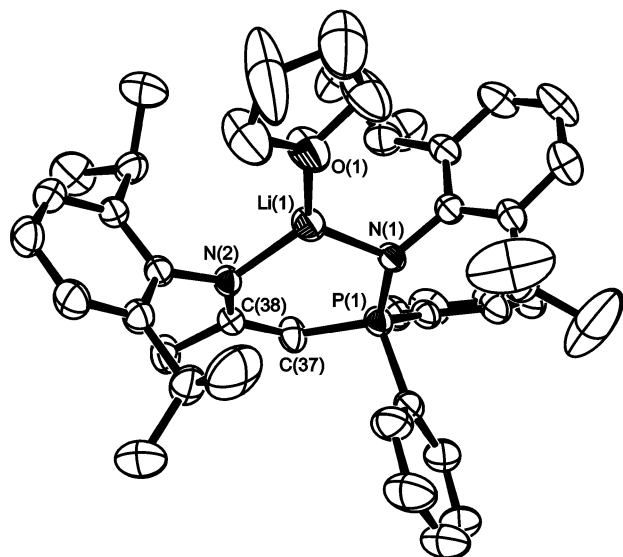


Fig. 3 ORTEP²³ drawing of **5**; 30% thermal ellipsoids are shown. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Li(1)–O(1) 1.894(6), Li(1)–N(2) 1.914(6), Li(1)–N(1) 1.925(6), P(1)–N(1) 1.597(2), P(1)–C(37) 1.727(3), P(1)–C(13) 1.813(3), P(1)–C(19) 1.831(3), C(37)–C(38) 1.399(4), N(2)–C(38) 1.321(3); O(1)–Li(1)–N(2) 126.1(3), O(1)–Li(1)–N(1) 125.2(3), N(2)–Li(1)–N(1) 108.5(3), C(1)–N(1)–Li(1) 114.6(2), P(1)–N(1)–Li(1) 116.2(2), C(38)–N(2)–Li(1) 122.7(3), C(25)–N(2)–Li(1) 116.7(2).

seen in **2**, consistent with some delocalization of the anionic charge over the NC₂PN linkage.

Reaction of **5** with NiBr₂(dme) proceeds smoothly to give the complex formulated on the basis of NMR and analytical data as red/black [Ni((C₆H₃*i*-Pr₂)NC(Me)CHPPH₂(NC₆H₃*i*-Pr₂))-(μ-Br)₂Li(thf)₂]**6**. An X-ray structure determination confirmed this formulation (Fig. 4). The structure of **6** is similar to that reported very recently for diketimine analog [Ni((C₆H₃*i*-Pr₂)NCMe)₂CH(μ-Cl)₂Li(thf)(Et₂O)].¹⁹ The geometry about Ni is pseudo-tetrahedral, with two N and two Br atoms making up the coordination sphere. The Ni–N distances in **6** of 2.000(7) and 1.988(6) Å are shorter than those seen in **3** consistent with the anionic nature of the ligand in **6**. This is also reflected in the shortening of the central C–imine–C distance, which was found to be 1.385(14) compared to the distance of 1.513(5) Å found in **4**. In a similar fashion, the P–C bond involving the central carbon is also shortened to 1.727(10) Å, compared to that of 1.803(4) Å found in **4**. Interestingly, the P–N distance in **6** is slightly longer at 1.628(7) vs. 1.605(3) Å found in **4**. These features of the anionic ligand also gives rise to a larger bite-angle (N–Ni–N) of the chelate (101.0(3)°) ligand. Similarly the Ni–Br bond lengths (2.4585(18), 2.4428(19) Å) are longer compared to those in **3** as well, presumably a result of the bridging to Li. The longer Ni–Br distances also accommodate a smaller Br–Ni–Br angle of 96.12(5)°. The Li–Br distances were found to be 2.550(19) and 2.517(18) Å while the Li–O distances were typical.

