Journal of Organometallic Chemistry 693 (2008) 3029–3034

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Palladium(II) aryl-amido complexes of diphosphinoazines in unsymmetrical PNP' pincer-type configuration

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ARTICLE INFO

Article history:
Received 11 April 2008
Received in revised form 6 June 2008
Accepted 17 June 2008
Available online 25 June 2008

Keywords:
Diphosphinoazines
Pincer complexes
Aryl-amido complexes
Palladium
Polydentate ligands

ABSTRACT

Square planar palladium(II) aryl-amido complexes of diphosphinoazines in monoanionic unsymmetrical PNP' pincer-type coordination were prepared by reactions of phenyl-, *o*-tolyl-, or 2,6-dimethylphenyllithium with previously described chloro-amido complexes of diphosphinoazines having isopropyl, cyclohexyl and *tert*-butyl substituents on phosphorus atoms. The compounds were characterized by NMR showing free rotation around metal–aryl bond in the complexes; the presence of C_{ipso}–Pd bond was detected by two-dimensional experiments. In addition to that, crystal and molecular structure of one phenyl-amido complex, $[Pd(C_6H_5)\{P(C_6H_{11})_2CH{=}C(Bu^t)NN{=}C(Bu^t)CH_2P(C_6H_{11})_2\}]$, was determined by X-ray diffraction together with the structure of a chloro-amido complex $[PdCl\{PBu^t_2CH{=}C(Bu^t)NN{=}C(Bu^t)CH_2PBu^t_2\}]$. In both structures the ligand trans to the amide nitrogen is well surrounded by substituents on phosphorus atoms, the former complex showing significant interactions between two cyclohexyl hydrogen atoms and the π-system of the phenyl ring. The values od Pd–C and Pd–N bond distances in this complex are the same as those in a monodentate analog $[Pd(PMe_3)_2(C_6H_5)(NHC_6H_5)]$ which contrasts with the different values in a similar PNP symmetrical pincer complex reported in the literature.

1. Introduction

More than 30 years since the first report by Shaw [1], transition metal complexes with pincer ligands continue to attract attention in modern coordination and organometallic chemistry and also find applications in new or considerably improved catalytic processes [2]. The most frequent combinations of atoms involved in pincer-type coordination modes are PCP and NCN systems but other two-electron donors like O, S, Se or C (of N-heterocyclic carbene) are now quite commonly found at the ends of pincer arms. Similarly, the central formally monoanionic carbon atom can be replaced by other elements. The important case represents nitrogen which can form monoanionic amide complexes. Chemistry of PNP systems has, indeed, seen significant advance in recent years [3]. There are some examples of PCP aryl pincer complexes with amide ligands [4], the reverse cases, that is PNP amido complexes with aryl–metal bonds, are also known. The important examples can be found in the articles of Ozerov on the use of iridium and rhodium PNP pincers for activation of aromatic C–H bonds [5] and Liang on similar platinum complexes [6]. There is also related work of Harkins and Peters dealing with NNN pincer complexes of platinum [7].

We have recently used ligands of diphosphinoazine type in one of their coordination modes, the monoanionic ene-hydrazone form (PNP'), to support transition metals as unsymmetrical tridentate pincer-like ligands. Palladium(II) chloro-amido complexes [8] and rhodium(I) carbonyl-amido complexes [9] were prepared, the former compounds were used as catalysts for the Heck reaction of bromo and activated chloro arenes [10]. Here we present synthesis and characterization of new palladium(II) aryl-amido diphosphinoazine complexes with varied substitution both on phosphine donor arms and on the aryl ligand.

2. Experimental

2.1. General

All manipulations were carried out in an inert atmosphere of nitrogen or argon using standard Schlenk techniques. Hexane was distilled from Na, THF from sodium benzophenone ketyl. Starting palladium complexes **1**–**3** were prepared according to a literature method [8]. Solutions of phenyllithium (**4**), 2-methylphenyllithium (**5**), and 2,6-dimethylphenyllithium (**6**) were prepared in situ from the corresponding arylbromides (Aldrich, used as received) and *n*-butyllithium in hexane (Aldrich) at −78 °C. ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$, spectra were measured on a Varian Mercury 300 spectrometer at 299.98, 80.98 and 75.44 MHz, respectively, in

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doi:10.1016/j.jorganchem.2008.06.024

C_6D_6 solvent. Chemical shifts are reported in ppm (δ) relative to TMS, referenced to hexamethyldisilane and external H_3PO_4 ($^{31}P\{^1H\}$). A monocrystal of **3** suitable for X-ray analysis was obtained by slow evaporation of solvent at room temperature.

2.2. Synthesis of the palladium complexes

2.2.1. [Pd(C_6H_5){$PPr^i_2CH{=}C(Bu^t)NN{=}C(Bu^t)CH_2PPr^i_2$}] (**7**)

Solution of [PdCl{$PPr^i_2CH{=}C(Bu^t)NN{=}C(Bu^t)CH_2PPr^i_2$}] (0.2 g, 0.35 mmol) in hexane (10 ml) was treated with phenyllithium (0.6 ml of 0.7 M solution in hexane, 0.42 mmol). The mixture turned orange immediately, it was further stirred 15 h at room temperature. Water (0.1 ml) was added to destroy the excess of phenyllithum and the solvent evaporated in vacuum. The residue was extracted with hexane (3 ml), filtered and evaporated to dryness in vacuum giving 0.21 g (95%) of a red-brown product.

