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New (aminomethyl)phosphines via selective hydrophosphination and/or phosphorus based Mannich condensation reactions

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ABSTRACT

Controlled stepwise reaction of a geminal substituted alkene or primary amine group afforded a small library of new functionalised tertiary and ditertiary phosphines. Accordingly, Mannich based condensation of the commercially available disubstituted arene $C_6H_4(NH_2)\{2\text{-}C(Me)=CH_2\}$ with $HOCH_2PR_2$ (R_2 = Cg: 1,3,5,7-tetramethyl-2,4,8-trioxa-6-phosphaadamantyl; Ph_2) afforded the (aminomethyl)phosphines $C_6H_4(NHCH_2PCg)\{2\text{-}C(Me)=CH_2\}$ **L$_1$** and $C_6H_4(NHCH_2PPh_2)\{2\text{-}C(Me)=CH_2\}$ **L$_2$** in approx. 60% yield. In addition to the formation of **L$_2$**, the diphosphine **L$_3$** was also identified and independently synthesised upon reaction of $C_6H_4(NH_2)\{2\text{-}C(Me)=CH_2\}$ with two equiv. of $HOCH_2PPh_2$ in CH_3OH under reflux. Alternatively, reaction of $C_6H_4(NH_2)\{2\text{-}C(Me)=CH_2\}$ with H-PR_2 (R_2 = Cg or Ph_2) in the presence of AIBN [2,2`-azobis(2-methylpropionitrile)] as free radical initiator, afforded the primary amine functionalised phosphines $C_6H_4(NH_2)\{2\text{-}CH(Me)CH_2PCg\}$ **L$_4$** and $C_6H_4(NH_2)\{2\text{-}CH(Me)CH_2PPh_2\}$ **L$_5$** in 85% and 66% isolated yields respectively. In both cases only the anti-Markovnikov addition products were observed. Subsequent reaction of **L$_5$** with $HOCH_2PR_2$ (R_2 = Ph_2) afforded the unsymmetrical ditertiary phosphine $C_6H_4(NHCH_2PPh_2)\{2\text{-}CH(Me)CH_2PPh_2\}$ **L$_6$**. Some preliminary coordination studies towards $[RuCl(\mu\text{-}Cl)(\eta^6\text{-}C_{10}H_{14})]_2$, [AuCl(tht)] (tht = tetrahydrothiophene) and $[MCl_2(\eta^4\text{-cod})]$ (M = Pd, Pt; cod = cycloocta-1,5-diene) demonstrate these new ligands behave as classic P-donors leaving the pendant amino or alkenyl groups non-coordinating. All compounds have been characterised by multinuclear NMR, FT–IR, mass spectrometry and microanalysis. Single crystal X-ray studies have been performed on **L$_3$**, **L$_5$**, **L$_6$**, **1**, **3b**$\cdot 0.5CH_2Cl_2$, **4a**$\cdot 1.5CH_2Cl_2$, **5** and **6**$\cdot 0.5CDCl_3 \cdot 0.5C_4H_{10}O$

Keywords: P ligands; Late-transition metals; X-ray crystallography; Organometallic complexes; Hydrophosphinations

1. Introduction

The coordination and organometallic chemistry of late transition metal complexes using tertiary phosphines as ancillary ligands continues to attract much attention. In the quest for developing new P-based ligands, a plethora of synthetic methodologies have thus far been developed allowing precise control of factors such as the incorporation of suitable electronic groups, sterically bulky substituents, functional groups, chirality and solubility properties [1]. For a number of years, our research group has been interested in developing atom economical and facile procedures to phosphorus based ligands [2]. In particular we [3], and others [4], have successfully used Mannich based condensations for accessing new (aminomethyl) derivatised phosphines through C−N bond formation (Scheme 1, pathway a). Recently there has also been much interest in hydrophosphinations (Scheme 1, pathway b) as an entry route to P−C bond formation using suitable P−H precursors [5]. Single [6] or double [7] hydrophosphination of alkenes have been developed as well as metal catalysed double hydrophosphination of alkynes [8] leading to unsymmetric ditertiary phosphines. Webster et al [9] employed simple iron catalysts to promote catalytic intramolecular hydrophosphination of alkene or alkyne functionalised primary phosphines. Furthermore the scope of this approach has also been extended to the alternative use of phosphine oxides [$R_2P(O)$−H or $(RO)_2P(O)$−H] and applied in alkene [10a,10b], alkyne [10b], nitrile [11], or azobenzene [12] hydrophosphination reactions. Asymmetric palladium(II) catalysed hydrophosphinations have also achieved much recent prominence [13] for the preparation of chiral phosphine ligands.

Herein we describe, using a commercially available starting material, the straightforward synthesis and characterisation of new amino- or alkenyl-functionalised tertiary monodentate and bidentate phosphines using Mannich based condensation and/or hydrophosphination protocols. We demonstrate the facile nature of the syntheses of these ligands opposed to alternative P–C bond forming synthetic methods [14]. Furthermore we show these ligands function in a classical P-monodentate or μ-P,P-bridging manner through conducting some brief coordination studies to Ru^{II}, Au^{I}, Pd^{II}, and Pt^{II} metal centres. All new compounds have been structurally verified by a combination of spectroscopic and crystallographic techniques.

< *Insert Scheme 1 and Scheme 1 caption here* >

2. Experimental

2.1. Materials

All reactions were conducted under an inert atmosphere except for the coordination studies which were carried out in air using reagent grade quality solvents. The compounds $[MCl_2(\eta^4\text{-}cod)]$ (cod = cycloocta-1,5-diene) [15], $[RuCl(\mu\text{-}Cl)(\eta^6\text{-}C_{10}H_{14})]_2$ [16], and [AuCl(tht)] (tht = tetrahydrothiophene) [17] were all prepared according to known procedures. $HOCH_2PR_2$ (R_2 = Cg or Ph_2) [3a, 18] were prepared, either in situ or preformed, according to literature methods. 2-isopropenylaniline was obtained from Sigma-Aldrich and used directly without further purification.

2.2. Instrumentation

Infrared spectra were recorded as KBr pellets on either a Perkin-Elmer System 2000 (4000–400 cm^{-1} range) or a Spectrum 100S (4000–250 cm^{-1} range) Fourier-Transform spectrometer. ^1H NMR spectra (400 MHz) were recorded on a Bruker DPX-400 FT spectrometer with chemical shifts (δ) in ppm to high frequency of $Si(CH_3)_4$ and coupling constants (*J*) in Hz. $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker DPX-400 FT spectrometer with chemical shifts (δ) in ppm to high frequency of 85% H_3PO_4. NMR spectra were measured in $CDCl_3$ at 298 K. Elemental analyses (Perkin-Elmer 2400 CHN or Exeter

Analytical, Inc. CE-440 Elemental Analyzers) were performed by the Loughborough University Analytical Service within the Department of Chemistry. Mass spectra were recorded within the Department of Chemistry at Loughborough University and by the EPSRC National Mass Spectrometry Service at Swansea University.

2.3 Syntheses

2.3.1 **Preparation of $C_6H_4(NHCH_2PCg)\{2\text{-}C(Me)\text{=}CH_2\}$ (L_1).** A solution of $CgPCH_2OH$ (0.635 g, 2.57 mmol) in CH_3OH (10 ml) was added to $C_6H_4(NH_2)\{2\text{-}C(Me)\text{=}CH_2\}$ ((0.342 g, 2.57 mmol) and the resulting solution stirred for 24 h at r.t. The solvent volume was reduced in vacuo to ~5 ml and the suspension kept in the freezer for 12 h. The resulting solid was collected by suction filtration and dried in vacuo. Yield: 0.600 g, 64%. ^1H NMR [$CDCl_3$]: δ 7.21 (1H, *virtual* t, $^3J_{HH}$ 7.2, arom. *H*), 7.05 (1H, d, $^3J_{HH}$ 6.8, arom. *H*), 6.75 (2H, arom. *H*), 5.33 (1H, s, =C*H*), 5.05 (1H, s, =C*H*), 4.74 (1H, bs, N*H*), 3.52 (1H, d, $^2J_{HH}$ 12.7, PCH_2N), 3.02 (1H, d, $^2J_{HH}$ 12.7, PCH_2N), 2.17–1.21 (19H, m, CH_2 + CH_3, Cg). $^{31}P\{^1H\}$ NMR [$CDCl_3$]: δ –33.3, –33.5. FT–IR (KBr): ν_{NH} 3428 cm^{-1}. EI–MS (*m/z*) $[MH]^+$ 362. Anal. (%) Calcd. for $C_{20}H_{28}NO_3P{\cdot}0.5H_2O$: C, 64.85; H, 7.89; N, 3.78. Found: C, 64.63; H, 7.32; N, 3.86.

2.3.2 **Preparation of $C_6H_4(NHCH_2PPh_2)\{2\text{-}C(Me)\text{=}CH_2\}$ (L_2).** A solution of $C_6H_4(NH_2)\{2\text{-}C(Me)\text{=}CH_2\}$ (0.300 g, 2.25 mmol) in CH_3OH (7.5 ml) was added to a CH_3OH solution (7.5 ml) of Ph_2PCH_2OH (0.487 g, 2.25 mmol) by cannula. The resulting mixture was stirred for 24 h and the solvent concentrated under reduced pressure to ~5 ml. The suspension was kept in the freezer for 12 h and the solid collected by suction filtration and dried in vacuo. Yield: 0.449 g, 60%. ^1H NMR [$CDCl_3$]: δ 7.54–7.32 (10H, m, arom. *H*), 7.20 (1H, dt, $^3J_{HH}$ 7.3, $^4J_{HH}$ 1.5, arom. *H*), 6.99 (1H, dd, $^3J_{HH}$ 7.4, $^4J_{HH}$ 1.5, arom. *H*), 6.81 (1H, d, $^3J_{HH}$ 8.1, arom. *H*), 6.72 (1H, vt, $^3J_{HH}$ 7.4 arom. *H*), 5.06 (1H, d, $^2J_{HH}$ 1.3, =C*H*), 4.74 (1H, d, $^2J_{HH}$ 1.3, =C*H*), 4.23 (1H, bs, N*H*), 3.83 (2H, d, $^2J_{HP}$ 4.5, PCH_2N), 1.86 (3H, s, CH_3). $^{31}P\{^1H\}$ NMR [$CDCl_3$]: δ –18.5. FT–IR (KBr): ν_{NH} 3401 cm^{-1}. EI–MS (*m/z*) $[MH]^+$ 332. Anal. (%) Calcd. for $C_{22}H_{22}NP{\cdot}0.5H_2O$: C, 78.65; H, 6.41; N, 4.16. Found: C, 79.09; H, 6.52; N, 4.21.

