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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 $C_6H_4(NH_2)\{2-C(Me)=CH_2\}$ with $HOCH_2PR_2$ ($R_2 = Cg$: 1,3,5,7-tetramethyl-2,4,8-trioxa-6-phosphaadamantyl; Ph_2) afforded the (aminomethyl)phosphines $C_6H_4(NHCH_2PCg)\{2-C(Me)=CH_2\}$ **L**₁ and $C_6H_4(NHCH_2PPh_2)\{2-C(Me)=CH_2\}$ **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 $C_6H_4(NH_2)\{2-C(Me)=CH_2\}$ with two equiv. of $HOCH_2PPh_2$ in CH_3OH under reflux. Alternatively, reaction of $C_6H_4(NH_2)\{2-C(Me)=CH_2\}$ 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 $C_6H_4(NH_2)\{2-CH(Me)CH_2PCg\}$ **L**₄ and $C_6H_4(NH_2)\{2-CH(Me)CH_2PPh_2\}$ **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 $C_6H_4(NHCH_2PPh_2)\{2-CH(Me)CH_2PPh_2\}$ **L**₆. Some preliminary coordination studies towards $[RuCl(\mu-Cl)(\eta^6-C_{10}H_{14})]_2$, $[AuCl(tht)]$ (tht = tetrahydrothiophene) and $[MCl_2(\eta^4-cod)]$ ($M = Pd, Pt$; 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**·0.5 CH_2Cl_2 , **4a**·1.5 CH_2Cl_2 , **5** and **6**·0.5 $CDCl_3$ ·0.5 $C_4H_{10}O$

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 [MCl₂(η^4 -cod)] (cod = cycloocta-1,5-diene) [15], [RuCl(μ -Cl)(η^6 -C₁₀H₁₄)₂] [16], and [AuCl(tht)] (tht = tetrahydrothiophene) [17] were all prepared according to known procedures. HOCH₂PR₂ (R₂ = Cg or Ph₂) [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(CH₃)₄ and coupling constants (J) in Hz. ³¹P{¹H} NMR spectra were recorded on a Bruker DPX-400 FT spectrometer with chemical shifts (δ) in ppm to high frequency of 85% H₃PO₄. NMR spectra were measured in CDCl₃ 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 $C_6H_4(NHCH_2PCg)\{2-C(Me)=CH_2\}$ (L_1). A solution of $CgPCH_2OH$ (0.635 g, 2.57 mmol) in CH_3OH (10 ml) was added to $C_6H_4(NH_2)\{2-C(Me)=CH_2\}$ (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, =*CH*), 5.05 (1H, s, =*CH*), 4.74 (1H, bs, *NH*), 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 $C_6H_4(NHCH_2PPh_2)\{2-C(Me)=CH_2\}$ (L_2). A solution of $C_6H_4(NH_2)\{2-C(Me)=CH_2\}$ (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, $^3J_{\text{HH}}$ 7.4 arom. *H*), 5.06 (1H, d, $^2J_{\text{HH}}$ 1.3, =CH), 4.74 (1H, d, $^2J_{\text{HH}}$ 1.3, =CH), 4.23 (1H, bs, NH), 3.83 (2H, d, $^2J_{\text{HP}}$ 4.5, PCH₂N), 1.86 (3H, s, CH₃). $^{31}\text{P}\{^1\text{H}\}$ NMR [CDCl₃]: δ -18.5. FT-IR (KBr): ν_{NH} 3401 cm⁻¹. EI-MS (*m/z*) [MH]⁺ 332. Anal. (%) Calcd. for C₂₂H₂₂NP·0.5H₂O: C, 78.65; H, 6.41; N, 4.16. Found: C, 79.09; H, 6.52; N, 4.21.

2.3.3 Preparation of C₆H₄{N(CH₂PPh₂)₂}{2-C(Me)=CH₂} (L₃). A solution of C₆H₄(NH₂){2-C(Me)=CH₂} (0.300 g, 2.25 mmol) and Ph₂PCH₂OH (0.974 g, 4.51 mmol) in CH₃OH (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 [CDCl₃]: δ 7.67–6.95 (24H, m, arom. *H*), 5.00 (1H, s, =CH), 4.84 (1H, d, $^2J_{\text{HH}}$ 1.4, =CH), 4.41 (4H, s, PCH₂N), 1.81 (3H, s, CH₃) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR [CDCl₃]: δ -27.3. EI-MS (*m/z*) [MH]⁺ 530. Anal. (%) Calcd. for C₃₅H₃₄NP₂: C, 79.26; H, 6.30; N, 2.72. Found: C, 79.38; H, 6.28; N, 2.64.