Anal. Calc. for $C_{33}H_{61}N_2P_2Pd$ (**7** · ½ C_6H_{14}): C, 60.58; H, 9.40; N, 4.28. Found: C, 60.55; H, 9.39; N, 4.25%. $^{31}P-\{^1H\}$ NMR (C_6D_6): 40.9, 62.8 [AB, ^2J(PP) = 369 Hz]; ^1H NMR (C_6D_6): 0.81 [6H, dd, ^3J(HH) = 7.2 Hz, ^3J(PH) = 14.3 Hz, CH_3 Pr^i], 0.90 [6H, dd, ^3J(HH) = 6.9 Hz, ^3J(PH) = 8.7 Hz, CH_3 Pr^i], 0.95 [6H, dd, ^3J(HH) = 7.1 Hz, ^3J(PH) = 10.7 Hz, CH_3 Pr^i], 1.09 [6H, dd, ^3J(HH) = 7.1 Hz, ^3J(PH) = 14.3 Hz, CH_3 Pr^i], 1.23 [9H, s, CH_3 Bu^t], 1.60 [9H, s, CH_3 Bu^t], 1.80 [2H, br m, CH, Pr^i], 1.89 [2H, br m, CH, Pr^i], 2.07 [2H, dd, ^2J(PH) = 10.8 Hz, ^4J(PH) = 3.0 Hz, CH_2], 3.72 [1H, dd, ^2J(PH) = 5.3 Hz, ^4J(PH) = 2.0 Hz, CH], 6.92–7.55 [5H, m, CH, Ph]; $^{13}C-\{^1H\}$ NMR (C_6D_6): 11.33 [dd, ^1J(CP) = 11.7 Hz, ^3J(PC) = 1.4 Hz, CH_2P], 17.36 [d, ^2J(PC) = 1.7 Hz, $(CH_3)_2CH$], 17.77 [s, $(CH_3)_2CH$], 18.00 [d, ^2J(PC) = 2.6 Hz, $(CH_3)_2CH$], 18.05 [d, ^2J(PC) = 4.3 Hz, $(CH_3)_2CH$], 22.88 [dd, ^1J(PC) = 17.6 Hz, ^3J(PC) = 2.6 Hz $PCH(CH_3)_2$], 23.70 [dd, ^1J(PC) = 27.1 Hz, ^3J(PC) = 3.5 Hz, $PCH(CH_3)_2$], 29.43 [s, $(CH_3)_3C$], 31.61 [s, $(CH_3)_3C$], 39.26 [d, ^3J(PC) = 6.8 Hz, $C(CH_3)_3$], 39.43 [d, ^3J(PC) = 2.6 Hz, $C(CH_3)_3$], 67.55 [d, ^1J(PC) = 45.8 Hz, PCH=], 122.20 [s, C_{para}], 126.91 [s, C_{meta}], 139.33 [t, ^5J(CP) = 3.2 Hz, C_{ortho}], 142.80 [s, C–N], 148.14 [dd, ^2J(PC) = 12.7 Hz, ^2J(PC) = 8.4 Hz, C_{ipso}], 189.32 [d, ^2J(PC) = 18.7 Hz, C=N].

2.2.2. [Pd(2-$CH_3C_6H_4$){$PPr^i_2CH{=}C(Bu^t)NN{=}C(Bu^t)CH_2PPr^i_2$}] (**8**)

Solution of [PdCl{$PPr^i_2CH{=}C(Bu^t)NN{=}C(Bu^t)CH_2PPr^i_2$}] (0.16 g, 0.29 mmol) in THF (10 ml) was treated with 2-methylphenyllithium (0.55 ml of 0.63 M solution in THF, 0.35 mmol). The mixture was stirred 15 h at room temperature. Water (0.1 ml) was added and the solvent evaporated in vacuum. The residue was extracted with hexane (4 ml), filtered and evaporated to dryness in vacuum giving 0.18 g (97%) of a dark red product.

$^{31}P-\{^1H\}$ NMR (C_6D_6): 58.1, 79.3 [AB, ^2J(PP) = 420 Hz]; ^1H NMR (C_6D_6): 1.01 [6 H, dd, ^3J(HH) = 6.9 Hz, ^3J(PH) = 14.4 Hz, CH_3, Pr^i], 1.11 [6H, dd, ^3J(HH) = 6.9 Hz, ^3J(PH) = 15.0 Hz, CH_3, Pr^i], 1.13 [9 H, s, CH_3, Bu^t], 1.25 [6H, dd, ^3J(HH) = 7.4 Hz, ^3J(PH) = 15.5 Hz, CH_3, Pr^i], 1.36 [6H, dd, ^3J(HH) = 7.2 Hz, ^3J(PH) = 16.8 Hz, CH_3, Pr^i], 1.44 [9H, s, CH_3, Bu^t], 1.90 [2H, dd, ^2J(PH) = 10.2 Hz, ^4J(PH) = 3.6 Hz, CH_2], 2.16 [4 H, bm, CH, Pr^i], 2.11 [3H, s, CH_3, 2-$CH_3C_6H_4$], 3.83 [1H, dd, ^2J(PH) = 6.3 Hz, ^4J(PH) = 2.4 Hz, CH], 6.84 – 7.12 [4H, m, CH, 2-$CH_3C_6H_4$]; $^{13}C-\{^1H\}$ NMR (C_6D_6): 10.33 [dd, ^1J(CP) = 10.8 Hz, ^3J(PC) = 2.5 Hz, CH_2P], 17.73 [d, ^2J(PC) = 2.3 Hz, $(CH_3)_2CH$], 18.34 [d, ^2J(PC) = 2.3 Hz, $(CH_3)_2CH$], 18.60 [d, ^2J(PC) = 2.9 Hz, $(CH_3)_2CH$], 18.82 [d, ^2J(PC) = 4.0 Hz, $(CH_3)_2CH$], 19.15 [s, CH_3], 23.99 [dd, ^1J(PC) = 17.3 Hz, ^3J(PC) = 3.2 Hz, $PCH(CH_3)_2$], 24.92 [dd, ^1J(PC) = 27.3 Hz, ^3J(PC) = 4.2 Hz, $PCH(CH_3)_2$], 29.06 [s, $(CH_3)_3$ C], 31.41 [s, $(CH_3)_3C$], 39.41 [d, ^3J(PC) = 11.5 Hz, $C(CH_3)_3$], 39.52 [s, $C(CH_3)_3$], 71.93 [d, ^1J(PC) = 45.2 Hz, PCH=], 125.89 [s, CH=], 126.02 [s, CH=], 128.91 [s, CH=], 130.19 [s, CH=], 135.48 [s, >C=], 140.77 [s, PdC=], 149.07 [s, C–N], 190.55 [dd, ^2J(PC) = 21.5 Hz, ^4J(PC) = 1.1 Hz, C=N].

2.2.3. [Pd{2,6-$(CH_3)_2C_6H_3$}{$PPr^i_2CH{=}C(Bu^t)NN{=}C(Bu^t)CH_2PPr^i_2$}] (**9**)

Solution of [PdCl{$PPr^i_2CH{=}C(Bu^t)NN{=}C(Bu^t)CH_2PPr^i_2$}] (0.3 g, 0.54 mmol) in hexane (10 ml) was treated with 2,6-dimethylphenyllithium (0.9 ml of 0.64 M solution in hexane:diethyl ether (5:2), 0.42 mmol). The mixture was stirred 15 h at room temperature. Water (0.1 ml) was added and the solvent evaporated in vacuum. The residue was extracted with hexane (2 ml), filtered and evaporated to dryness in vacuum giving 0.24 g (71%) of a red product.