2.3.3 **Preparation of $C_6H_4\{N(CH_2PPh_2)_2\}\{2\text{-}C(Me){=}CH_2\}$ (L_3).** A solution of $C_6H_4(NH_2)\{2\text{-}C(Me){=}CH_2\}$ (0.300 g, 2.25 mmol) and Ph_2PCH_2OH (0.974 g, 4.51 mmol) in CH_3OH (10 ml) was refluxed for 12 d, cooled and the volume concentrated under reduced pressure resulting in a colourless solid. Yield: 0.695 g, 58%. ^1H NMR [$CDCl_3$]: δ 7.67–6.95 (24H, m, arom. *H*), 5.00 (1H, s, =C*H*), 4.84 (1H, d, $^2J_{HH}$ 1.4, =C*H*), 4.41 (4H, s, PCH_2N), 1.81 (3H, s, CH_3) ppm. $^{31}P\{^1H\}$ NMR [$CDCl_3$]: δ –27.3. EI–MS (*m/z*) $[MH]^+$ 530. Anal. (%) Calcd. for $C_{35}H_{34}NP_2$: C, 79.26; H, 6.30; N, 2.72. Found: C, 79.38; H, 6.28; N, 2.64.

2.3.4 **Preparation of $C_6H_4(NH_2)\{2\text{-}CH(Me)CH_2PCg\}$ (L_4).** The compounds $C_6H_4(NH_2)\{2\text{-}C(Me){=}CH_2\}$ (0.500 g, 3.75 mmol), CgPH (0.812 g, 3.75 mmol) and AIBN [2,2`-azobis(2-methylpropionitrile)] (0.085 g, 0.53 mmol) were placed in a Schlenk tube. The mixture was freeze–pump–thawed (3 times) and stirred at 110 ^oC for 24 h. The yellow oily product solidified upon cooling in the freezer. Yield: 1.112 g, 85%. ^1H NMR [$CDCl_3$]: δ 7.17 (1H, dd, $^3J_{HH}$ 3.2, $^4J_{HH}$ 0.6, arom. *H*), 7.05 (1H, dd, $^3J_{HH}$ 3.2, $^4J_{HH}$ 0.6, arom. *H*), 6.83 (1H, vt, $^3J_{HH}$ 3.2, arom. *H*), 6.71 (1H, d, $^3J_{HH}$ 3.2, arom. *H*), 3.61 (2H, bs, N*H*), 3.02 (1H, m, C*H*), 2.27–1.12 (23H, m, CH_2, CH_3, Cg). $^{31}P\{^1H\}$ NMR [$CDCl_3$]: δ –31.7, –31.9. FT–IR (KBr): ν_{NH} 3460, 3369 cm^{-1}. EI–MS (*m/z*) $[MH]^+$ 350. Anal. (%) Calcd. for $C_{19}H_{28}NO_3P$: C, 65.96; H, 8.30; N, 4.04. Found: C, 65.31; H, 8.08; N, 4.01.

2.3.5 **Preparation of $C_6H_4(NH_2)\{2\text{-}CH(Me)CH_2PPh_2\}$ (L_5).** The compounds $C_6H_4(NH_2)\{2\text{-}C(Me)=CH_2\}$ (0.500 g, 3.75 mmol), $HPPh_2$ (0.698 g, 3.75 mmol) and AIBN (0.085 g, 0.53 mmol) were placed in a Schlenk tube. The mixture was freeze–pump–thawed (3 times) and stirred at 110 ^{o}C for 3 d. After that time more AIBN was added (0.024 g, 0.15 mmol) and left for a further 2 d. The colourless oily product solidified upon addition of CH_3OH (10 ml) and was purified by adding Et_2O (5 ml). The resulting solid was collected by suction filtration and dried in vacuum. Yield: 0.789 g, 66%. ^{1}H NMR [$CDCl_3$]: δ 7.57–7.33 (10H, arom. *H*), 7.25 (1H, dd, $^3J_{HH}$ 7.7, $^4J_{HH}$ 1.4, arom. C*H*), 7.06 (1H, dt, $^3J_{HH}$ 7.6, $^4J_{HH}$ 1.5, arom. *H*), 6.84 (1H, dt, $^3J_{HH}$ 7.5, $^4J_{HH}$ 1.2, arom. *H*), 6.65 (1H, dd, $^3J_{HH}$ 7.9, $^4J_{HH}$ 1.2, arom. *H*), 2.95 (2H, bs, N*H*), 2.75 (1H, m, C*H*), 2.49 (1H, dt, $^2J_{HH}$ 13.6, $^3J_{HH}$ 4.0, $^2J_{HP}$ 3.2, CH_2), 2.23 (1H, ddd, $^2J_{HH}$ 13.6, $^3J_{HH}$ 10.0, $^2J_{HP}$ 3.2, CH_2), 1.49 (3H, d, $^3J_{HH}$ 6.8, CH_3). ^{31}P{^{1}H} NMR [$CDCl_3$]: δ –19.5. FT–IR (KBr): ν_{NH} 3462, 3377 cm^{-1}. EI–MS (*m/z*) [MH]$^+$ 320. Anal. (%) Calcd. for $C_{21}H_{22}NP\cdot0.25CH_3OH$: C, 77.96; H, 7.08; N, 4.28. Found: C, 77.65; H, 6.64; N, 3.99.

2.3.6 **Preparation of $C_6H_4(NHCH_2PPh_2)\{2\text{-}CH(Me)CH_2PPh_2\}$ (L_6).** Method 1: $\mathbf{L_5}$ (0.100 g, 0.313 mmol) and Ph_2PCH_2OH (0.081 g, 0.38 mmol) were placed in a Schlenk tube and degassed CH_3OH (10 ml) added. The mixture was refluxed for 3 d and concentrated under reduced pressure to ~1 ml. The resulting solid was filtered off under vacuum. Yield: 0.074 g, 46%. Method 2: $\mathbf{L_2}$ (0.200 g, 0.60 mmol), $HPPh_2$ (0.224 g, 1.21 mmol) and AIBN (0.018 g, 0.108 mmol) were placed in a Schlenk tube and degassed CH_3OH (10 ml) added. The mixture was refluxed for 5 d, stirred for a further 2 d at r.t. and concentrated under reduced pressure to dryness. The resulting oil was solidified with Et_2O (10 ml) and filtered off under vacuum. Yield: 0.052 g, 17% (not optimised). ^{1}H NMR [$CDCl_3$]: δ 7.60–7.27 (10H, m, arom. *H*), 7.25 (1H, dd, $^3J_{HH}$ 7.7, $^4J_{HH}$ 1.4, arom. *H*), 7.06 (1H, dt, $^3J_{HH}$ 7.7, $^4J_{HH}$ 1.4, arom. *H*), 6.84

(1H, dt, $^3J_{HH}$ 7.7, $^4J_{HH}$ 1.4, arom. *H*), 6.65 (1H, dd, $^3J_{HH}$ 7.7, $^4J_{HH}$ 1.4, arom. *H*), 3.30 (1H, bs, N*H*), 2.84–2.70 (1H, m, C*H*), 2.56–2.44 (1H, dt, $^2J_{HH}$ 12.3, $^2J_{HP}$ 4.0, $^3J_{HH}$ 4.0, CH_2), 2.26 (1H, ddd, $^2J_{HH}$ 12.3, $^2J_{HP}$ 4.0, $^3J_{HH}$ 8.0, CH_2), 1.52 (3H, d, $^3J_{HH}$ 6.8, CH_3). ^{31}P{^{1}H} NMR [$CDCl_3$]: δ –19.6, –19.8. FT–IR (KBr): ν_{NH} 3400 cm^{-1}. EI–MS (*m/z*) [MOH]$^+$ 534, [MO_2H]$^+$ 550. Anal. (%) Calcd. for $C_{34}H_{33}NP_2$: C, 78.90; H, 6.43; N, 2.71. Found: C, 78.80; H, 6.45; N, 2.80.

2.3.7 **Preparation of 1.** The solids $\mathbf{L_2}$ (0.084 g, 0.26 mmol) and [RuCl(μ-Cl)(η^6-$C_{10}H_{14}$)]$_2$ (0.092 g, 0.13 mmol) were dissolved in CH_2Cl_2 (10 ml) and the solution stirred for 1 h. The solvent was reduced in volume to ~1 ml and Et_2O (20 ml) added to afford a red solid **1** which was collected by suction filtration and dried in vacuum. Yield: 0.132 g, 69%. ^{1}H NMR [$CDCl_3$]: δ 7.93–7.37 (10H, m, arom. *H*), 7.00–6.81 (1H, m, arom. *H*), 6.78 (1H, dd, $^3J_{HH}$ 7.8, $^4J_{HH}$ 1.5, arom. *H*), 6.49 (1H, t, $^3J_{HH}$ 7.8, arom. *H*), 6.34 (1H, d, $^3J_{HH}$ 7.8, arom. *H*), 5.33 (2H, d, $^3J_{HH}$ 6.2, arom. C*H*), 5.20 (2H, d, $^3J_{HH}$ 6.2, arom. C*H*), 4.98 (1H, s, =C*H*), 4.56 (1H, s, =C*H*), 4.48 (2H, s, PCH_2N), 4.18 (1H, bs, N*H*), 2.57 (1H, sept., $^3J_{HH}$ 7.0, C*H*), 1.94 (3H, s, CH_3), 1.70 (3H, s, CH_3), 0.87 (6H, d, $^3J_{HH}$ 7.0, CH_3). ^{31}P{^{1}H} NMR [$CDCl_3$]: δ 25.2. FT–IR (KBr): ν_{NH} 3390 cm^{-1}. EI–MS (*m/z*) [M–Cl]$^+$ 602. Anal. (%) Calcd. for $C_{32}H_{36}NPRuCl_2\cdot0.75CH_2Cl_2$: C, 56.09; H, 5.39; N, 2.00. Found: C, 56.53; H, 5.38; N, 1.99.