2.3.4 Preparation of C₆H₄(NH₂){2-CH(Me)CH₂PCg} (L₄). The compounds C₆H₄(NH₂){2-C(Me)=CH₂} (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 °C for 24 h. The yellow oily product solidified upon cooling in the freezer. Yield: 1.112 g, 85%. ^1H NMR [CDCl₃]: δ 7.17 (1H, dd, $^3J_{\text{HH}}$ 3.2, $^4J_{\text{HH}}$ 0.6, arom. *H*), 7.05 (1H, dd, $^3J_{\text{HH}}$ 3.2, $^4J_{\text{HH}}$ 0.6, arom. *H*), 6.83 (1H, vt, $^3J_{\text{HH}}$ 3.2, arom. *H*), 6.71 (1H, d, $^3J_{\text{HH}}$ 3.2, arom. *H*), 3.61 (2H, bs, NH), 3.02 (1H, m, CH), 2.27–1.12 (23H, m, CH₂, CH₃, Cg). $^{31}\text{P}\{^1\text{H}\}$ NMR [CDCl₃]: δ -31.7, -31.9. FT-IR (KBr): ν_{NH} 3460, 3369 cm⁻¹. EI-MS (*m/z*) [MH]⁺ 350. Anal. (%) Calcd. for C₁₉H₂₈NO₃P: C, 65.96; H, 8.30; N, 4.04. Found: C, 65.31; H, 8.08; N, 4.01.

2.3.5 Preparation of $C_6H_4(NH_2)\{2-CH(Me)CH_2PPh_2\}$ (L_5). The compounds $C_6H_4(NH_2)\{2-C(Me)=CH_2\}$ (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 °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%. 1H NMR [$CDCl_3$]: δ 7.57–7.33 (10H, arom. *H*), 7.25 (1H, dd, $^3J_{HH}$ 7.7, $^4J_{HH}$ 1.4, arom. *CH*), 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, *NH*), 2.75 (1H, m, *CH*), 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). $^{31}P\{^1H\}$ NMR [$CDCl_3$]: δ –19.5. FT–IR (KBr): ν_{NH} 3462, 3377 cm^{-1} . EI–MS (m/z) [MH]⁺ 320. Anal. (%) Calcd. for $C_{21}H_{22}NP \cdot 0.25CH_3OH$: C, 77.96; H, 7.08; N, 4.28. Found: C, 77.65; H, 6.64; N, 3.99.