$^{31}P-\{^1H\}$ NMR (C_6D_6): 38.5, 62.5 [AB, ^2J(PP) = 377 Hz]; ^1H NMR (C_6D_6): 0.97 [6H, dd, ^3J(HH) = 6.8 Hz, ^3J(PH) = 14.2 Hz, CH_3, Pr^i], 1.00 [6H, dd, ^3J(HH) = 7.3 Hz, ^3J(PH) = 14.6 Hz, CH_3, Pr^i], 1.16 [6H, dd, ^3J(HH) = 7.2 Hz, ^3J(PH) = 11.7 Hz, CH_3, Pr^i], 1.21 [6H, dd, ^3J(HH) = 7.4 Hz, ^3J(PH) = 14.3 Hz, CH_3, Pr^i], 1.23 [9H, s, CH_3, Bu^t], 1.58 [9H, s, CH_3, Bu^t], 2.05 [4H, br m, CH, Pr^i], 2.07 [2H, dd, ^2J(PH) = 10.5 Hz, ^4J(PH) = 2.7 Hz, CH_2], 2.22 [6H, s, CH_3, 2,6-$(CH_3)_2C_6H_3$], 3.65 [1H, dd, ^2J(PH) = 5.0 Hz, ^4J(PH) = 1.1 Hz, CH], 6.73–6.90 [3H, m, CH, 2,6-$(CH_3)_2C_6H_3$]; $^{13}C-\{^1H\}$ NMR (C_6D_6): 11.64 [d, ^1J(CP) = 12.7 Hz, CH_2P], 17.88 [d, ^2J(PC) = 2.0 Hz, $(CH_3)_2CH$], 18.22 [s, $(CH_3)_2CH$], 18.57 [d, ^2J(PC) = 4.0 Hz, $(CH_3)_2CH$], 18.80 [d, ^2J(PC) = 6.0 Hz, $(CH_3)_2CH$], 23.21 [dd, ^1J(PC) = 16.0 Hz, ^3J(PC) = 2.8 Hz, $PCH(CH_3)_2$], 23.71 [s, CH_3], 24.99 [dd, ^1J(PC) = 24.1 Hz, ^3J(PC) = 4.2 Hz, $PCH(CH_3)_2$], 29.48 [s, $(CH_3)_3C$], 31.57 [s, $(CH_3)_3C$], 39.12 [d, ^3J(PC) = 12.9 Hz, $C(CH_3)_3$], 39.32 [d, ^3J(PC) = 2.6 Hz, $C(CH_3)_3$], 66.52 [d, ^1J(PC) = 45.3 Hz, PCH=], 126.67 [s, C_{para}], 128.31 [s, C_{meta}], 138.16 [s, C_{ortho}], 141.57 [d, ^2J(PC) = 1.7 Hz, C_{ipso}], 149.01 [s, C–N], 187.85 [d, ^2J(PC) = 18.1 Hz, C=N].

2.2.4. [Pd(C_6H_5){$P(C_6H_{11})_2CH{=}C(Bu^t)NN{=}C(Bu^t)CH_2P(C_6H_{11})_2$}] (**10**)

Solution of [PdCl{$P(C_6H_{11})_2CH{=}C(Bu^t)NN{=}C(Bu^t)CH_2P$-$(C_6H_{11})_2$}] (0.2 g, 0.27 mmol) in hexane (10 ml) was treated with phenyllithium (0.45 ml of 0.7 M solution in hexane, 0.32 mmol). The mixture turned orange immediately; it was stirred for further 15 h at room temperature. Water (0.1 ml) was added and the solvent evaporated in vacuum. The residue was extracted with hexane (4 ml), filtered and evaporated to dryness in vacuum giving 0.14 g (66%) of a red-brown product. A monocrystal suitable for X-ray analysis was obtained by slow evaporation of solvent at room temperature.

Anal. Calc. for $C_{48}H_{84}N_2P_2Pd$ (**10** · C_6H_{14}): C, 67.23; H, 9.87; N, 3.27. Found: C, 60.27; H, 9.90; N, 3.25%. $^{31}P-\{^1H\}$ NMR (C_6D_6): 32.4, 51.9 [AB, ^2J(PP) = 369 Hz]; ^1H NMR (C_6D_6): 0.78–2.37 [44H, m, CH_2 + CH, C_6H_{11}], 1.28 [9H, s, CH_3, Bu^t], 1.64 [9H, s, CH_3, Bu^t], 2.16 [2H, dd, ^2J(PH) = 10.8 Hz, ^4J(PH) = 2.7 Hz, CH_2], 3.82 [1H, dd, ^2J(PH) = 5.1 Hz, ^4J(PH) = 2.1 Hz, CH], 6.94–7.65 [5H, m, CH, Ph]; $^{13}C-\{^1H\}$ NMR (C_6D_6): 12.80 [d, ^1J(CP) = 11.8 Hz, CH_2P], 29.54 [s, $(CH_3)_3C$], 31.70 [s, $(CH_3)_3C$], 33.01 [dd, ^1J(PC) = 17.5 Hz, ^3J(PC) = 2.5 Hz, PCH], 33.69 [dd, ^1J(PC) = 27.4 Hz, ^3J(PC) = 3.5 Hz, PCH], 39.31 [d, ^3J(PC) = 13.2 Hz, $C(CH_3)_3$], 39.55 [d, ^3J(PC) = 2.9 Hz, $C(CH_3)_3$], 68.73 [d, ^1J(PC) = 46.1 Hz, PCH=], 122.30 [s, C_{para}], 126.89 [s, C_{meta}], 139.47 [t, ^5J(CP) = 3.0 Hz, C_{ortho}], 143.42 [s, C–N], 149.68 [dd, ^2J(PC) = 12.6 Hz, ^2J(PC) = 8.2 Hz, C_{ipso}], 188.97 [d, ^2J(PC) = 18.7 Hz, C=N].