2.3.8 **Preparation of 2a.** To a CH_2Cl_2 (10 ml) solution of [AuCl(tht)] (0.115 g, 0.36 mmol) was added $\mathbf{L_2}$ (0.117 g, 0.35 mmol) as a solid in one portion. The colourless solution was stirred for 1 h, evaporated under vacuum to ~1–2 ml. Addition of Et_2O (15 ml) afforded solid **2a** which was collected by suction filtration and dried under vacuum. Yield: 0.120 g, 59%. ^{1}H NMR [$CDCl_3$]: δ 7.71–7.46 (10H, m, arom. *H*), 7.15 (1H, dt, $^3J_{HH}$ 8.0, $^4J_{HH}$ 1.2, arom. *H*), 6.99 (1H, dd, $^3J_{HH}$ 7.6, $^4J_{HH}$ 1.6, arom. *H*), 6.87 (1H, t, $^3J_{HH}$ 8.8, arom. *H*), 6.75 (1H, d, $^3J_{HH}$

8.4, arom. H), 5.11 (1H, s, =CH), 4.75 (1H, s, =CH), 4.22 (2H, d, $^{2}J_{PH}$ 4.0, CH_2), 1.87 (3H, s, CH_3). $^{31}P\{^{1}H\}$ NMR [$CDCl_3$]: δ 25.0. FT–IR (KBr): ν_{NH} 3381, ν_{AuCl} 327 cm^{-1}. Anal. (%) Calcd. for $C_{22}H_{22}NPAuCl$: C, 46.86; H, 3.94; N, 2.48. Found: C, 46.34; H, 3.66; N, 2.52. Preparation of **2b.** To a CH_2Cl_2 (10 ml) solution of [AuCl(tht)] (0.069 g, 0.22 mmol) was added $\mathbf{L_3}$ (0.057 g, 0.11 mmol) as a solid in one portion. The colourless solution was stirred for 30 min, evaporated under vacuum to ~1-2 ml. Addition of Et_2O (25 ml) and n-hexanes (25 ml) afforded solid **2** which was collected by suction filtration and dried under vacuum. Yield: 0.056 g, 52%. ^{1}H NMR [$CDCl_3$]: δ 7.57–7.35 (20H, m, arom. H), 7.13 (1H, d, $^{3}J_{HH}$ 7.2, arom. H), 7.05 (1H, dt, $^{3}J_{HH}$ 7.2, $^{4}J_{HH}$ 2.0, arom. H), 6.89 (1H, t, $^{3}J_{HH}$ 7.6, arom. H), 6.87 (1H, dt, $^{3}J_{HH}$ 7.6, $^{4}J_{HH}$ 2.0 arom. H), 4.96 (4H, s, CH_2), 4.94 (1H, s, =CH), 4.65 (1H, s, =CH), 1.57 (3H, s, CH_3). $^{31}P\{^{1}H\}$ NMR [$CDCl_3$]: δ 16.1. FT–IR (KBr): ν_{AuCl} 332 cm^{-1}. Anal. (%) Calcd. for $C_{35}H_{33}NP_2Au_2Cl_2$: C, 42.27; H, 3.35; N, 1.41. Found: C, 42.27; H, 3.37; N, 1.45.

2.3.9 **Preparation of 3a.** To a CH_2Cl_2 (10 ml) solution of [$PdCl_2(\eta^4$-cod)] (0.043 g, 0.15 mmol) was added $\mathbf{L_2}$ (0.100 g, 0.30 mmol) as a solid in one portion. The orange solution was stirred for 1 h, evaporated under vacuum to ~1-2 ml and addition of Et_2O (20 ml) afforded **3a** which was collected by suction filtration and dried under vacuum. Yield: 0.087 g, 69%. ^{1}H NMR [$CDCl_3$]: δ 7.85–6.94 (m, arom. H), 6.78 (2H, dt, CH), 6.58 (1H, d, $^{3}J_{HH}$ 8.4, arom. H), 6.41 (1H, d, $^{3}J_{HH}$ 8.4, arom. H), 5.13 (1H, dd, =CH), 5.01 (1H, dd, =CH), 4.78 (2H, multiplet, =CH), 4.68 (1H, bs, NH), 4.43 (4H, s, PCH_2N), 4.38 (4H, s, PCH_2N), 1.92 (6H, s, CH_3), 1.86 (6H, s, CH_3). $^{31}P\{^{1}H\}$ NMR [$CDCl_3$]: δ 26.8, 14.3 (ca. 45:55 ratio of cis/trans isomers). FT–IR (KBr): ν_{NH} 3402, ν_{NH} 307, 283 cm^{-1}. EI–MS (*m/z*) $[M–Cl]^+$ 803. Anal. (%) Calcd. for $C_{44}H_{44}N_2P_2PdCl_2\cdot0.25CH_2Cl_2$: C, 61.69; H, 5.22; N, 3.25. Found: C, 61.24; H, 5.20; N, 3.26. In a similar manner the platinum(II) complex **3b** was synthesised (75%). ^{1}H NMR [$CDCl_3$]: δ 7.88–7.42 (20H, m, arom. H), 7.08 (3H, m, arom. H), 6.64 (1H, d, $^{3}J_{HH}$ 6.8 arom. H), 5.09

(1H, s, =C*H*), 4.76 (1H, s, =C*H*), 4.23 (4H, vt, $^3J_{PtH}$ 40, $^2J_{PH}$ 1.6, CH_2), 1.92 (3H, s, CH_3). ^{31}P{^{1}H} NMR [$CDCl_3$]: δ 7.3 ($^1J_{PPt}$ 3661). FT–IR (KBr): ν_{PtCl} 316, 290 cm^{-1}. Anal. (%) Calcd. for $C_{44}H_{44}N_2P_2PtCl_2$: C, 56.89; H, 4.78; N, 3.02. Found: C, 57.65; H, 4.94; N, 2.82.

2.3.10 **Preparation of 4a.** To a CH_2Cl_2 (10 ml) solution of [$PdCl_2$(η^4-cod)] (0.041 g, 0.14 mmol) was added **L_3** (0.077 g, 0.15 mmol) as a solid in one portion. The yellow solution was stirred for 1 h, evaporated under vacuum to ~1-2 ml whereupon a yellow solid started to deposit. Addition of Et_2O (20 ml) afforded solid **4a** which was collected by suction filtration and dried under vacuum. Yield: 0.094 g, 92%. ^{1}H NMR [$CDCl_3$]: δ 7.81–7.42 (20H, m, arom. *H*), 7.03 (3H, m, arom. *H*), 6.59 (1H, d, $^3J_{HH}$ 7.8, arom. *H*), 4.72 (1H, s, =C*H*), 4.62 (1H, s, =C*H*), 3.92 (4H, s, CH_2), 1.57 (3H, s, CH_3). ^{31}P{^{1}H} NMR [$CDCl_3$]: δ 10.0. FT–IR (KBr): ν_{PtCl} 307, 294 cm^{-1}. Anal. (%) Calcd. for $C_{35}H_{33}NP_2PdCl_2$: C, 59.46; H, 4.71; N, 1.98. Found: C, 58.97; H, 4.59; N, 2.06. In a similar manner the platinum(II) complex **4b** was synthesised (94%). ^{1}H NMR [$CDCl_3$]: δ 7.88–7.42 (20H, m, arom. *H*), 7.08 (3H, m, arom. *H*), 6.64 (1H, d, $^3J_{HH}$ 6.8 arom. *H*), 4.74 (1H, s, =C*H*), 4.67 (1H, s, =C*H*), 4.03 (4H, vt, $^3J_{PtH}$ 40.0, $^2J_{PH}$ 1.6, CH_2), 1.46 (3H, s, CH_3). ^{31}P{^{1}H} NMR [$CDCl_3$]: δ –6.1 ($^1J_{PPt}$ 3417). FT–IR (KBr): ν_{PtCl} 313, 289 cm^{-1}. Anal. (%) Calcd. for $C_{35}H_{33}NP_2PtCl_2\cdot0.5Et_2O$: C, 53.37; H, 4.61; N, 1.68. Found: C, 53.85; H, 4.64; N, 1.60.

2.3.11 **Preparation of 5.** From **L_6** (0.050 g, 0.096 mmol) and [$PtCl_2$(η^4-cod)] (0.036 g, 0.096 mmol) in CH_2Cl_2 and precipitation with Et_2O. Yield: 0.060 g, 80%. ^{1}H NMR [$CDCl_3$]: δ 7.92–6.95 (20H, m, arom. *H*), 6.47 (2H, t, $^3J_{HH}$ 6.0, arom. *H*), 6.34 (1H, dd, $^3J_{HH}$ 8.0, $^4J_{HH}$ 1.2, arom. *H*), 6.18 (1H, d, $^3J_{HH}$ 9.2, arom. *H*), 5.32–5.27 (1H, m, PCH_2N), 4.30 (1H, m, N*H*), 3.57–3.47 (1H, m, C*H*), 3.42 (1H, bt, $^3J_{HH}$ 12.8, PCH_2N), 2.67 (1H, q, $^3J_{HH}$ 13.6, C*H*), 1.97 (1*H*, q, $^3J_{HH}$ 8.4, C*H*), 1.78 (3H, dd, $^3J_{HH}$ 16.0, *J* 2.0, CH_3). ^{31}P{^{1}H} NMR [$CDCl_3$]: δ 26.9

($^{1}J_{PPt}$ 3768, $^{2}J_{PP}$ 9), 11.3 ($^{1}J_{PPt}$ 3479, $^{2}J_{PP}$ 9). FT–IR (KBr): ν_{NH} 3358, ν_{PtCl} 316, 291 cm^{-1}. EI–MS (*m/z*) $[M–Cl]^+$ 747. Anal. (%) Calcd. for $C_{34}H_{33}NP_2PtCl_2$: C, 52.12; H, 4.24; N, 1.79. Found: C, 51.74; H, 4.13; N, 1.76.

2.3.12 **Preparation of 6.** From $\mathbf{L_6}$ (0.0052 g, 0.010 mmol) and $[RuCl(\mu\text{-}Cl)(\eta^6\text{-}C_{10}H_{14})]_2$ (0.0060 g, 0.0098 mmol) in $CDCl_3$ (0.5 ml). After NMR data acquisition, vapour diffusion with Et_2O afforded red crystals. Yield: 0.0079 g, 73%. ^{1}H NMR [$CDCl_3$]: δ 7.78 (2H, t, arom. *H*), 7.70 (2H, t, arom. *H*), 7.61 (2H, t, arom. *H*), 7.48 (2H, t, arom. *H*), 7.40 (5H, s, arom. *H*), 7.29-7.20 (5H, m, arom. *H*), 7.11 (2H, t, arom. *H*), 6.62 (1H, d, $^{3}J_{HH}$ 8.4, arom. *H*), 6.45 (1H, t, $^{3}J_{HH}$ 7.2, arom. *H*), 6.20 (1H, d, $^{3}J_{HH}$ 7.6, arom. *H*), 5.86 (1H, d, $^{3}J_{HH}$ 8.0, arom. *H*), 5.40–4.99 (8H, m, CH_{cymene}), 4.18 (2H, s, PCH_2N), 2.88 (2H, m, PCH_2), 2.51 [3H, m, C*H* and C*H*$(CH_3)_2$], 1.88 (3H, s, $C_6H_4CH_3$), 1.79 (3H, s, $C_6H_4CH_3$), 0.96–0.50 (15H, m, CH_3 and $CH(CH_3)_2$]. $^{31}P\{^{1}H\}$ NMR [$CDCl_3$]: δ 25.1, 21.6. Anal. (%) Calcd. for $C_{54}H_{61}NP_2Ru_2Cl_4\cdot0.25CDCl_3$: C, 56.17; H, 5.33; N, 1.21. Found: C, 55.77; H, 5.11; N, 1.33.