2.3.6 Preparation of $C_6H_4(NHCH_2PPh_2)\{2-CH(Me)CH_2PPh_2\}$ (L_6). Method 1: 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: 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). 1H 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, $^3J_{\text{HH}}$ 7.7, $^4J_{\text{HH}}$ 1.4, arom. *H*), 6.65 (1H, dd, $^3J_{\text{HH}}$ 7.7, $^4J_{\text{HH}}$ 1.4, arom. *H*), 3.30 (1H, bs, *NH*), 2.84–2.70 (1H, m, *CH*), 2.56–2.44 (1H, dt, $^2J_{\text{HH}}$ 12.3, $^2J_{\text{HP}}$ 4.0, $^3J_{\text{HH}}$ 4.0, *CH*₂), 2.26 (1H, ddd, $^2J_{\text{HH}}$ 12.3, $^2J_{\text{HP}}$ 4.0, $^3J_{\text{HH}}$ 8.0, *CH*₂), 1.52 (3H, d, $^3J_{\text{HH}}$ 6.8, *CH*₃). $^{31}\text{P}\{^1\text{H}\}$ NMR [CDCl_3]: δ –19.6, –19.8. FT-IR (KBr): ν_{NH} 3400 cm^{-1} . EI-MS (m/z) [$\text{MOH}]^+$ 534, [$\text{MO}_2\text{H}]^+$ 550. Anal. (%) Calcd. for $\text{C}_{34}\text{H}_{33}\text{NP}_2$: 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 **L**₂ (0.084 g, 0.26 mmol) and $[\text{RuCl}(\mu\text{-Cl})(\eta^6\text{-C}_{10}\text{H}_{14})]_2$ (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%. ^1H NMR [CDCl_3]: δ 7.93–7.37 (10H, m, arom. *H*), 7.00–6.81 (1H, m, arom. *H*), 6.78 (1H, dd, $^3J_{\text{HH}}$ 7.8, $^4J_{\text{HH}}$ 1.5, arom. *H*), 6.49 (1H, t, $^3J_{\text{HH}}$ 7.8, arom. *H*), 6.34 (1H, d, $^3J_{\text{HH}}$ 7.8, arom. *H*), 5.33 (2H, d, $^3J_{\text{HH}}$ 6.2, arom. *CH*), 5.20 (2H, d, $^3J_{\text{HH}}$ 6.2, arom. *CH*), 4.98 (1H, s, =*CH*), 4.56 (1H, s, =*CH*), 4.48 (2H, s, *PCH*₂*N*), 4.18 (1H, bs, *NH*), 2.57 (1H, sept., $^3J_{\text{HH}}$ 7.0, *CH*), 1.94 (3H, s, *CH*₃), 1.70 (3H, s, *CH*₃), 0.87 (6H, d, $^3J_{\text{HH}}$ 7.0, *CH*₃). $^{31}\text{P}\{^1\text{H}\}$ NMR [CDCl_3]: δ 25.2. FT-IR (KBr): ν_{NH} 3390 cm^{-1} . EI-MS (m/z) [$\text{M-Cl}]^+$ 602. Anal. (%) Calcd. for $\text{C}_{32}\text{H}_{36}\text{NPRuCl}_2 \cdot 0.75\text{CH}_2\text{Cl}_2$: 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 $[\text{AuCl}(\text{tht})]$ (0.115 g, 0.36 mmol) was added **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%. ^1H NMR [CDCl_3]: δ 7.71–7.46 (10H, m, arom. *H*), 7.15 (1H, dt, $^3J_{\text{HH}}$ 8.0, $^4J_{\text{HH}}$ 1.2, arom. *H*), 6.99 (1H, dd, $^3J_{\text{HH}}$ 7.6, $^4J_{\text{HH}}$ 1.6, arom. *H*), 6.87 (1H, t, $^3J_{\text{HH}}$ 8.8, arom. *H*), 6.75 (1H, d, $^3J_{\text{HH}}$

8.4, arom. H), 5.11 (1H, s, =CH), 4.75 (1H, s, =CH), 4.22 (2H, d, $^2J_{\text{PH}}$ 4.0, CH₂), 1.87 (3H, s, CH₃). $^{31}\text{P}\{^1\text{H}\}$ NMR [CDCl₃]: δ 25.0. FT-IR (KBr): ν_{NH} 3381, ν_{AuCl} 327 cm⁻¹. Anal. (%) Calcd. for C₂₂H₂₂NPAuCl: C, 46.86; H, 3.94; N, 2.48. Found: C, 46.34; H, 3.66; N, 2.52.

Preparation of **2b**. To a CH₂Cl₂ (10 ml) solution of [AuCl(tht)] (0.069 g, 0.22 mmol) was added **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 Et₂O (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%. ^1H NMR [CDCl₃]: δ 7.57–7.35 (20H, m, arom. H), 7.13 (1H, d, $^3J_{\text{HH}}$ 7.2, arom. H), 7.05 (1H, dt, $^3J_{\text{HH}}$ 7.2, $^4J_{\text{HH}}$ 2.0, arom. H), 6.89 (1H, t, $^3J_{\text{HH}}$ 7.6, arom. H), 6.87 (1H, dt, $^3J_{\text{HH}}$ 7.6, $^4J_{\text{HH}}$ 2.0 arom. H), 4.96 (4H, s, CH₂), 4.94 (1H, s, =CH), 4.65 (1H, s, =CH), 1.57 (3H, s, CH₃). $^{31}\text{P}\{^1\text{H}\}$ NMR [CDCl₃]: δ 16.1. FT-IR (KBr): ν_{AuCl} 332 cm⁻¹. Anal. (%) Calcd. for C₃₅H₃₃NP₂Au₂Cl₂: 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 CH₂Cl₂ (10 ml) solution of [PdCl₂(η^4 -cod)] (0.043 g, 0.15 mmol) was added **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 Et₂O (20 ml) afforded **3a** which was collected by suction filtration and dried under vacuum. Yield: 0.087 g, 69%. ^1H NMR [CDCl₃]: δ 7.85–6.94 (m, arom. H), 6.78 (2H, dt, CH), 6.58 (1H, d, $^3J_{\text{HH}}$ 8.4, arom. H), 6.41 (1H, d, $^3J_{\text{HH}}$ 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, PCH₂N), 4.38 (4H, s, PCH₂N), 1.92 (6H, s, CH₃), 1.86 (6H, s, CH₃). $^{31}\text{P}\{^1\text{H}\}$ NMR [CDCl₃]: 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 C₄₄H₄₄N₂P₂PdCl₂·0.25CH₂Cl₂: 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%). ^1H NMR [CDCl₃]: δ 7.88–7.42 (20H, m, arom. H), 7.08 (3H, m, arom. H), 6.64 (1H, d, $^3J_{\text{HH}}$ 6.8 arom. H), 5.09