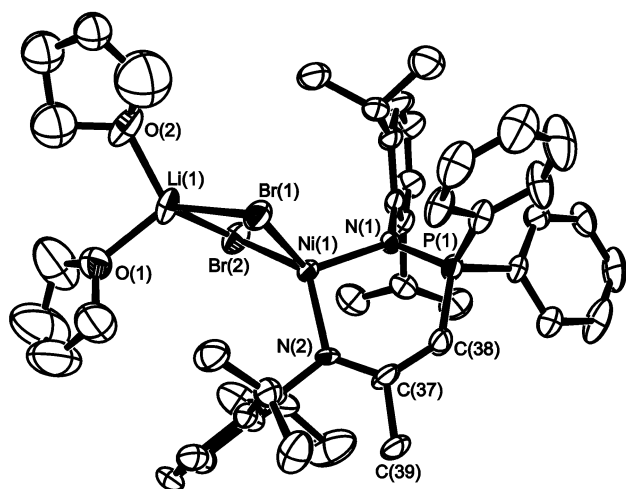


Fig. 4 ORTEP²³ drawing of **6**; 30% thermal ellipsoids are shown. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Ni(1)–N(2) 1.988(6), Ni(1)–N(1) 2.000(7), Ni(1)–Br(2) 2.4428(19), Ni(1)–Br(1) 2.4585(18), Br(1)–Li(1) 2.550(19), Br(2)–Li(1) 2.517(18), P(1)–N(1) 1.628(7), P(1)–C(38) 1.727(10), P(1)–C(1) 1.825(11), P(1)–C(7) 1.826(9), N(1)–C(18) 1.431(10), N(2)–C(37) 1.337(11), N(2)–C(25) 1.432(11), O(1)–Li(1) 1.98(2), O(2)–Li(1) 1.925(19); N(2)–Ni(1)–N(1) 101.0(3), N(2)–Ni(1)–Br(2) 129.6(2), N(1)–Ni(1)–Br(2) 108.71(19), N(2)–Ni(1)–Br(1) 105.5(2), N(1)–Ni(1)–Br(1) 117.1(2), Br(2)–Ni(1)–Br(1) 96.12(5), Ni(1)–Br(1)–Li(1) 83.8(4), Ni(1)–Br(2)–Li(1) 84.8(4), C(18)–N(1)–P(1) 121.6(5), C(18)–N(1)–Ni(1) 120.2(5), P(1)–N(1)–Ni(1) 118.2(4), C(37)–N(2)–Ni(1) 124.0(7), C(25)–N(2)–Ni(1) 115.2(5).

In related syntheses **5** was generated *in situ* and reacted with NiBr₂(dme) and an equivalent of PPh₃. This yielded deep red crystals of **7** in 57% yield. This species was diamagnetic. The ³¹P{¹H} NMR spectrum of **7** showed resonances at δ 24.6 and 18.0 with a P–P coupling of 39 Hz. ¹³C{¹H} NMR data revealed a resonance at δ 6.12 which suggested metallation of the central carbon of the ligand. X-Ray data confirmed the formulation as NiBr((C₆H₃*i*-Pr₂)NC(Me)CHPPH₂(NC₆H₃*i*-Pr₂))(PPh₃)**7**. The structure of **7** is pseudo-square planar at Ni with coordination of the phosphinimine-imine ligand *via* the phosphinimine–N and the central C atoms (Fig. 5(a)). Similar four-membered MCPN rings have been observed for Rh–²⁴ and