2.4. X-ray crystallography

Suitable crystals of $\mathbf{L_3}$ were obtained from an in situ NMR aliquot of the reaction between 1 equiv. $C_6H_4(NH_2)\{2\text{-}C(Me)=CH_2\}$ and two equiv. of Ph_2PCH_2OH in MeOH. Compounds $\mathbf{L_5}$ and $\mathbf{L_6}$ were crystallised upon allowing a CH_3OH filtrate to stand for several days. Red block crystals of the ruthenium(II) complex **1** were obtained by vapour diffusion of Et_2O into a $CHCl_3$ solution. The complexes **3b**$\cdot0.5CH_2Cl_2$, **4a**$\cdot1.5CH_2Cl_2$ and **5** were obtained by vapour diffusion of Et_2O into a CH_2Cl_2 solution whereas complex **6**$\cdot0.5CDCl_3\cdot0.5C_4H_{10}O$ was obtained by vapour diffusion of Et_2O into a $CDCl_3$ solution. Details of the data collection parameters and crystal data for $\mathbf{L_3}$, $\mathbf{L_5}$, $\mathbf{L_6}$, **1**, **3b**$\cdot0.5CH_2Cl_2$, **4a**$\cdot1.5CH_2Cl_2$, **5** and **6**$\cdot0.5CDCl_3\cdot0.5C_4H_{10}O$ are given in Table 1. Measurements for $\mathbf{L_3}$, $\mathbf{L_5}$, $\mathbf{L_6}$, **1**, **3b**$\cdot0.5CH_2Cl_2$,

4a·1.5CH_2Cl_2, **5** and **6**·0.5$CDCl_3$·0.5$C_4H_{10}O$ were made on modern CCD diffractometers using graphite-monochromated radiation from a rotating anode source (for **5**) or sealed tube source (all others) [19]. Intensities were corrected semi-empirically for absorption, based on symmetry-equivalent and repeated reflections [19, 20]. The structures were solved [21] by direct or dual-space methods and refined on F^2 values for all unique data by full-matrix least squares [21, 22]. All non-hydrogen atoms were refined anisotropically. Carbon-bound hydrogen atoms were constrained in a riding model with U_{eq} set to 1.2U_{eq} of the carrier atom (1.5 U_{eq} for methyl hydrogen). N*H* coordinates were freely refined, except for those in **3b**·0.5CH_2Cl_2 which were constrained with U_{eq} set to 1.2U_{eq} of the carrier atom. For **1** C–CH_3 and =CH_2 atoms were modelled as 50/50 disordered on atoms C(31) and C(32). For **3b**·0.5CH_2Cl_2 one molecule of CH_2Cl_2 was modelled as 2-fold disordered with a major component 63.6(16)%. The H atoms on the terminal =CH_2 and C–CH_3 groups at C(9)/C(10) and C(9A)/C(10A) were also modelled as two-fold disordered with major components 58(11)% and 54(11)% respectively. In these two cases, as in **1** above, the C–C bond lengths were very similar and the sites could also not be distinguished based on H atom electron density. For **4a**·1.5CH_2Cl_2 one of the CH_2Cl_2 molecules of crystallisation was modelled as two-fold disordered with major component occupancy 57.6(10)%. For **6**·0.5$CDCl_3$·0.5$C_4H_{10}O$ the solvent of crystallisation was modelled using the Platon Squeeze procedure [23]. This recovered 85 electrons in one void which corresponds roughly to one $CDCl_3$ and one Et_2O per unit cell, which agreed with point atom observations.

2. Results and Discussion

3.1. Ligand Synthesis

The amino(methyl)phosphines $\mathbf{L_1}$ and $\mathbf{L_2}$ were synthesised in ~60% yield upon reaction of one equiv. of $HOCH_2PR_2$ [readily prepared from equimolar amounts of $(CH_2O)_n$ and Ph_2PH

[18] or CgPH [3d] respectively] and one equivalent of $C_6H_4(NH_2)\{2\text{-}C(Me){=}CH_2\}$ in CH_3OH (Scheme 1). There has been much interest in the Cg group, as seen here in $\mathbf{L_1}$, for its steric properties [3a], diverse coordination behaviour [2, 3a, 6g] and versatility in homogeneous metal catalysed reactions [24a]. For $\mathbf{L_2}$, small amounts of the disubstituted phosphine $\mathbf{L_3}$ were also formed during the reaction as observed by in situ NMR spectroscopy [δ(P) −27.0]. To confirm this assignment, reaction of two equiv. of Ph_2PCH_2OH with one equiv. of $C_6H_4(NH_2)\{2\text{-}C(Me){=}CH_2\}$ in refluxing CH_3OH afforded $\mathbf{L_3}$ in 58% yield. Other characterising data for $\mathbf{L_1}$–$\mathbf{L_3}$ are given in the Experimental Section and are broadly as expected. In the ^1H NMR spectra of $\mathbf{L_1}$ and $\mathbf{L_2}$ the PCH_2N methylene protons showed an ABX splitting pattern (A and B for the diastereotopic protons and X for the P).

< Insert Scheme 2 and Scheme 2 caption here >

The X-ray structure of $\mathbf{L_3}$ has been determined (Fig. 1) and supports the spectroscopic and analytical characterising data. Both phosphorus atoms are pyramidal as reflected by the C−P−C bond angles whilst P−C and C−N bond lengths and P−C−N/C−N−C bond angles are in agreement with previously reported ligands of this type [3]. The C(7)–C(8) bond length of 1.329(3) Å is consistent with a C=C double bond and is shorter than that found in $\mathbf{L_5}$ and $\mathbf{L_6}$ (vide infra).

< Insert Table 1 and Table 1 caption here >

<Insert Figure 1 and Figure 1 caption here >

The primary amine functionalised tertiary phosphines $\mathbf{L_4}$ and $\mathbf{L_5}$ were prepared by free radical catalysed hydrophosphination using equimolar amounts of $C_6H_4(NH_2)\{2\text{-}$

$C(Me)=CH_2$} and secondary phosphines (H-PR_2, R_2 = Cg or Ph_2) with AIBN at 110 ºC for 5 d. Cui and co-workers recently showed that a NHC-Yb(III) amide complex hydrophosphinates $Ph_2C=CH_2$, when reacted with Ph_2PH, at r.t. for 4 h with 100% conversion [6c]. No efforts toward double hydrophosphination of $C_6H_4(NH_2)${2-$C(Me)=CH_2$} with primary phosphines have been attempted. Compound $\mathbf{L_5}$ was obtained as a yellowish oil which solidified upon adding CH_3OH and the resulting colourless solid was purified with Et_2O (see Experimental Section). The $^{31}P\{^1H\}$ NMR spectrum of $\mathbf{L_5}$ showed a singlet at δ(P) –19.5, similar to that found for $\mathbf{L_2}$. The linear isomer of $\mathbf{L_5}$ was formed in excellent regioselectivity with no observable NMR evidence for the branched isomer. Hence three well defined sets of resonances in the region between δ(H) 2.75–2.23 for $\mathbf{L_5}$, corresponding to the methine and diastereotopic methylene protons, support the terminal addition of the "H"/"PPh_2" groups across the $C(Me)=CH_2$ bond. Suitable crystals of $\mathbf{L_5}$ were obtained from a CH_3OH filtrate with the molecular structure shown in Fig. 2. The C–C and C–C–C parameters for C(8)–C(7), C(7)–C(6) and C(7)–C(9) are in agreement with typical single C–C bond lengths and C–C–C angles.

< Insert Figure 2 and Figure 2 caption here >

To demonstrate the free –NH_2 group is susceptible to further reaction, initial NMR monitoring of the reaction between $\mathbf{L_5}$ with Ph_2PCH_2OH, in a 1:1 stoichiometry, showed no reaction. Nevertheless, after several hours, a solid precipitated which, after NMR inspection, revealed two closely spaced peaks around δ(P) –19 [25] assigned to the unsymmetrical diphosphine $\mathbf{L_6}$. The yield could be increased after some optimisation work. No one-pot approach to the preparation of $\mathbf{L_6}$ has been attempted in this study. This procedure therefore has potential scope for expanding this class of ligand through simple manipulation of the appropriate secondary phosphine or hydroxymethylditertiary phosphine. Crystals of $\mathbf{L_6}$ were obtained from a CH_3OH filtrate. The P–C/C–C bond lengths and the P–C–C/C–C–C bond angles are fairly similar to those found in $\mathbf{L_5}$ whereas the C–N and P–C–N values are in accordance with literature values [3]. The C(7)–C(8) and C(7)–C(9) bond lengths are consistent with single C–C bonds.

< Insert Figure 3 and Figure 3 caption here >

3.2. Metal coordination studies

The ligating ability of $\mathbf{L_2}$ and $\mathbf{L_3}$ was assessed through a range of simple coordination studies towards $[RuCl(\mu\text{-}Cl)(\eta^6\text{-}C_{10}H_{14})]_2$, [AuCl(tht)] and $[MCl_2(\eta^4\text{-cod})]$ (M = Pd, Pt) in the appropriate stoichiometry, in CH_2Cl_2 and at r.t., affording the complexes **1**–**4b** in 52–94% isolated yields. The characterising details for these compounds is as expected and furthermore, in the case of the dichloropalladium(II) complex **3a** both cis (**3a**) and trans (**3aa**) isomers were observed whereas for the dichloroplatinum(II) complex **3b** only the cis isomer was observed in solution.

< Insert Table 2 and Table 2 caption here >

< Insert Chart 1 and Chart 1 caption here >

The molecular structures of the ruthenium(II) complex **1** (Fig. 4), **3b**·$0.5CH_2Cl_2$ (Fig. 5) and the dichloropalladium(II) complex **4a**·$1.5CH_2Cl_2$ (Fig. 6) have each been determined by single crystal X-ray crystallography (Table 2 and Figure Captions for selected geometrical parameters). The structures are broadly as anticipated reflecting their piano-stool (for **1**) or square-planar arrangements (for **3b**·$0.5CH_2Cl_2$ and **4a**·$1.5CH_2Cl_2$) around the metal centre.

Moreover, in all three structures the alkenyl C=C bond length is in the region 1.311(15)–1.361(15) Å consistent with the absence of any binding to the metal centre in any of these examples. We note that the $–CH_3$ and $=CH_2$ groups are often disordered in the solid state, since they occupy similar volumes within the unit cell.