(1H, s, =CH), 4.76 (1H, s, =CH), 4.23 (4H, vt, $^3J_{\text{PtH}}$ 40, $^2J_{\text{PH}}$ 1.6, CH₂), 1.92 (3H, s, CH₃). $^{31}\text{P}\{^1\text{H}\}$ NMR [CDCl₃]: δ 7.3 ($^1J_{\text{PPt}}$ 3661). FT-IR (KBr): ν_{PtCl} 316, 290 cm⁻¹. Anal. (%) Calcd. for C₄₄H₄₄N₂P₂PtCl₂: 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 CH₂Cl₂ (10 ml) solution of [PdCl₂(η^4 -cod)] (0.041 g, 0.14 mmol) was added L₃ (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 Et₂O (20 ml) afforded solid **4a** which was collected by suction filtration and dried under vacuum. Yield: 0.094 g, 92%. ^1H NMR [CDCl₃]: δ 7.81–7.42 (20H, m, arom. H), 7.03 (3H, m, arom. H), 6.59 (1H, d, $^3J_{\text{HH}}$ 7.8, arom. H), 4.72 (1H, s, =CH), 4.62 (1H, s, =CH), 3.92 (4H, s, CH₂), 1.57 (3H, s, CH₃). $^{31}\text{P}\{^1\text{H}\}$ NMR [CDCl₃]: δ 10.0. FT-IR (KBr): ν_{PtCl} 307, 294 cm⁻¹. Anal. (%) Calcd. for C₃₅H₃₃NP₂PdCl₂: 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%). ^1H NMR [CDCl₃]: δ 7.88–7.42 (20H, m, arom. H), 7.08 (3H, m, arom. H), 6.64 (1H, d, $^3J_{\text{HH}}$ 6.8 arom. H), 4.74 (1H, s, =CH), 4.67 (1H, s, =CH), 4.03 (4H, vt, $^3J_{\text{PtH}}$ 40.0, $^2J_{\text{PH}}$ 1.6, CH₂), 1.46 (3H, s, CH₃). $^{31}\text{P}\{^1\text{H}\}$ NMR [CDCl₃]: δ -6.1 ($^1J_{\text{PPt}}$ 3417). FT-IR (KBr): ν_{PtCl} 313, 289 cm⁻¹. Anal. (%) Calcd. for C₃₅H₃₃NP₂PtCl₂·0.5Et₂O: 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 L₆ (0.050 g, 0.096 mmol) and [PtCl₂(η^4 -cod)] (0.036 g, 0.096 mmol) in CH₂Cl₂ and precipitation with Et₂O. Yield: 0.060 g, 80%. ^1H NMR [CDCl₃]: δ 7.92–6.95 (20H, m, arom. H), 6.47 (2H, t, $^3J_{\text{HH}}$ 6.0, arom. H), 6.34 (1H, dd, $^3J_{\text{HH}}$ 8.0, $^4J_{\text{HH}}$ 1.2, arom. H), 6.18 (1H, d, $^3J_{\text{HH}}$ 9.2, arom. H), 5.32–5.27 (1H, m, PCH₂N), 4.30 (1H, m, NH), 3.57–3.47 (1H, m, CH), 3.42 (1H, bt, $^3J_{\text{HH}}$ 12.8, PCH₂N), 2.67 (1H, q, $^3J_{\text{HH}}$ 13.6, CH), 1.97 (1H, q, $^3J_{\text{HH}}$ 8.4, CH), 1.78 (3H, dd, $^3J_{\text{HH}}$ 16.0, J 2.0, CH₃). $^{31}\text{P}\{^1\text{H}\}$ NMR [CDCl₃]: δ 26.9