2.2.5. [Pd(2-$CH_3C_6H_4$){$P(C_6H_{11})_2CH{=}C(Bu^t)NN{=}C(Bu^t)CH_2P(C_6H_{11})_2$}] (**11**)

Solution of [PdCl{$P(C_6H_{11})_2CH{=}C(Bu^t)NN{=}C(Bu^t)CH_2P$-$(C_6H_{11})_2$}] (0.17 g, 0.23 mmol) in THF (10 ml) was treated with 2-methylphenyllithium (0.45 ml of 0.63 M solution in THF, 0.28 mmol). The mixture was stirred 15 h at room temperature. Water (0.1 ml) was added and the solvent evaporated in vacuum. The residue was extracted with hexane (4 ml), filtered and evaporated to dryness in vacuum giving 0.10 g (56%) of a red product.

$^{31}P-\{^1H\}$ NMR (C_6D_6): 49.9, 69.0 [AB, ^2J(PP) = 420 Hz]; ^1H NMR (C_6D_6): 0.95–2.35 [44H, m, CH_2 + CH, C_6H_{11}], 1.20 [9H, s, CH_3, Bu^t], 1.51 [9H, s, CH_3, Bu^t], 2.01 [2H, dd, ^2J(PH) = 10.7 Hz, ^4J(PH) =

3.8 Hz, CH_2], 2.10 [3H, s, CH_3, 2-$CH_3C_6H_4$], 3.95 [1H, dd, ^2J(PH) = 6.2 Hz, ^4J(PH) = 2.3 Hz, CH], 6.98–7.09 [4H, m, CH, 2-$CH_3C_6H_4$]; ^{13}C-{^{1}H} NMR (C_6D_6): 11.62 [d, ^1J(CP) = 13.3 Hz, CH_2P], 19.16 [s, CH_3], 29.20 [s, $(CH_3)_3$C], 31.57 [s, $(CH_3)_3$C], 33.91 [dd, ^1J(PC) = 17.2 Hz, ^3J(PC) = 3.1 Hz, PCH], 34.39 [dd, ^1J(PC) = 27.0 Hz, ^3J(PC) = 4.3 Hz, PCH], 39.53 [d, ^3J(PC) = 14.6 Hz, C$(CH_3)_3$], 39.68 [d, ^3J(PC) = 2.0 Hz, C$(CH_3)_3$], 73.01 [d, ^1J(PC) = 45.2 Hz, PCH=], 125.96 [s, CH=], 126.09 [s, CH=], 128.98 [s, CH=], 130.26 [s, CH=], 135.57 [s, >C=], 140.85 [s, PdC=], 149.28 [s, C–N], 190.27 [d, ^2J(PC) = 22.1 Hz, C=N].

2.2.6. [Pd{2,6-$(CH_3)_2C_6H_3$}{P($C_6H_{11})_2$CH=C(Bu^t)NN=C(Bu^t)CH_2-P($C_6H_{11})_2$}] (**12**)

Solution of [PdCl{P($C_6H_{11})_2$CH=C(Bu^t)NN=C(Bu^t)CH_2P-($C_6H_{11})_2$}] (0.25 g, 0.34 mmol) in hexane (15 ml) was treated with 2,6-dimethylphenyllithium (0.6 ml of 0.64 M solution in hexane:diethyl ether (5:2), 0.38 mmol). The mixture faded a little then it was stirred 20 h at room temperature. Water (0.1 ml) was added and the solvent evaporated in vacuum. The residue was extracted with hexane (4 ml), filtered and evaporated to dryness in vacuum giving 0.17 g (61%) of a red product.

^{31}P–{^{1}H} NMR (C_6D_6): 48.9, 65.9 [AB, ^2J(PP) = 423 Hz]; ^{1}H NMR (C_6D_6): 0.95–2.32 [44H, m, CH_2 + CH, C_6H_{11}], 1.19 [9H, s, CH_3, Bu^t], 1.48 [9H, s, CH_3, Bu^t], 2.00 [2H, dd, ^2J(PH) = 10.5 Hz, ^4J(PH) = 3.3 Hz, CH_2], 2.23 [6H, s, CH_3, 2,6-$(CH_3)_2C_6H_3$], 3.91 [1H, dd, ^2J(PH) = 6.5 Hz, ^4J(PH) = 2.0 Hz, CH], 6.72 [3H, m, CH, 2,6-$(CH_3)_2C_6H_3$]; ^{13}C–{^{1}H} NMR (C_6D_6): 11.56 [d, ^1J(CP) = 10.9 Hz, CH_2P], 23.71 [s, CH_3], 29.20 [s, $(CH_3)_3$C], 31.52 [s, $(CH_3)_3$C], 33.38 [dd, ^1J(PC) = 16.4 Hz, ^3J(PC) = 3.2 Hz, PCH], 33.92 [dd, ^1J(PC) = 26.4 Hz, ^3J(PC) = 3.9 Hz, PCH], 39.51 [d, ^3J(PC) = 15.0 Hz, C$(CH_3)_3$], 39.72 [d, ^3J(PC) = 2.0 Hz, C$(CH_3)_3$], 72.43 [d, ^1J(PC) = 45.8 Hz, PCH=], 126.70 [s, C_{para}], 128.31 [s, C_{meta}], 138.15 [s, C_{ortho}], 148.88 [s, C–N], 190.49 [d, ^2J(PC) = 21.0 Hz, C=N].

2.2.7. [Pd(C_6H_5){PBu^t_2CH=C(Bu^t)NN=C(Bu^t)CH_2PBu^t_2}] (**13**)

Solution of [PdCl{PBu^t_2CH=C(Bu^t)NN=C(Bu^t)CH_2PBu^t_2}] (0.23 g, 0.37 mmol) in hexane (15 ml) was treated with phenyllithium (0.65 ml of 0.7 M solution in hexane, 0.46 mmol). The colour of the mixture faded immediately then slowly turned red-brown, it was further stirred 20 h at room temperature. Water (0.1 ml) was added and the solvent evaporated in vacuum. The residue was extracted with hexane (4 ml), filtered and evaporated to dryness in vacuum giving 0.15 g (62%) of a red-brown product.