< *Insert Figure 4 and Figure 4 caption here* >

< *Insert Figure 5 and Figure 5 caption here* >

< *Insert Figure 6 and Figure 6 caption here* >

The coordination capability of the asymmetric aminomethylphosphine $\mathbf{L_6}$ was also investigated towards $[PtCl_2(\eta^4\text{-cod})]$ and $[RuCl(\mu\text{-}Cl)(\eta^6\text{-}C_{10}H_{14})]_2$. The synthesis of the cis isomer **5** (isolated in 80% yield) was achieved by reacting $[PtCl_2(\eta^4\text{-cod})]$ and one equiv. of $\mathbf{L_6}$. In the $^{31}P\{^1H\}$ NMR spectrum, two resonances at δ(P) 26.9 and 11.3 were observed with associated J_{PtP} coupling constants of 3768 and 3479 respectively. Known reported compounds with medium sized chelate rings showed two phosphorus signals flanked by ^{195}Pt satellites with values similar to **5** [25, 26]. The FT–IR spectrum shows two ν_{PtCl} vibrations (316 and 291 cm^{-1}) consistent with cis-chelation and an ν_{NH} vibration at 3358 cm^{-1}. Bridge cleavage of the dimer $[RuCl(\mu\text{-}Cl)(\eta^6\text{-}C_{10}H_{14})]_2$ with 1 equiv. of $\mathbf{L_6}$ in $CDCl_3$ gave the new bimetallic complex **6** as confirmed by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. The phosphorus chemical shifts for the two inequivalent ^{31}P centres (δ 25.1 and 21.6) are very similar to that found in **1** and furthermore show a downfield shift with respect to the free ligand $\mathbf{L_6}$. The ^1H NMR spectrum of **6** showed the anticipated resonances for the two inequivalent *p*-cymene ligands. The bridging behaviour observed here for $\mathbf{L_6}$ contrasts with that previously observed for $C_6H_4(NHCH_2PPh_2)(2\text{-}PPh_2)$ [25] in which both P-monodentate and P,P-chelating modes towards late transition metal centres were observed.

The structures of the dichloroplatinum(II) complex **5** (Fig. 7) and the dinuclear ruthenium(II) complex **6**·$0.5CDCl_3\cdot0.5C_4H_{10}O$ (Fig. 8) were confirmed by single crystal X-ray crystallography (Table 2). The square planar environment around the Pt(II) centre is clearly evident from the relevant bond angles and **5** displays typical Pt–P and Pt–Cl bond lengths. The phosphine forms a nine-membered metallacycle at the platinum(II) centre. The X-ray structure of **6**·$0.5CDCl_3\cdot0.5C_4H_{10}O$ confirms a bimetallic arrangement of $[RuCl_2(\eta^6\text{-}C_{10}H_{14})]$ metal fragments supported by a bridging $\mathbf{L_6}$ diphosphine ligand. The Ru–P and Ru–Cl bond lengths in **6**·$0.5CDCl_3\cdot0.5C_4H_{10}O$ are similar to previously reported examples [27] and both ruthenium(II) metal centres show piano-stool arrangements.

< Insert Figure 7 and Figure 7 caption here >

< Insert Figure 8 and Figure 8 caption here >

4. Conclusions

In summary, we have shown that new functionalised (aminomethyl)phosphines are readily obtainable through simple Mannich based condensation or hydrophosphination reactions of a 1,2-disubstituted arene. The resulting phosphine ligands display classic ligating behaviour at various late transition metal centres. Given the diversity of known R substituents this approach should be amenable to other ligand systems by careful choice of R_2PCH_2OH and R_2PH precursors.

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Appendix A. Supplementary material

A complete set of X-ray crystallographic structural data for compounds $\mathbf{L_3}$, $\mathbf{L_5}$, $\mathbf{L_6}$, **1**, **3b**·$0.5CH_2Cl_2$, **4a**·$1.5CH_2Cl_2$, **5** and **6**·$0.5CDCl_3$·$0.5C_4H_{10}O$ (CCDC 1562158–65) are available free of charge via http://www.ccdc.cam.ac.uk/data_request/cif or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK; fax: (+44) 1223 336 033 or e-mail: deposit@ccdc.cam. ac.uk.

References

[1] J.H. Downing, M.B. Smith, M. B., In Comprehensive Coordination Chemistry II, Vol. 1, (2004) 253, Amsterdam, Elsevier.

[2] For example, see: G.M. Brown, M.R.J. Elsegood, M.B. Smith, K. Blann, Inorg. Chem. Commun. 14 (2011) 940.

[3] (a) G.M. Brown, M.R.J. Elsegood, A.J. Lake, N.M. Sanchez-Ballester, M.B. Smith, T.S. Varley, K. Blann, Eur. J. Inorg. Chem. (2007) 1405;

(b) M.B. Smith, S.H. Dale, S.J. Coles, T. Gelbrich, M.B. Hursthouse, M.E. Light, P.N. Horton, CrystEngCommun 9 (2007) 165;

(c) M.B. Smith, S.H. Dale, S.J. Coles, T. Gelbrich, M.B. Hursthouse, M.E. Light, CrystEngCommun 8 (2006) 140;

(d) M.R.J. Elsegood, M.B. Smith, P.M. Staniland, Inorg. Chem. 45 (2006) 6761.

[4] (a) P. Qiu, J.Y. Zhao, X. Shi, X.H. Duan, New J. Chem. 40 (2016) 6568;

(b) E.I. Musina, T.I. Fesenko, I.D. Strelnik, F.M. Polyancev, S.K. Latypov, P. Lönnecke, E. Hey-Hawkins, A.A. Karasik, O.G. Sinyashin, Dalton Trans. 44 (2015) 13565;

(c) P. Das, M.-H. Ho, M. O'Hagan, W.J. Shaw, R.M. Bullock, S. Raugei, M.L. Helm, Dalton Trans. 43 (2014) 2744;

(d) H. Schubert, W. Leis, H.A. Mayer, L. Wesemann, Chem. Commun. 50 (2014) 2738;

(e) A.A. Karasik, A.S. Balueva, E.I. Musina, O.G. Sinyashin, Mendeleev Commun. 23 (2013) 237;

(f) R. Starosta, M. Florek, J. Król, M. Puchalska, A. Kochel, New J. Chem. 34 (2010) 1441.

[5] (a) C.A. Bange, R. Waterman, Chem. Eur. J. 22 (2016) 12598;

(b) A.A. Trifonov, I.V. Basalov, A.A. Kissel, Dalton Trans. 45 (2016) 19172;

(c) J.T. Fleming, L.J. Higham, Coord. Chem. Rev. 297-298 (2015) 127;

(d) B.P. Nell, D.R. Tyler, Coord. Chem. Rev. 279 (2014) 23;

(e) V. Koshti, S. Gaikwad, S.H. Chikkali, Coord. Chem. Rev. 265 (2014) 52;

(f) L. Rosenberg, ACS Catal. 3 (2013) 2845.

[6] (a) M. Espinal-Viguri, M.F. Mahon, S.N.G. Tyler, R.L. Webster, Tetrahedron 73 (2017) 64;

(b) Q. Liu, C. Wang, X. Zhang, M. Xue, Y. Yao, Y. Zhang, Q. Shen, New J. Chem. 40 (2016) 10447;

(c) J. Yuan, H. Hu, C. Cui, Chem. Eur. J. 22 (2016) 5778;

(d) J.R.F. Pritzwald-Stegmann, P. Lönnecke, E. Hey-Hawkins, Dalton Trans. 45 (2016) 2208;

(e) L.A. Oparina, N.K. Gusarova, O.V. Vysotskaya, A.V. Artem’ev, N.A. Kolyvanov, B.A. Trofimov, Synthesis 46 (2014) 653;

(f) K.J. Gallagher, R.L. Webster, Chem. Commun. 50 (2014) 12109;

(g) T.J. Cunningham, M.R.J. Elsegood, P.F. Kelly, M.B. Smith, P.M. Staniland, Eur. J. Inorg. Chem. (2008) 2326;

(h) N. Bampos, L.D. Field, B.A. Messerle, R.J. Smernik, Inorg. Chem. 32 (1993) 4084.

[7] I.V. Basalov, B. Liu, T. Roisnel, A.V. Cherkasov, G.K. Fukin, J.-F. Carpentier, Y. Sarazin, A.A. Trifonov, Organometallics 35 (2016) 3261.

[8] (a) J. Yuan, L. Zhu, J. Zhang, J. Li, C. Cui, Organometallics 36 (2017) 455;

(b) M. Itazaki, S. Katsube, M. Kamitani, H. Nakazawa, Chem. Commun. 52 (2016) 3163;

(c) A. Di Giuseppe, R. De Luca, R. Castarlenas, J.J. Pérez-Torrente, M. Crucianelli, L.A. Oro, Chem. Commun. 52 (2016) 5554.

[9] M. Espinal-Viguri, A.K. King, J.P. Lowe, M.F. Mahon, R.L. Webster, ACS Catal. 6 (2016) 7892.

[10] (a) M.-S. Li, Q. Zhang, D.-Y. Hu, W.-W. Zhong, M. Cheng, J.-X. Ji, W. Wei, Tetrahedron Lett. 57 (2016) 2642;

(b) P.-Y. Geant, B.S. Mohamed, C. Périgaud, S. Peyrottes, J.-P. Uttaro, C.Mathé, New J. Chem. 40 (2016) 5318.

[11] M.M.I. Basiouny, J.A.R. Schmidt, Organometallics 36 (2017) 721.

[12] G. Hong, X. Zhu, C. Hu, A.N. Aruma, S. Wu, L. Wang, J. Org. Chem. 81 (2016) 6867.

[13] (a) X.-R. Li, X.-Y. Yang, Y. Li, S.A. Pullarkat, P.-H. Leung, Dalton Trans. 46 (2017) 1311;

(b) S.A. Pullarkat, Synthesis 48 (2016) 493;

(c) X. Wei, J. Lu, W.-L. Duan, Synthesis 48 (2016) 4155;

(d) Y.-C. Song, G.-F. Dai, F. Xiao, W.-L. Duan, Tetrahedron Lett. 57 (2016) 2990.

[14] (a) Y.-B. Yu, L. Cheng, Y.-P. Li, Y. Fu, S.-F. Zhu, Q.-L. Zhou, Chem. Commun. 52 (2016) 4812;

(b) F.-L. Zhu, Y. Zou, D.-Y. Zhang, Y.-H. Wang, X.-H. Hu, S. Chen, J. Xu, X.-P. Hu, Angew. Chem. Int. Ed. 53 (2014) 1410.

[15] (a) D. Drew, J.R. Doyle, Inorg. Synth. 13 (1972) 47;

(b) J.X. McDermott, J.F. White, G.M. Whitesides, J. Am. Chem. Soc. 98 (1976) 6521.

[16] M.A. Bennet, T.N. Huang, T.W. Matheson, A.R. Smith, Inorg. Synth. 21 (1982) 74.

[17] R. Uson, A. Laguna, M. Laguna, Inorg. Synth. 26 (1989) 85.

[18] H. Hellmann, J. Bader, H. Birkner, O. Schumacher, Justus Liebigs Ann. Chem. 659 (1962) 49.

[19] (a) APEX II Program for Diffractometer Control. Bruker AXS Inc., Madison, WI (2006–2014);

(b) CrysAlis PRO, Rigaku Oxford Diffraction, (2015);

(c) CrysAlis PRO, Agilent Technologies, (2013).