($^1J_{\text{Pt}}$ 3768, $^2J_{\text{PP}}$ 9), 11.3 ($^1J_{\text{Pt}}$ 3479, $^2J_{\text{PP}}$ 9). FT-IR (KBr): ν_{NH} 3358, ν_{PtCl} 316, 291 cm^{-1} . EI-MS (m/z) $[\text{M}-\text{Cl}]^+$ 747. Anal. (%) Calcd. for $\text{C}_{34}\text{H}_{33}\text{NP}_2\text{PtCl}_2$: 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 **L**₆ (0.0052 g, 0.010 mmol) and $[\text{RuCl}(\mu\text{-Cl})(\eta^6\text{-C}_{10}\text{H}_{14})]_2$ (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%. ^1H 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, $^3J_{\text{HH}}$ 8.4, arom. *H*), 6.45 (1H, t, $^3J_{\text{HH}}$ 7.2, arom. *H*), 6.20 (1H, d, $^3J_{\text{HH}}$ 7.6, arom. *H*), 5.86 (1H, d, $^3J_{\text{HH}}$ 8.0, arom. *H*), 5.40–4.99 (8H, m, $\text{CH}_{\text{cymene}}$), 4.18 (2H, s, PCH_2N), 2.88 (2H, m, PCH_2), 2.51 [3H, m, *CH* and $\text{CH}(\text{CH}_3)_2$], 1.88 (3H, s, $\text{C}_6\text{H}_4\text{CH}_3$), 1.79 (3H, s, $\text{C}_6\text{H}_4\text{CH}_3$), 0.96–0.50 (15H, m, CH_3 and $\text{CH}(\text{CH}_3)_2$). $^{31}\text{P}\{^1\text{H}\}$ NMR [CDCl_3]: δ 25.1, 21.6. Anal. (%) Calcd. for $\text{C}_{54}\text{H}_{61}\text{NP}_2\text{Ru}_2\text{Cl}_4 \cdot 0.25\text{CDCl}_3$: 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 **L**₃ were obtained from an in situ NMR aliquot of the reaction between 1 equiv. $\text{C}_6\text{H}_4(\text{NH}_2)\{2\text{-C}(\text{Me})=\text{CH}_2\}$ and two equiv. of $\text{Ph}_2\text{PCH}_2\text{OH}$ in MeOH. Compounds **L**₅ and **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**·0.5 CH_2Cl_2 , **4a**·1.5 CH_2Cl_2 and **5** were obtained by vapour diffusion of Et_2O into a CH_2Cl_2 solution whereas complex **6**·0.5 CDCl_3 ·0.5 $\text{C}_4\text{H}_{10}\text{O}$ was obtained by vapour diffusion of Et_2O into a CDCl_3 solution. Details of the data collection parameters and crystal data for **L**₃, **L**₅, **L**₆, **1**, **3b**·0.5 CH_2Cl_2 , **4a**·1.5 CH_2Cl_2 , **5** and **6**·0.5 CDCl_3 ·0.5 $\text{C}_4\text{H}_{10}\text{O}$ are given in Table 1. Measurements for **L**₃, **L**₅, **L**₆, **1**, **3b**·0.5 CH_2Cl_2 ,

4a·1.5CH₂Cl₂, **5** and **6**·0.5CDCl₃·0.5C₄H₁₀O 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 1.2 U_{eq} of the carrier atom (1.5 U_{eq} for methyl hydrogen). NH coordinates were freely refined, except for those in **3b**·0.5CH₂Cl₂ which were constrained with U_{eq} set to 1.2 U_{eq} of the carrier atom. For **1** C–CH₃ and =CH₂ atoms were modelled as 50/50 disordered on atoms C(31) and C(32). For **3b**·0.5CH₂Cl₂ one molecule of CH₂Cl₂ was modelled as 2-fold disordered with a major component 63.6(16)%. The H atoms on the terminal =CH₂ and C–CH₃ 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**·1.5CH₂Cl₂ one of the CH₂Cl₂ molecules of crystallisation was modelled as two-fold disordered with major component occupancy 57.6(10)%. For **6**·0.5CDCl₃·0.5C₄H₁₀O the solvent of crystallisation was modelled using the Platon Squeeze procedure [23]. This recovered 85 electrons in one void which corresponds roughly to one CDCl₃ and one Et₂O per unit cell, which agreed with point atom observations.