Anal. Calc. for $C_{48}H_{84}N_2P_2Pd$: C, 61.20; H, 9.37; N, 4.20. Found: C, 61.37; H, 9.42; N, 4.23%. ^{31}P-{^{1}H} NMR (C_6D_6): 56.3, 93.2 [AB, ^2J(PP) = 373 Hz]; ^{1}H NMR (C_6D_6): 1.08 [18H, d, ^3J(PH) = 12.3 Hz, CH_3, Bu^t], 1.19 [18H, d, ^3J(PH) = 13.2 Hz, CH_3, Bu^t], 1.31 [9H, s, CH_3, Bu^t], 1.44 [9H,s, CH_3, Bu^t], 2.07 [2H, dd, ^2J(PH) = 10.2 Hz, ^4J(PH) = 2.1 Hz, CH_2], 4.35 [1H, t, ^4J(PH) = 3.2 Hz, CH], 6.86–7.73 [5H, m, CH, Ph]; ^{13}C–{^{1}H} NMR (C_6D_6): 14.47 [d, ^1J(PC) = 7.2 Hz, CH_2P], 29.49 [d, ^2J(PC) = 4.0 Hz, $(CH_3)_3$CP], 29.54 [d, ^2J(PC) = 3.5 Hz, $(CH_3)_3$CP], 30.91 [s, $(CH_3)_3$C], 30.96 [s, $(CH_3)_3$C], 35.76 [dd, ^1J(PC) = 16.4 Hz, ^3J(PC) = 4.9 Hz, PC$(CH_3)_3$], 36.20 [dd, ^1J(PC) = 6.6 Hz, ^3J(PC) = 3.5 Hz, PC$(CH_3)_3$], 39.04 [d, ^3J(PC) = 3.5 Hz, $(CH_3)_3$C], 39.20 [d, ^3J(PC) = 11.2 Hz, $(CH_3)_3$C], 79.38 [d, ^1J(PC) = 44.4 Hz, PCH=], 122.34 [s, C_{para}], 126.22 [s, C_{meta}], 142.11 [t, ^5J(PC) = 2.9 Hz, C_{ortho}], 147.25 [dd, ^2J(PC) = 11.1 Hz, ^2J(PC) = 8.7 Hz, C_{ipso}], 149.70 [s, C–N], 185.25 [d, ^2J(PC) = 18.7 Hz, C=N].

2.2.8. [Pd(2-$CH_3C_6H_4$){PBu^t_2CH=C(Bu^t)NN=C(Bu^t)CH_2PBu^t_2}] (**14**)

Solution of [PdCl{PBu^t_2CH=C(Bu^t)NN=C(Bu^t)CH_2PBu^t_2}] (0.20 g, 0.32 mmol) in THF (10 ml) was treated with 2-methylphenyllithium (0.805 ml of 0.63 M solution in THF, 0.50 mmol). The mixture was stirred 3 h at reflux, then 15 h at room temperature. Water (0.2 ml) was added and the solvent evaporated in vacuum. The residue was extracted with hexane (4 ml), filtered and evaporated to dryness in vacuum giving 0.21 g (95%) of a red product.

^{31}P–{^{1}H} NMR (C_6D_6): 68.2, 105.5 [AB, ^2J(PP) = 416 Hz]; ^{1}H NMR (C_6D_6): 1.20 [9H, s, CH_3, Bu^t], 1.34 [18H, d, ^3J(PH) = 12.3 Hz, CH_3, Bu^t], 1.41 [18H, d, ^3J(PH) = 6.3 Hz, CH_3, Bu^t], 1.47 [9H,s, CH_3, Bu^t], 1.99 [2H, dd, ^2J(PH) = 9.8 Hz, ^4J(PH) = 3.2 Hz, CH_2], 2.10 [3H, s, CH_3, 2-$CH_3C_6H_4$], 4.34 [1H, t, ^4J(PH) = 3.6 Hz, CH], 6.97–7.10 [4H, m, CH, 2-$CH_3C_6H_4$]; ^{13}C–{^{1}H} NMR (C_6D_6): 12.76 [dd, ^1J(CP) = 6.9 Hz, ^3J(PC) = 1.7 Hz, CH_2P], 19.14 [s, CH_3], 29.68 [dd, ^2J(PC) = 4.0 Hz, ^4J(PC) = 1.4 Hz, $(CH_3)_3$CP], 30.02 [dd, ^2J(PC) = 3.2 Hz, ^4J(PC) = 1.0 Hz, $(CH_3)_3$CP], 30.34 [s, $(CH_3)_3$C], 31.14 [s, $(CH_3)_3$C], 36.58 [dd, ^1J(PC) = 17.0 Hz, ^3J(PC) = 5.2 Hz, PC$(CH_3)_3$], 36.90 [dd, ^1J(PC) = 5.5 Hz, ^3J(PC) = 4.3 Hz, PC$(CH_3)_3$], 39.36 [dd, ^3J(PC) = 14.0 Hz, ^5J(PC) = 1.3 Hz, C$(CH_3)_3$], 39.64 [d, ^3J(PC) = 2.6 Hz, C$(CH_3)_3$], 81.10 [d, ^1J(PC) = 43.5 Hz, PCH=], 125.90 [s, CH=], 126.03 [s, CH=], 128.12 [s, CH=], 130.21 [s, CH=], 135.49 [s, >C=], 140.77 [s, PdC=], 157.61 [s, C–N], 187.93 [dd, ^2J(PC) = 20.2 Hz, ^4J(PC) = 1.3 Hz, C=N].

2.2.9. [Pd{2,6-$(CH_3)_2C_6H_3$}{PBu^t_2CH=C(Bu^t)NN=C(Bu^t)CH_2PBu^t_2}] (**15**)

Solution of [PdCl{PBu^t_2CH=C(Bu^t)NN=C(Bu^t)CH_2PBu^t_2}] (0.23 g, 0.37 mmol) in hexane (15 ml) was treated with 2,6-dimethylphenyllithium (0.7 ml of 0.64 M solution in hexane:diethyl ether (5:2), 0.45 mmol). The mixture was stirred 3 h at reflux, then 15 h at room temperature. Water (0.1 ml) was added and the solvent evaporated in vacuum. The residue was extracted with hexane (4 ml), filtered and evaporated to dryness in vacuum giving 0.15 g (58%) of a red product.