[20] (a) SAINT software for CCD diffractometers, Bruker AXS Inc., Madison, WI, (2006–2014);

(b) SADABS software, L. Krause, R. Herbst-Irmer, G.M. Sheldrick, D.J. Stalke, Appl. Cryst. 48 (2015) 3.

[21] (a) G.M. Sheldrick, Acta Crystallogr., Sect. A 71 (2015) 3;

(b) G.M. Sheldrick, Acta Crystallogr. Sect. A 64 (2008) 112.

[22] G.M. Sheldrick, SHELXTL user manual, version 6.12, Bruker AXS Inc., Madison, WI, (2001).

[23] (a) A.L. Spek, Acta Crystallogr. Sect. A 46 (1990) C34;

(b) P.v.d. Sluis, A.L. Spek, Acta Crystallogr. Sect. A 46 (1990) 194.

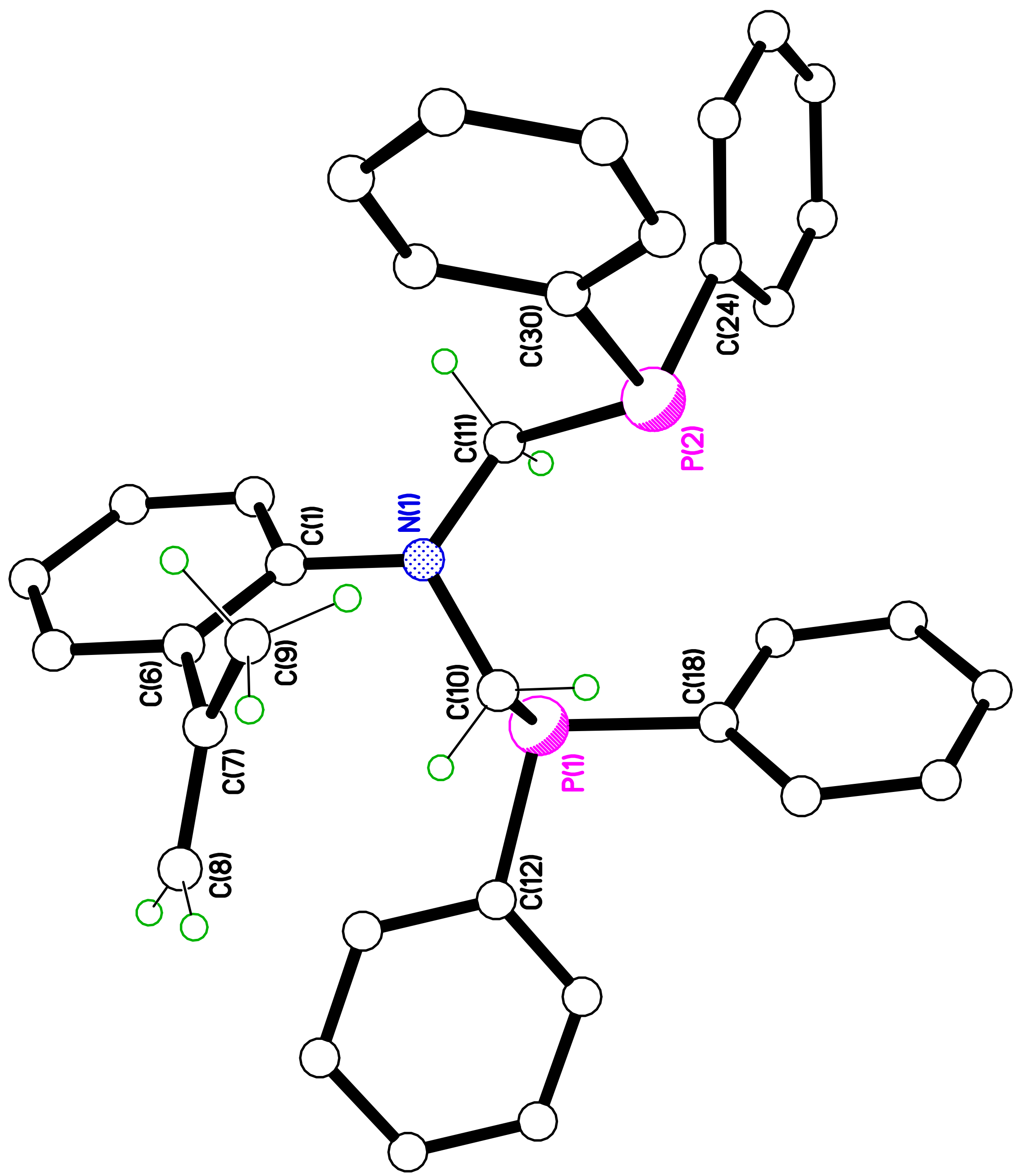
[24] (a) T.A. Shuttleworth, A.M. Miles-Hobbs, P.G. Pringle, H.A. Sparkes, Dalton Trans. 46 (2017) 125;

(b) T.J. Cunningham, M.R.J. Elsegood, P.F. Kelly, M.B. Smith, P.M. Staniland, Dalton Trans. 39 (2010) 5216.

[25] Q. Zhang, S.M. Aucott, A.M.Z. Slawin, J.D. Woollins, Eur. J. Inorg. Chem. (2002) 1635.

[26] I.D. Kostas, G. Antonopoulou, C. Potamitis, C.P. Raptopoulou, V. Psycharis, J. Organomet. Chem. 828 (2017) 133.

[27] S.E. Durran, M.B. Smith, A.M.Z. Slawin, J.W. Steed, J. Chem. Soc., Dalton Trans. (2000) 2771.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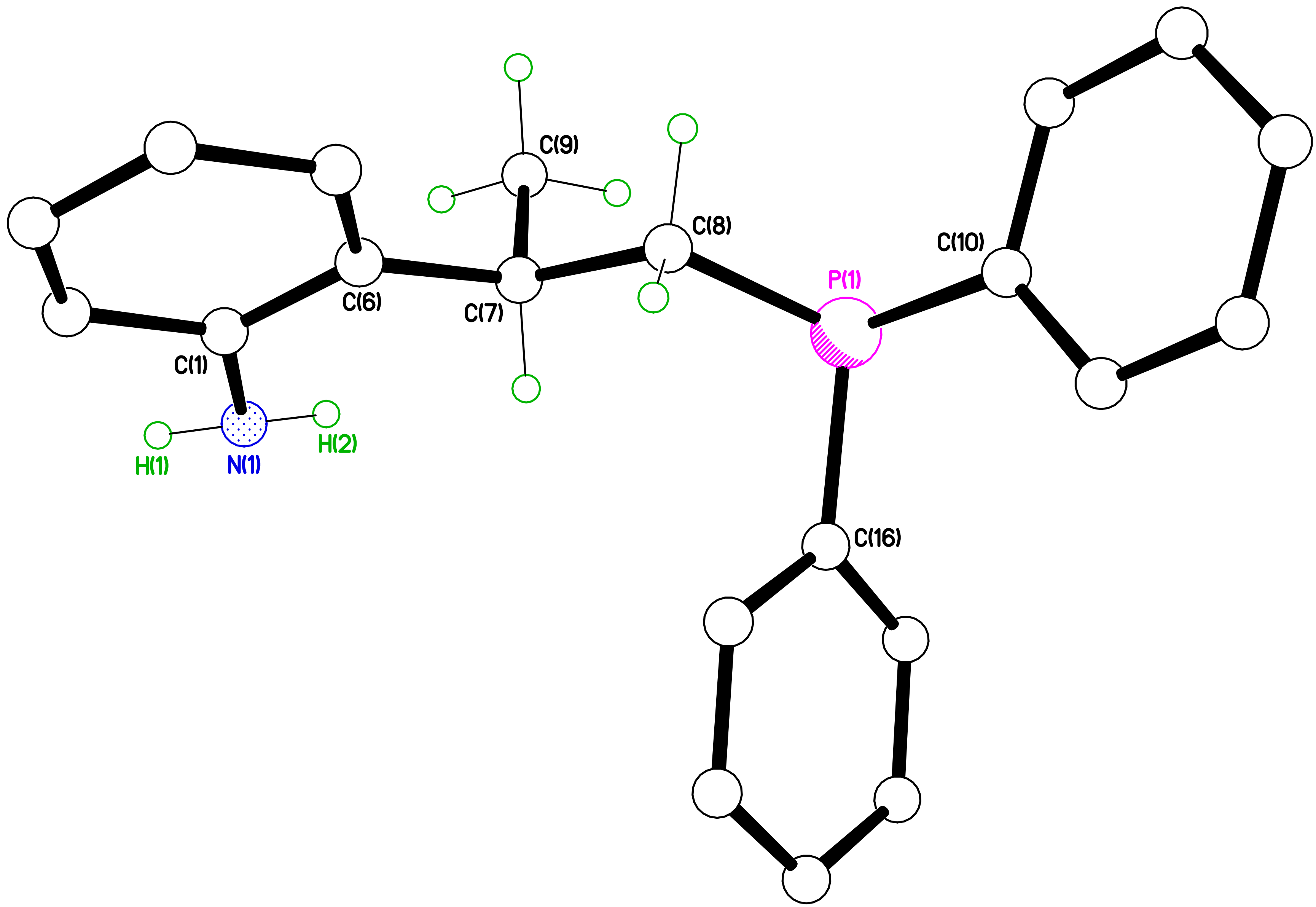