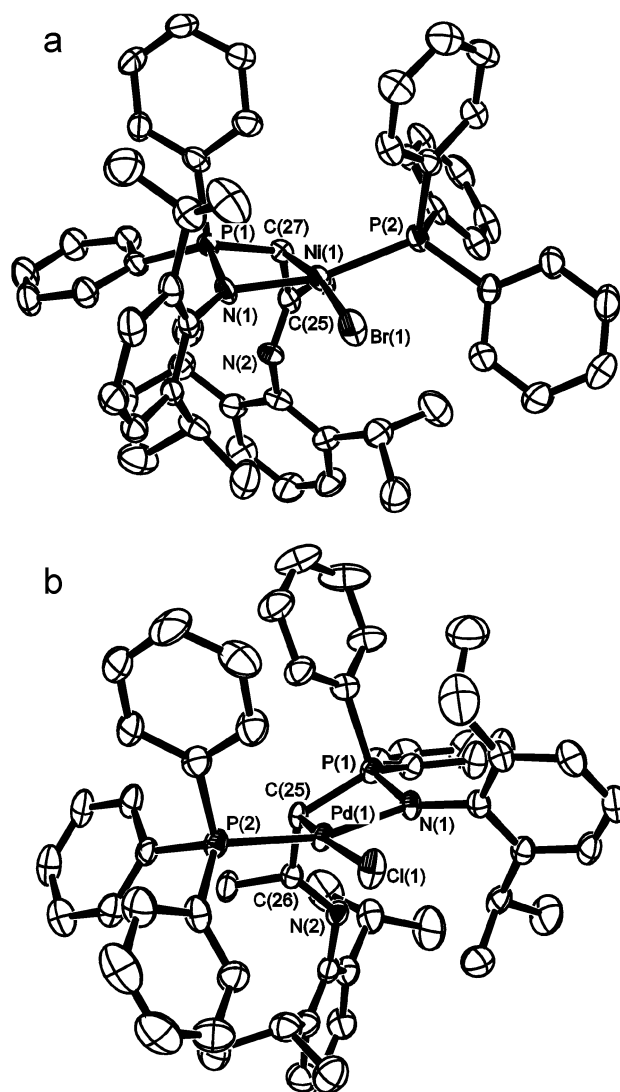


Fig. 5 (a) ORTEP²³ drawing of **7** and (b) **8**; 30% thermal ellipsoids are shown. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): **7**: Ni(1)–N(1) 1.946(5), Ni(1)–C(27) 2.023(6), Ni(1)–P(2) 2.201(3), Ni(1)–Br(1) 2.341(3), Ni(1)–P(1) 2.570(3), P(1)–N(1) 1.589(6), P(1)–C(27) 1.778(7), P(1)–C(1) 1.807(6), P(1)–C(7) 1.822(7), P(2)–C(44) 1.829(7), P(2)–C(52) 1.830(7), P(2)–C(46) 1.839(7), N(1)–C(28) 1.425(8), N(2)–C(25) 1.268(8), N(2)–C(13) 1.421(9), C(25)–C(27) 1.485(9); N(1)–Ni(1)–C(27) 78.8(2), N(1)–Ni(1)–P(2) 165.37(18), C(27)–Ni(1)–P(2) 98.44(17), N(1)–Ni(1)–Br(1) 93.58(16), C(27)–Ni(1)–Br(1) 170.00(16), P(2)–Ni(1)–Br(1) 90.53(7), N(1)–Ni(1)–P(1) 38.12(15), C(27)–Ni(1)–P(1) 43.54(19), P(2)–Ni(1)–P(1) 133.37(7), Br(1)–Ni(1)–P(1) 130.59(9), C(28)–N(1)–Ni(1) 131.0(4), P(1)–N(1)–Ni(1) 92.7(2), C(25)–N(2)–C(13) 124.3(6). **8**: Pd(1)–N(1) 2.115(4), Pd(1)–C(25) 2.141(5), Pd(1)–P(2) 2.2720(18), Pd(1)–Cl(1) 2.3347(18), Pd(1)–P(1) 2.698(2), P(1)–N(1) 1.592(4), P(1)–C(25) 1.791(5), P(1)–C(7) 1.808(6), P(1)–C(1) 1.848(6), P(2)–C(52) 1.815(6), P(2)–C(40) 1.828(6), P(2)–C(46) 1.839(6), N(1)–C(13) 1.439(6), N(2)–C(26) 1.279(6), N(2)–C(28) 1.440(7), C(25)–C(26) 1.484(7); N(1)–Pd(1)–C(25) 74.39(17), N(1)–Pd(1)–P(2) 165.15(12), C(25)–Pd(1)–P(2) 101.15(14), N(1)–Pd(1)–Cl(1) 95.89(12), C(25)–Pd(1)–Cl(1) 168.63(13), P(2)–Pd(1)–Cl(1) 89.71(7), N(1)–Pd(1)–P(1) 36.12(11), C(25)–Pd(1)–P(1) 41.49(13), P(2)–Pd(1)–P(1) 133.76(6), Cl(1)–Pd(1)–P(1) 130.58(5), C(13)–N(1)–P(1) 134.7(4), C(13)–N(1)–Pd(1) 131.2(3), P(1)–N(1)–Pd(1) 92.31(18), C(26)–N(2)–C(28) 121.4(4).