^{31}P–{^{1}H} NMR (C_6D_6): 66.4, 95.7 [AB, ^2J(PP) = 416 Hz]; ^{1}H NMR (C_6D_6): 1.19 [9H, s, CH_3, Bu^t], 1.38 [18H, d, ^3J(PH) = 12.6 Hz, CH_3, Bu^t], 1.40 [18H, d, ^3J(PH) = 9.3 Hz, CH_3, Bu^t], 1.46 [9H,s, CH_3, Bu^t], 1.96 [2H, dd, ^2J(PH) = 9.9 Hz, ^4J(PH) = 3.3 Hz,CH_2], 2.22 [6H, s, CH_3, 2,6-$(CH_3)_2C_6H_3$], 4.29 [1H, dd, ^2J(PH) = 4.2 Hz, ^4J(PH) = 3.0 Hz, CH], 6.72–6.94 [3H, m, CH, 2,6-$(CH_3)_2C_6H_3$]; ^{13}C–{^{1}H} NMR (C_6D_6): 11.93 [dd, ^1J(PC) = 8.1 Hz, ^3J(PC) = 1.8 Hz, CH_2P], 23.67 [s, CH_3], 29.49 [dd, ^2J(PC) = 4.1 Hz, ^4J(PC) = 1.2 Hz, $(CH_3)_3$CP], 30.34 [s, $(CH_3)_3$C], 31.24 [s, $(CH_3)_3$C], 36.22 [dd, ^1J(PC) = 17.3 Hz, ^3J(PC) = 5.1 Hz, PC$(CH_3)_3$], 36.47 [dd, ^1J(PC) = 3.9 Hz, ^3J(PC) = 1.4 Hz, PC$(CH_3)_3$], 39.45 [dd, ^3J(PC) = 13.7 Hz, ^5J(PC) = 0.9 Hz, C$(CH_3)_3$], 39.84 [d, ^3J(PC) = 2.6 Hz, $(CH_3)_3$C], 79.45 [d, ^1J(PC) = 43.5 Hz, PCH=], 126.67 [s, C_{para}], 128.31 [s, C_{meta}], 138.14 [s, C_{ortho}], 154.64 [s, C–N], 188.66 [d, ^2J(PC) = 21.0 Hz, C=N].

3. Crystallographic data

The diffraction-quality crystals of complexes were grown as mentioned above. The crystals were selected in mother liquor and quickly transferred into Fluorolube oil, then mounted on glass fibres in random orientation and cooled to 150(1) K. Diffraction data were collected using Nonius Kappa CCD diffractometer (Enraf-Nonius) at 150(1) K (Cryostream Cooler Oxford Cryosystem) and analyzed using the HKL program package [11]. The structures were solved by direct methods and refined by full-matrix least-squares techniques on F values (SIR92 [12] and CRYSTALS [13]). The graphical presentation of the structures were done in ORTEP-3 [14] and ACCELRYS DS Visualizer [15].

[PdCl{P($C_6H_{11})_2$CH=C(Bu^t)NN=C(Bu^t)CH_2P($C_6H_{11})_2$}] (**3**), M = 625.57 g/mol, monoclinic system, space group $P2_1/c$, a = 18.2271(3), b = 10.6897(2), c = 16.8968(2) Å, β = 103.347(1)°, Z = 4, V = 3203.29(9) Å^3, D_c = 1.30 g m^{-3}, μ(Mo Kα) = 0.78 mm^{-1}, crystal dimensions of 0.2 × 0.2 × 0.3 mm. All heavy atoms were refined anisotropically. All hydrogen atoms were localized from the expected geometry and were refined isotropically. This model

converged to the final $R = 0.0258$ and $R_w = 0.0312$ using 5836 independent reflections ($\theta_{max} = 27.51°$).

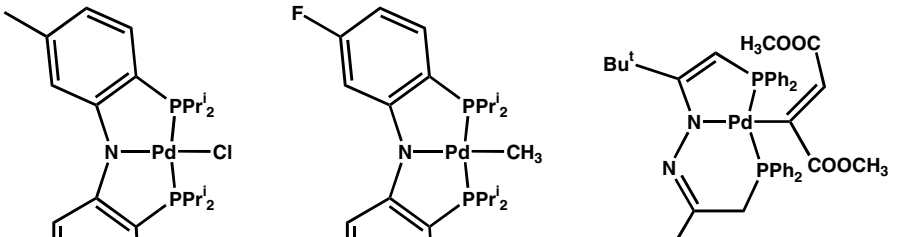
$[Pd(C_6H_5)\{P(C_6H_{11})_2CH{=}C(Bu^t)NN{=}C(Bu^t)CH_2P(C_6H_{11})_2\}] \cdot C_6H_{14}$ (**10** · C_6H_{14}), $M = 857.56$ g/mol, triclinic system, space group $P\bar{1}$, $a = 9.4293(2)$, $b = 14.9696(3)$, $c = 18.4260(5)$ Å, $\alpha = 93.591(1)°$, $\beta = 104.248(1)°$, $\gamma = 103.5659(1)°$, $Z = 2$, $V = 2430.5(1)$ Å^3, $D_c = 1.17$ g cm^{-3}, $\mu(MoK\alpha) = 0.48$ mm^{-1}, crystal dimensions of $0.2 \times 0.2 \times 0.3$ mm. The independent part is created by one molecule of the complex and one solvent molecule. All heavy atoms of the complex were refined anisotropically, the hydrogen atoms were localized from the expected geometry and were refined isotropically. The hexane carbon atoms were refined only isotropically and the positions of hydrogen atoms were calculated from the geometry and were not refined. This model converged to the final $R = 0.0412$ and $R_w = 0.0496$ using 8811 independent reflections ($\theta_{max} = 27.48°$).

4. Results and discussion

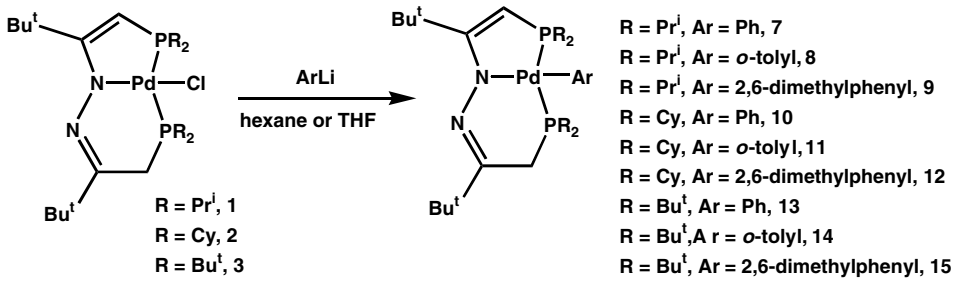
Reaction of palladium(II) chloro-amido complexes **1**–**3** with aryllithiums **4**–**6** led to new aryl-amido complexes **7**–**15** (Scheme 1) in which diphosphinoazines coordinated as monoanionic unsymmetrical pincer-type ligands with amide nitrogens in positions *trans* to the aryl carbon. Yields generally decreased with the bulkiness of the incoming aryl substituent and with steric congestion created by substituents on both phosphoruses, *tert*-butyl complexes being the most resistant to substitution. Nevertheless, using reflux conditions the *tert*-butyl complex **14** with 2-methylphenyl ligand could be obtained in 95% isolated yield.