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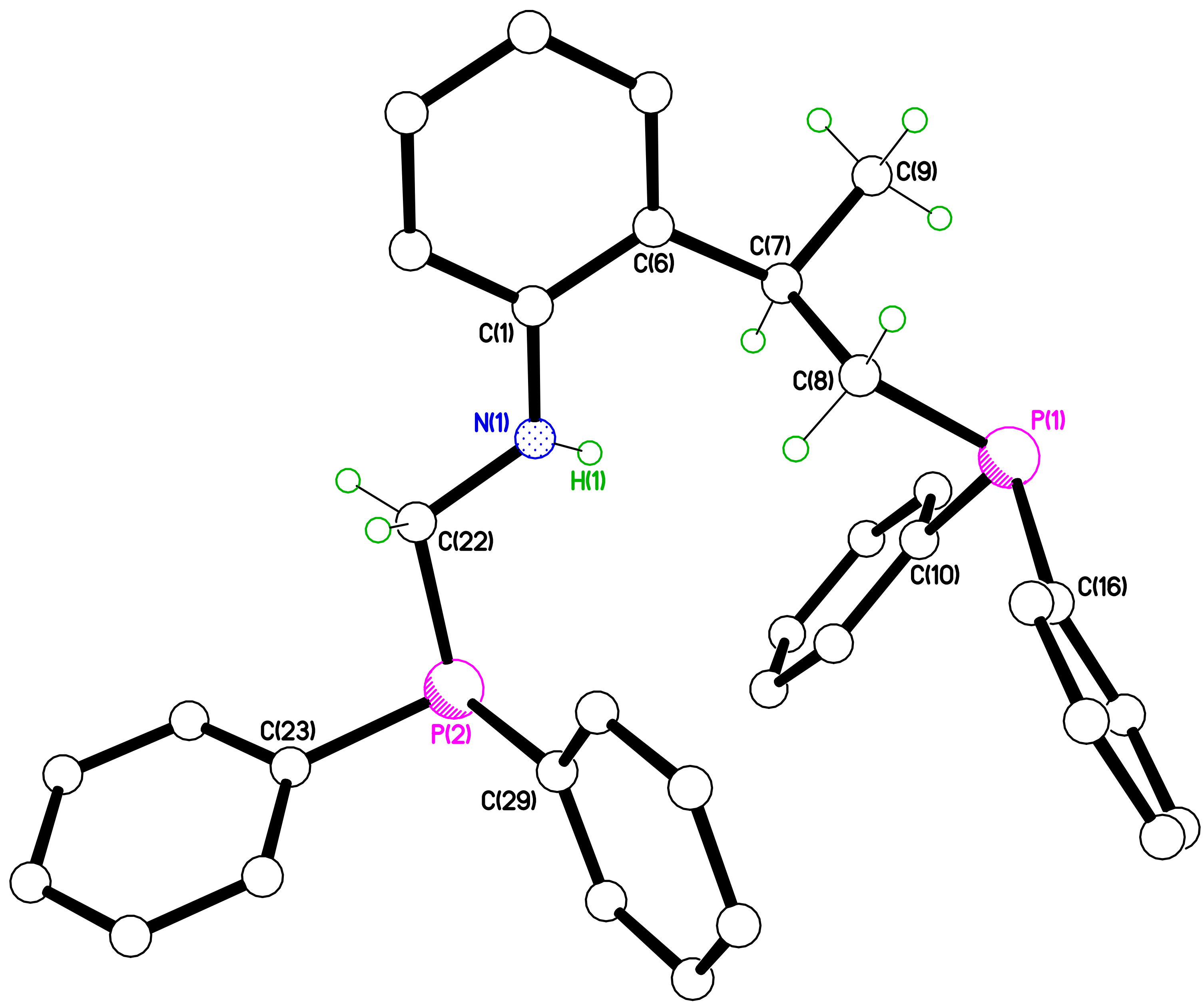
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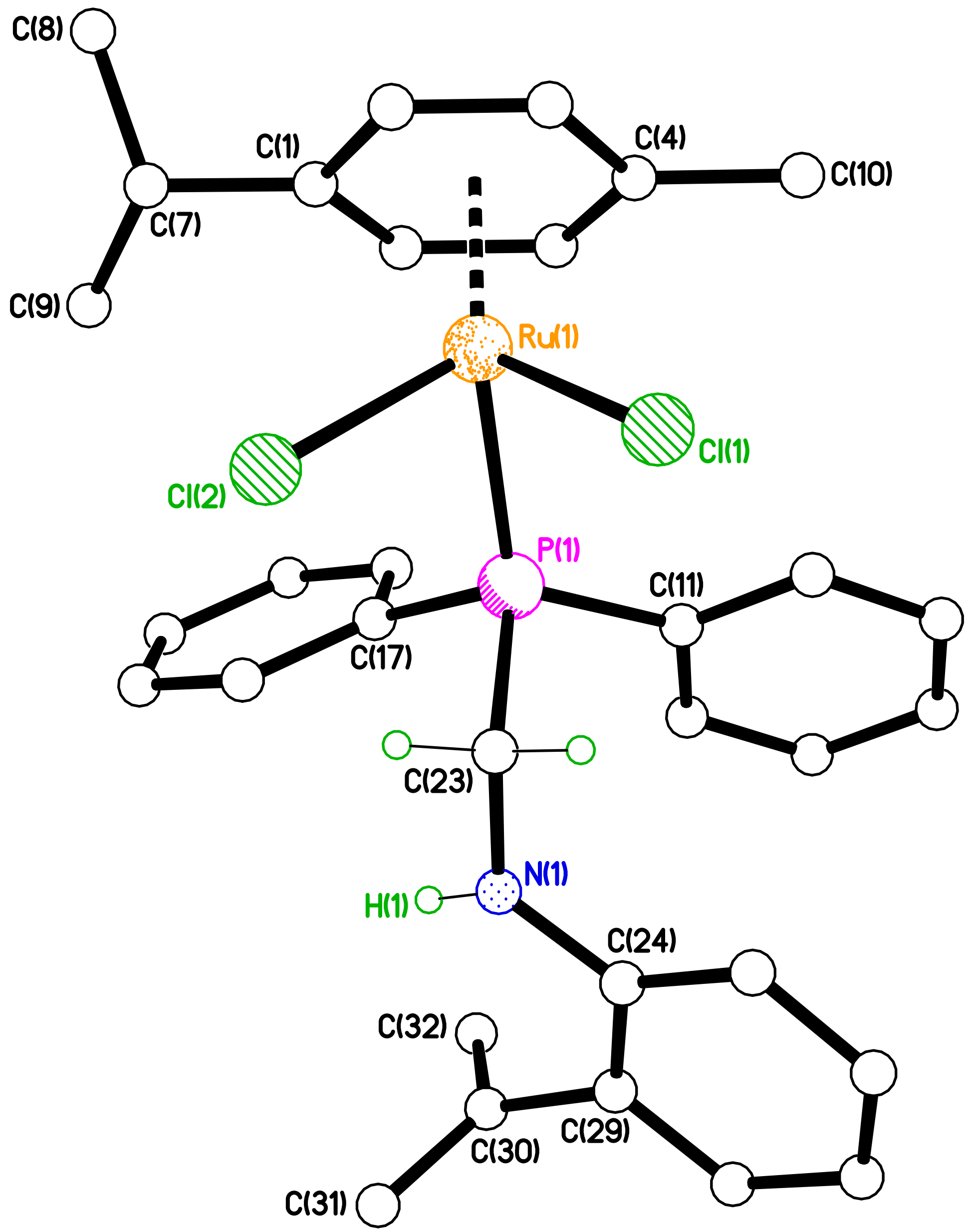
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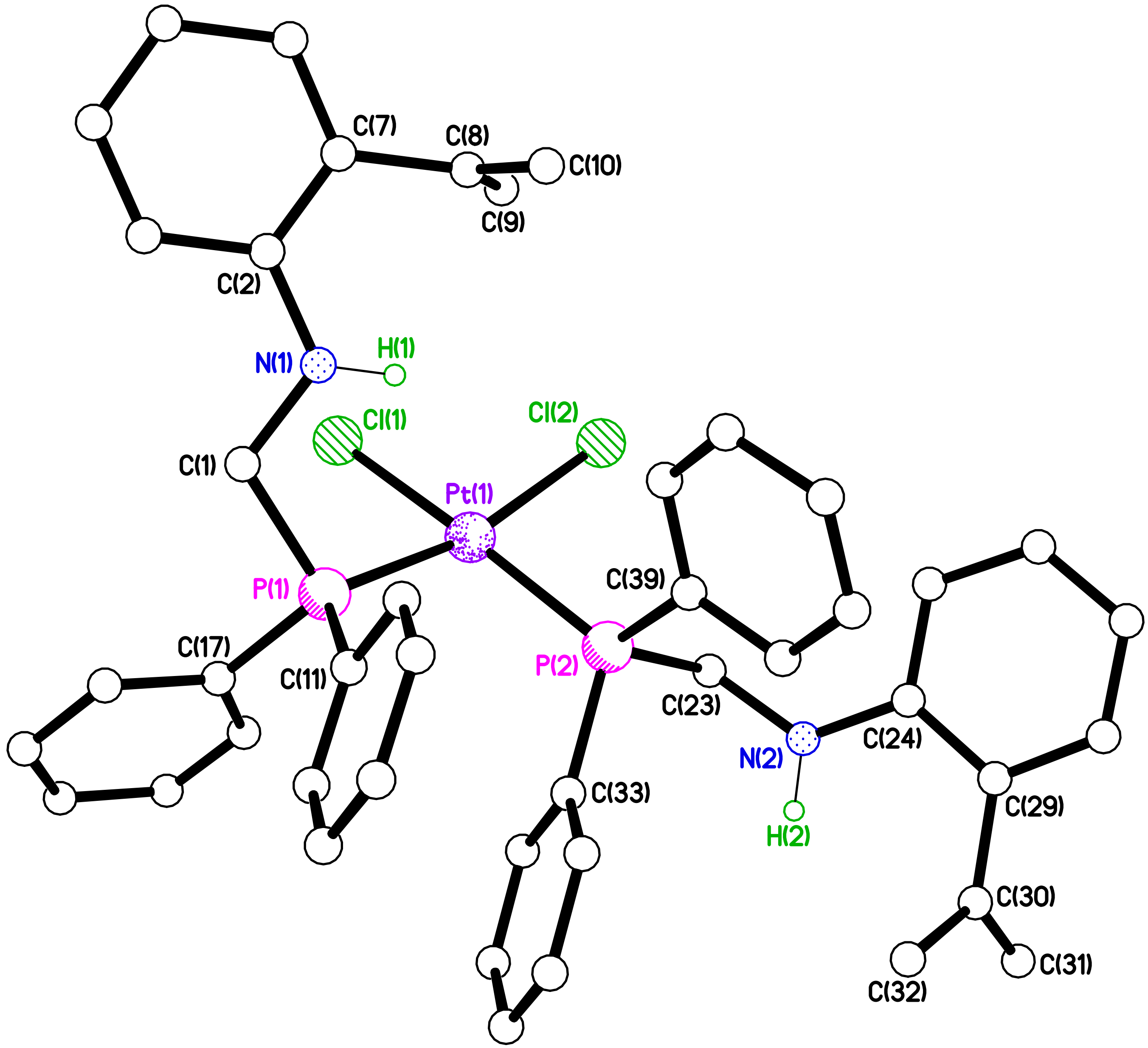