Ir–bis(phosphinimine)methane²⁵ complexes. The imine fragment of **7** does not bind to the metal but rather dangles free, adopting a position which is pseudo-*trans* to the axial phenyl ring on the P adjacent the central carbon. The Ni–N distance is 1.946(5) Å while the Ni–C distance is 2.023(6) Å. This tight four-membered chelate ring gives rise to the small bite angle of 78.8(2)° as well as the relatively short transannular Ni–P distance of 2.570(3) Å. Approximately *trans* to the C is a Br atom

(C–Ni–Br 170.00(16)°), while the ligand PPh₃ is pseudo-*trans* to the N (N–Ni–P 165.37(18)°). The Ni–P distance in this case is 2.201(3) Å while the Ni–Br distance is 2.341(3) Å, similar to that seen in **4**. The central-C of the ligand to imine-C bond is lengthened to 1.485(9) Å compared to that seen in **6** consistent with localization of the ligand anionic charge on the central carbon. In contrast, the P–N distance in **7** is 1.589(6) Å, slightly shorter than that seen in **4** and **6**. This may result from a decrease in the Lewis acidity of the Ni as a result of effective electron donation from the coordinated C atom.

In a similar fashion the analogous Pd species, brown crystals of PdBr((C₆H₃*i*-Pr₂)NC(Me)CHPPh₂(NC₆H₃*i*-Pr₂))(PPh₃) **8** were prepared in 57% isolated yield. The ³¹P{¹H} NMR spectrum of **8** showed resonances at δ 29.2 and 25.5 with a P–P coupling of 15 Hz, consistent with the formulation. X-Ray crystallographic studies of the revealed that **8** is structurally analogous to **7**, again with the phosphinimine-imine ligand bound in an N–C fashion through the phosphinimine N and the central C of the ligand (Fig. 5(b)). The Pd–N and Pd–C distances are 2.115(4) and 2.141(5) Å, respectively. The longer bond lengths in the Pd complex compared to **7** result in a N–Pd–C bite-angle that is significant larger (95.89(12)°) as well. Pd–P and Pd–Cl bond lengths are 2.2720(19) and 2.3347(18) Å. The transannular Pd–P distance is 2.698(2) Å, longer than corresponding distance in **7**, as expected. However, the P–N distance in **8** of 1.592(4) Å is similar to that seen in **7**.

These synthetic and structural studies reveal that it is possible to prepare a phosphinimine-imine ligand that is analogous to bulky diimine NacNac ligands. In this case, however the replacement of an imine-carbon with a PPh₂ fragment apparently significantly increases the steric congestion. The neutral metal complex of **3** could be prepared for Ni, where the metal adopts a pseudo-tetrahedral geometry, whereas attempts to prepare analogous square-planar Pd complexes failed. This was attributed to the enhanced steric congestion of this phosphinimine-imine ligand. Supporting this view, pseudo-square-planar Ni and Pd complexes of the anionic phosphinimine-iminate ligand were readily obtained. However, these species adopted an N–C binding mode. These results stand in contrast to the previously reported Pd–diketiminato chemistry, where ligand deprotonation afforded the bimetallic species [Pd((C₆H₃*i*-Pr₂)NCMe)₂CH(MeCN)₂(Pd(NCMe)₃)] [BF₄]₂.¹⁷ The present results suggest the increase in ligand size achieved by incorporation of the phosphinimine fragment accommodates the N,C binding mode. It is also possible however that the absence of effective charge delocalization to the P–N fragment, also results in increased localization of the charge on the central carbon again favoring the observed four-membered rings. In either case, these findings clearly suggest that such phosphinimine-imine ligands are not simple analogs of diimine ligands. As such, these species will provide the sheltered metal environment that is thought to make the diimine complexes effective olefin polymerization catalysts.^{5,17,26} Thus, while applications in polymerization catalysis appear unlikely, efforts to exploit these differences provided by these hybrid phosphinimine-imine and phosphinimine-iminato ligands are underway.

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