In ^{1}H NMR spectra, the proton shifts of CH_2P groups were in the range of 1.90–2.07 ppm whereas protons of =CHP groups resonated between 3.65 and 4.35 ppm. Both signals appeared as doublets of doublets coupled to both phosphorus atoms. The similar features could be found in ^{13}C NMR spectra. The CH_2P carbons appeared in the range of 10.33–12.80 ppm whereas =CHP carbons were considerably more deshielded (66.52–81.10 ppm) as expected and as is common with other known complexes with ene-hydrazone backbone. The signals of carbons next to phosphorus were doublets, ^1J(PC) being always greater for the carbon in a five-membered ring.

Signals of special importance were resonances of carbons of the aryl ligands, especially the *ipso* carbon directly bonded to palladium. With the exception of complexes **12** and **15**, its resonance was found in all the complexes. Comparison of carbon chemical shifts of complex **9** with those of complexes **12** and **15** strongly suggested, however, that the latter complexes had structures analogous to the former one. In all cases there was only one signal for each couple of *ortho* and *meta* carbons as well as for *para* carbons documenting a free rotation of aryl ligands around Pd–C bonds at room temperature. The fast rotation of aryl groups in our complexes contrasts with the work of van Koten et al. who found restricted rotation of *o*- and *m*-tolyl (but not phenyl and *p*-tolyl) groups in platinum NCN pincer complexes [17]. Whereas dimethylamino donor groups of the NCN pincers are certainly smaller than diisopropyl-, dicyclohexyl- or di-*tert*-butylphosphino groups of our PNP' pincers, the ligand framework of the former pincers is much more rigid. We believe that it is the possibility of comparably easy ring inversion, especially of the six-membered ring, that allows the aryl groups to mesh with substituents on phosphorus atoms while rotating. The signals of *ipso* carbons were doublets of doublets, the signals of *ortho* carbons were virtual triplets confirming thus the coupling to both phosphorus atoms. For example, the signal of C_{ipso} in complex **7** was found at 148.14 ppm with ^2J(CP) 12.7 Hz and 8.4 Hz whereas the signal of C_{ortho} was a virtual triplet at 139.33 with $|^3J(PC) + {}^3J(P'C)| = 3.2$ Hz. These values were



The NMR spectra of all products were in accordance with structures with ene-hydrazone monoanionic ligand backbone. Large ^2J(PP) coupling constants (369–423 Hz) confirmed *trans* arrangement of phosphine donor groups [16]. The ene-hydrazone coordination mode created two metallarings of inequal size (5-membered and 6-membered) as was confirmed by the presence of signals of both methylene and methine protons and carbons.



Scheme 1.

in accordance with data for a known *trans*-[Pd(PMe_3)$_2$(C_6H_5)(NHC_6H_5)] complex where the C_{ipso} signal was a triplet at 157.2 ppm with ^2J(CP) = 12 Hz [18].

In addition to the direct proof from the molecular structure determination of complex **10** (see below), the evidence for the presence of Pd–C_{ipso} bond in some other complexes was also provided by HMBC correlations. Complex **7** showed a four-bond coupling of the *ipso* carbon with methine protons and also a four-bond coupling with the methine protons of isopropyl groups, both in the five membered ring of the compound. In complex **8** this *ipso* carbon was coupled across five bonds with the methyl protons of isopropyl groups in the five membered ring whereas in complex **9** the C_{ipso} showed interaction with methylene protons in the six-membered ring.

We were able to grow single crystals of the cyclohexyl diphosphinoazine complex with phenyl ligand **10**. In addition to that, X-ray structure of one of the starting chloro-amido complexes **3** was determined (Figs. 1 and 2). The crystal structures confirmed the square-planar coordination sphere of the palladium central atom and the formation of five- and six-membered rings of the PNP' ligand suggested by NMR techniques.

So far only one structure of a palladium complex with a diphosphinoazine in monoanionic ene-hydrazone form [16] is reported in Cambridge Structure Database (CSD version 5.29, January 2008 release). However the Pd(II) coordination sphere in **3** and **10** can be compared also with other known PNP palladium complexes.

The angle P1–Pd–P8 in complex **3** is 170.75(2)° and Pd–N4 distance is 2.0648(15) Å which contrasts with the values of 163.54(2)° and 2.0258(19) Å, respectively, found by Ozerov [19] for a symmetrical pincer complex **16**. The smaller values for the latter complex are likely due to a higher ring strain of the structure with two condensed five membered rings, the Pd–Cl bond lengths being essentially equal. Palladium–nitrogen bond was found to be considerably longer (2.0938(15) Å) in the methyl-amido complex **17** than in complex **16**, which is explained by *trans* influence of the methyl ligand [20]. The same trend, i.e. lengthening of the Pd–N4 bond *trans* to a carbon ligand compared to the Pd–N4 bond *trans* to a chlorine, was also observed going from **3** to **10** (2.0648(15) Å vs. 2.123(2) Å) and also in a *trans*-vinyl complex **18** [16] although there the effect is smaller (2.087(11) Å) due to a more electron accepting

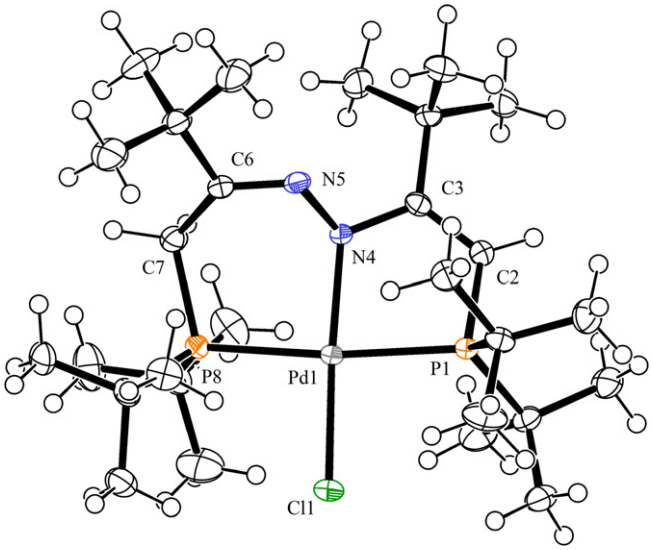


Fig. 1. ORTEP projection of **3**. Selected bond distances (Å) and angles (°): Pd–Cl 2.3302(6), Pd–P1 2.2795(6), Pd–P8 2.3181(6), Pd–N4 2.0648(15), P1–Pd–P8 170.75(2), N4–Pd-Cl 176.20(5).