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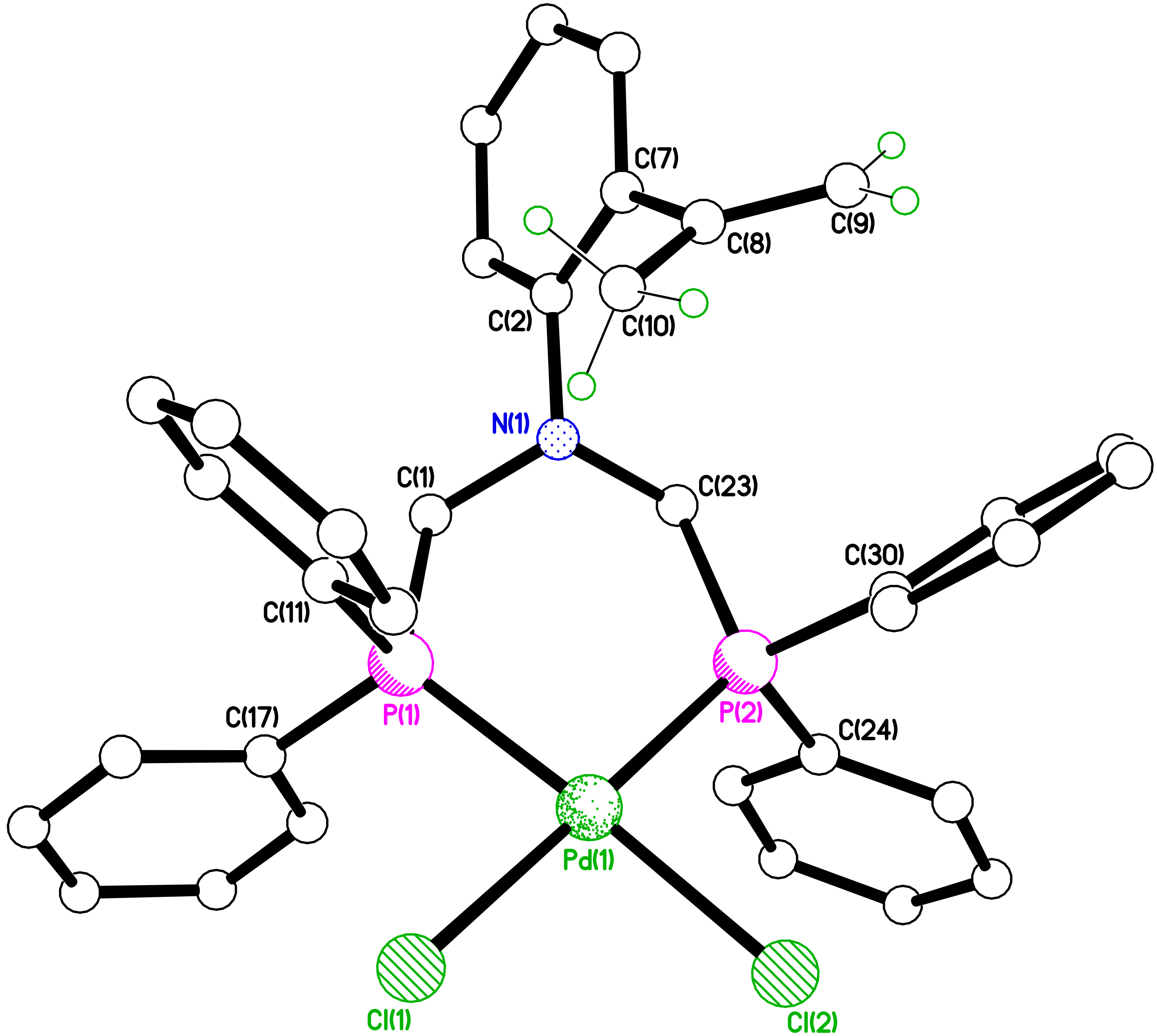
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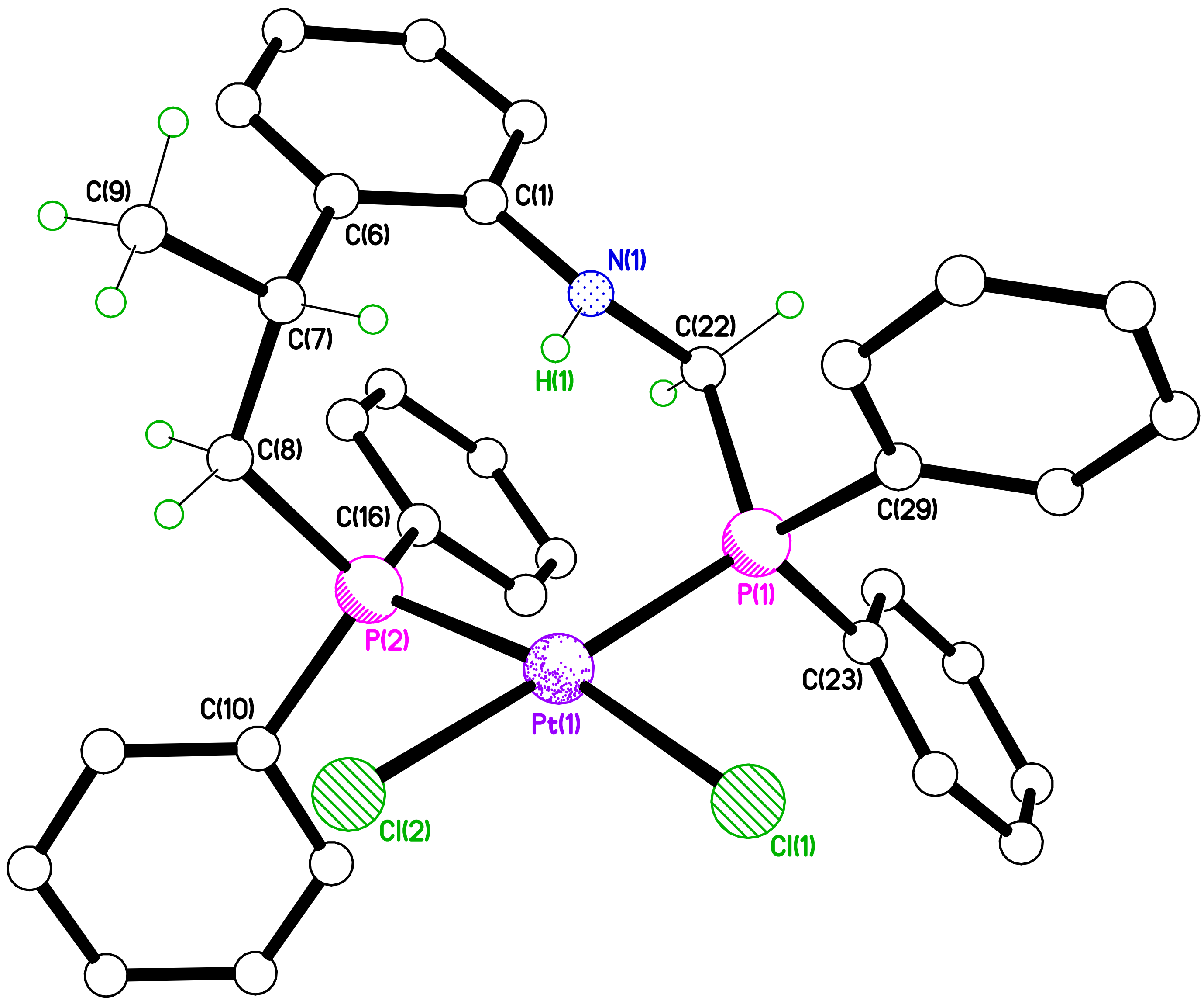
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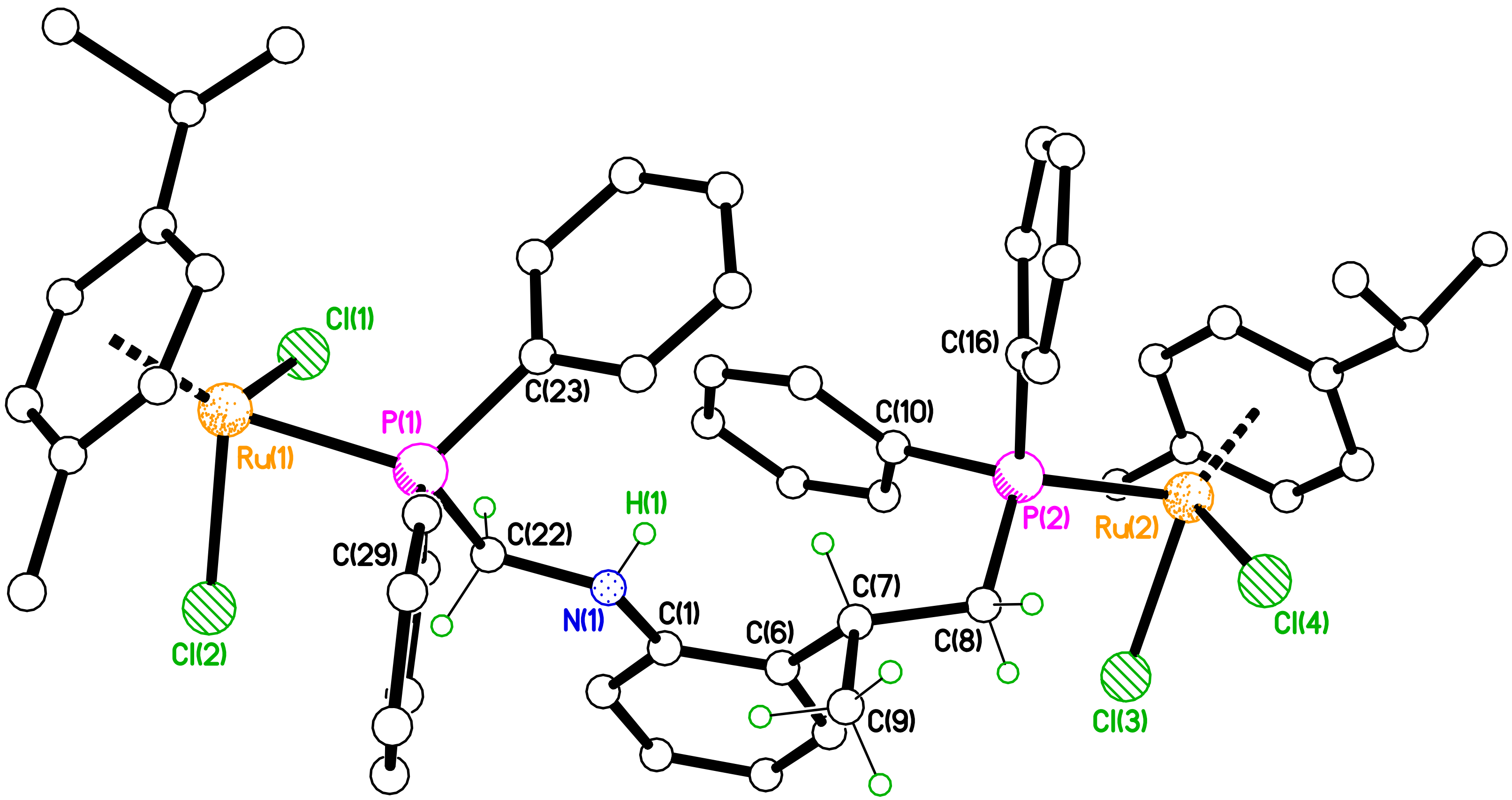
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