2. Results and Discussion

3.1. Ligand Synthesis

The amino(methyl)phosphines **L**₁ and **L**₂ were synthesised in ~60% yield upon reaction of one equiv. of HOCH₂PR₂ [readily prepared from equimolar amounts of (CH₂O)_n and Ph₂PH

[18] or CgPH [3d] respectively] and one equivalent of $C_6H_4(NH_2)\{2-C(Me)=CH_2\}$ in CH_3OH (Scheme 1). There has been much interest in the Cg group, as seen here in **L**₁, for its steric properties [3a], diverse coordination behaviour [2, 3a, 6g] and versatility in homogeneous metal catalysed reactions [24a]. For **L**₂, small amounts of the disubstituted phosphine **L**₃ were also formed during the reaction as observed by in situ NMR spectroscopy [$\delta(P) -27.0$]. To confirm this assignment, reaction of two equiv. of Ph_2PCH_2OH with one equiv. of $C_6H_4(NH_2)\{2-C(Me)=CH_2\}$ in refluxing CH_3OH afforded **L**₃ in 58% yield. Other characterising data for **L**₁–**L**₃ are given in the Experimental Section and are broadly as expected. In the ¹H NMR spectra of **L**₁ and **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 **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 **L**₅ and **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 **L**₄ and **L**₅ were prepared by free radical catalysed hydrophosphination using equimolar amounts of $C_6H_4(NH_2)\{2-$

C(Me)=CH₂} and secondary phosphines (H-PR₂, R₂ = Cg or Ph₂) with AIBN at 110 °C for 5 d. Cui and co-workers recently showed that a NHC-Yb(III) amide complex hydrophosphinates Ph₂C=CH₂, when reacted with Ph₂PH, at r.t. for 4 h with 100% conversion [6c]. No efforts toward double hydrophosphination of C₆H₄(NH₂){2-C(Me)=CH₂} with primary phosphines have been attempted. Compound **L**₅ was obtained as a yellowish oil which solidified upon adding CH₃OH and the resulting colourless solid was purified with Et₂O (see Experimental Section). The ³¹P{¹H} NMR spectrum of **L**₅ showed a singlet at δ(P) –19.5, similar to that found for **L**₂. The linear isomer of **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 **L**₅, corresponding to the methine and diastereotopic methylene protons, support the terminal addition of the “H”/“PPh₂” groups across the C(Me)=CH₂ bond. Suitable crystals of **L**₅ were obtained from a CH₃OH 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 –NH₂ group is susceptible to further reaction, initial NMR monitoring of the reaction between **L**₅ with Ph₂PCH₂OH, 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 **L**₆. The yield could be increased after some optimisation work. No one-pot approach to the preparation of **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 **L**₆ were obtained from a CH₃OH 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 **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 **L**₂ and **L**₃ was assessed through a range of simple coordination studies towards [RuCl(μ-Cl)(η⁶-C₁₀H₁₄)]₂, [AuCl(tht)] and [MCl₂(η⁴-cod)] (M = Pd, Pt) in the appropriate stoichiometry, in CH₂Cl₂ 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**·0.5CH₂Cl₂ (Fig. 5) and the dichloropalladium(II) complex **4a**·1.5CH₂Cl₂ (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**·0.5CH₂Cl₂ and **4a**·1.5CH₂Cl₂) 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 –CH₃ and =CH₂ 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 **L**₆ was also investigated towards [PtCl₂(η⁴-cod)] and [RuCl(μ-Cl)(η⁶-C₁₀H₁₄)₂]. The synthesis of the cis isomer **5** (isolated in 80% yield) was achieved by reacting [PtCl₂(η⁴-cod)] and one equiv. of **L**₆. In the ³¹P{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 ¹⁹⁵Pt 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(μ-Cl)(η⁶-C₁₀H₁₄)₂] with 1 equiv. of **L**₆ in CDCl₃ gave the new bimetallic complex **6** as confirmed by ¹H and ³¹P{¹H} NMR spectroscopy. The phosphorus chemical shifts for the two inequivalent ³¹P 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 **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 **L**₆ contrasts with that previously observed

for $C_6H_4(NHCH_2PPh_2)(2-PPh_2)$ [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**·0.5CDCl₃·0.5C₄H₁₀O (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**·0.5CDCl₃·0.5C₄H₁₀O confirms a bimetallic arrangement of [RuCl₂(η⁶-C₁₀H₁₄)] metal fragments supported by a bridging L₆ diphosphine ligand. The Ru–P and Ru–Cl bond lengths in **6**·0.5CDCl₃·0.5C₄H₁₀O 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 R₂PCH₂OH and R₂PH precursors.

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Appendix A. Supplementary material

A complete set of X-ray crystallographic structural data for compounds **L₃**, **L₅**, **L₆**, **1**, **3b**·0.5CH₂Cl₂, **4a**·1.5CH₂Cl₂, **5** and **6**·0.5CDCl₃·0.5C₄H₁₀O (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.

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