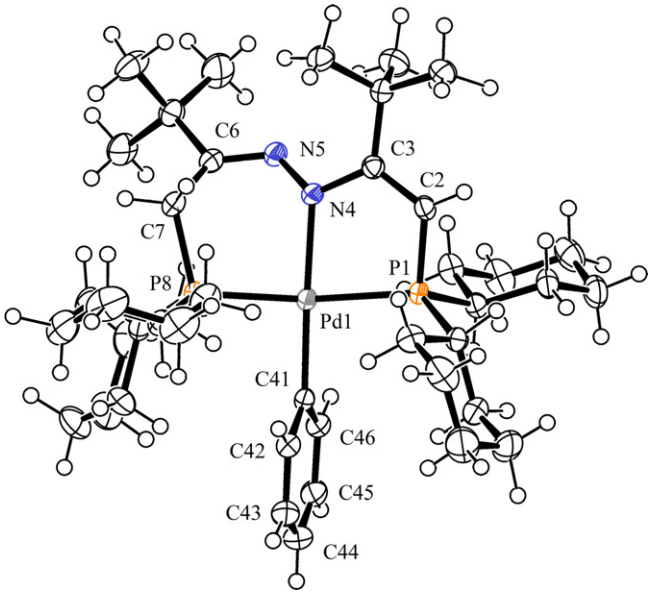


Fig. 2. ORTEP projection of **10**. The solvent molecule was omitted for clarity. Selected bond distances (Å) and angles (°): Pd–C41 2.033(3), Pd–P1 2.2785(6), Pd–P8 2.2705(6), Pd–N4 2.123(2), P1–Pd–P8 166.85(3), N4–Pd–C41 175.52(9).

character of the substituted vinyl ligand. An interesting comparison is offered with the structure determined by Boncella of a square-planar diphosphine palladium aryl-amido complex containing only monodentate ligands. The Pd–C as well as Pd–N bond lengths in the complex [Pd(PMe_3)$_2$(C_6H_5)(NHC_6H_5)] [21] are within experimental error equal to the values for complex **10** (2.033(3) Å and 2.123(2) Å, respectively). However, while P1–Pd–P8 angle in complex **10** amounts to 166.85(3)°, i.e. phosphine donor atoms are bent away from the phenyl ligand due to their involvement in the two metallarings, in complex [Pd(PMe_3)$_2$(C_6H_5)(NHC_6H_5)] the two trimethylphosphines are actually bent towards the phenyl (and away from the anilide ligand) the analogous P–Pd–P angle being approximately 185.8°. The explanation offered by authors [21] is steric (less repulsion from the phenyl than from the anilide ligand).

The five- and six-membered rings in the PNP' ligand can be described as any ring using the ring puckering parameters [22]. Both structures (**3** and **10**) adopt the E_5 conformation for the five-membered ring and the $B_{2,5}$ conformation for the six-membered ring (in the series of atoms Pd1–N4–C3–C2–P1 and Pd1–N4–N5–C6–C7–P8, respectively). In the case of **3** the six-membered ring is more puckered and its conformation reaches the border between $B_{2,5}$ and $^4T_2$ [22].

Both the *tert*-butyl and cyclohexyl groups are highly sterically demanding. Mutual interactions between these groups thus prevail in the molecular packing of **3** and **10**. The *tert*-butyl hydrogen atoms in **3** minimize the influence of the chlorine atom on the molecular assembly. The cyclohexyl groups in **10** do not surround the phenyl substituent as close as the *tert*-butyl groups envelop the chlorine atom in **3**. There are CH···π interactions between two cyclohexyl hydrogen atoms and the π-system of the phenyl ring. The adjacent complex molecules (two enantiomers generated by the center of symmetry) are mutually rotated by 180° making their phenyl substituents parallel (in the direction of internal diagonal). No interaction of the phenyl rings is apparent. The complex molecules are arranged stepwise in the X dimension creating thereby a solvent accessible void in the corners of the lattice cell (532 Å^3; calculated by Squeeze [23]). This void is filled with two hexane solvent molecules which represent a kind of the third nonpolar group within this structure (together with the cyclohexyl and *tert*-butyl groups).

5. Conclusions

Trans-aryl-amido palladium complexes were obtained by reactions of the corresponding easily accessible chloro-amido complexes with aryllithiums using as supporting pincers unsymmetrical PNP' diphosphinoazines in monoanionic ene-hydrazone form. The complexes are square-planar with aryl groups rotating freely in solution at room temperature despite relative bulkiness of the substituents on phosphorus atoms. The X-ray diffraction analysis of the phenyl substituted complex with bis(dicyclohexylphosphino)azine ligand revealed that the preferred conformation in the solid state is the one with the phenyl ring perpendicular to the coordination plane of the complex. This conformation also allows for CH···π interactions between cyclohexyl hydrogen atoms and the π-system of the phenyl ring.

Acknowledgements

The support of grant agencies (Grant Agency of the Czech Republic, 203/01/0554, 203/06/0738; Ministry of Education, Youth and Sports of the Czech Republic, LC06070 and MSM0021620857) is gratefully acknowledged.

Appendix A. Supplementary material

CCDC 684195 and 684196 contain the supplementary crystallographic data for [PdCl{P(C_6H_{11})$_2$CH=C(Bu^t)NN=C(Bu^t)CH_2P(C_6H_{11})$_2$}] (**3**) and [Pd(C_6H_5){P(C_6H_{11})$_2$CH=C(Bu^t)NN=C(Bu^t)CH_2P(C_6H_{11})$_2$}] · C_6H_{14} (**10** · C_6H_{14}). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.06.024.

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