Journal of Organometallic Chemistry 699 (2012) 39–47

Contents lists available at SciVerse ScienceDirect

Journal of Organometallic Chemistry

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

Square-planar metal(II) complexes containing ester functionalised bis(phosphino) amines: Mild P–N methanolysis and C_{arene}–H cyclometallation

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ARTICLE INFO

Article history:
Received 22 September 2011
Received in revised form
26 October 2011
Accepted 1 November 2011

Keywords:
Cyclometallation
Metathesis
Phosphine ligands
Square-planar complexes
X-ray crystallography

ABSTRACT

The synthesis of three new ester functionalised bis(phosphino)amines $Ph_2PN\{R\}PPh_2$ [R = C_6H_4(3-CO_2Me) **1a**; $C_6H_3(3,5\text{-}CO_2Me)_2$ **1b**; C_6H_4(4-CO_2Me) **1c**] upon stoichiometric reaction of Ph_2PCl and the appropriate $H_2N\{R\}$ in Et_2O is described. Reaction of 1 equiv. of **1a**–**c** with MCl_2(cod) (M = Pt, Pd) in CH_2Cl_2 afforded the dichlorometal(II) complexes $PtCl_2$(**1a**) **2a**, $PtCl_2$(**1b**) **2b**, $PtCl_2$(**1c**) **2c** and $PdCl_2$(**1b**) **2`b** respectively. The corresponding dibromo (and diiodo) platinum(II) complexes **3b** (and **4b**) were synthesised, in >80% isolated yields, from $PtBr_2$(cod) or PtI_2(cod). When a suspension of **2b** in MeOH was stirred at r.t. for ca. 16 h the mixed complex cis-$PtCl_2[Ph_2PNH\{R\}](Ph_2POMe)$ **5a** [R = $C_6H_3(3,5\text{-}CO_2Me)_2$] was cleanly generated. Metathesis of **5a** using excess NaBr or NaI in MeOH/acetone afforded cis-$PtBr_2[Ph_2PNH\{R\}](Ph_2POMe)$ **5b** or cis-$PtI_2[Ph_2PNH\{R\}](Ph_2POMe)$ **5c**. Methanolysis of $PtCl_2$(**1a**) **2a** at ambient temperature afforded, in low yield (18%), the regiospecific P,C-orthometallated complex cis-PtCl $[Ph_2PNH\{C_6H_3(3\text{-}CO_2Me)\}](Ph_2POMe)$ **6**. We speculate the C–H activated complex **6** is obtained via initial formation of cis-$PtCl_2[Ph_2PNH\{C_6H_4(3\text{-}CO_2Me)\}](Ph_2POMe)$ **7**. A similar observation was also found using **2c** whereupon examination of the isolated solid, by $^{31}P\{^1H\}$ NMR spectroscopy, revealed formation of three complexes namely orthometallated cis-$PtCl[Ph_2PNH\{C_6H_3(4\text{-}CO_2Me)\}](Ph_2POMe)$ **9**, cis-$PtCl[Ph_2PNH\{C_6H_4(4\text{-}CO_2Me)\}](Ph_2POMe)$ **10** and cis-$PtCl_2(Ph_2POMe)_2$ **8**. All new compounds reported here have been characterised by multinuclear NMR and IR spectroscopy, microanalysis and in six cases by single crystal X-ray crystallography. The X-ray structure of cis-$PtCl[Ph_2PNH\{C_6H_3(3\text{-}CO_2Me)\}](Ph_2POMe)$ **6** revealed selective C–H cycloplatination at the 6-position (as opposed to the 2-position) of the *N*-arene ring.

1. Introduction

Cyclometallated complexes represent an important class of compound widely encountered in modern organometallic and coordination chemistry [1]. Various examples of C–H activated (sp^2 or sp^3) achiral [2,3] or chiral [4] metal complexes have been reported and find numerous applications in areas ranging from organic transformations [3,5], directed self-assembly [6], catalysis [7], chemical sensing [8] and as luminescent materials [9].

Phosphorus based compounds such as tertiary phosphines [10], phosphinites [11], phosphites [12], iminophosphoranes [3,13] and PCP-pincer ligands [14] have widely been studied in a range of C–H activation processes. In contrast trivalent phosphorus ligands bearing one (or more) P–N bonds have recently been shown to undergo sp^2 or sp^3 C–H cyclometallation at Ru, Rh, Ir, Ni, Pd and Pt metal centres affording bidentate [15], tridentate [16] or tetradentate [17] carbometallated complexes. We have demonstrated in previous work that functionalised (phosphino)amines undergo thermally induced orthometallation at Pt^{II} and Rh^{III} metal centres affording rare examples of thermally stable M–P–N–C_{arene}–C_{arene} five-membered metallacycles [15e]. In this work we wished to explore whether chelating bis(phosphino)amines of the type $(Ph_2P)_2N\{R\}$ would themselves undergo C–H metallation, a reaction that has previously been observed for $(Ph_2P)_2CH_2$ [1]. We report here the synthesis of three bis(phosphino)amines bearing one (or two) –CO_2Me groups and a brief survey of their coordination chemistry at Pd^{II} and Pt^{II} metal centres. A general feature of (phosphino)amine chemistry is their air/moisture sensitivity due to the reactive nature of the heterolytic P–N bond [18]. We demonstrate here the selective methanolysis of a P–N bond [19] for some

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doi:10.1016/j.jorganchem.2011.11.003

of these strained four-membered ester functionalised bis(phosphino)amine complexes and furthermore disclose a facile C–H bond activation under remarkably mild conditions. Six single crystal X-ray structure determinations have been undertaken.

2. Experimental

2.1. Materials

Standard Schlenk techniques were used for the syntheses of ligands **1a**–**c** whilst all other reactions were performed under aerobic conditions using previously distilled solvents unless otherwise stated. The compounds $H_2NC_6H_4(3\text{-}CO_2Me)$, $H_2NC_6H_4(4\text{-}CO_2Me)$ and $H_2NC_6H_3(3,5\text{-}CO_2Me)_2$ were obtained from commercial suppliers and used directly. The complexes MX_2(cod) (M = Pt, Pd; X = Cl, Br, I) were prepared according to literature methods [20].

2.2. Instrumentation

Infrared spectra were recorded as KBr pellets in the range 4000–200 cm^{-1} on a Perkin–Elmer System 2000 Fourier-transform spectrometer, ^1H NMR spectra (250 or 400 MHz) were recorded on a Bruker AC250 or DPX-400 FT spectrometer with chemical shifts (δ) in ppm to high frequency of external $Si(CH_3)_4$ and coupling constants (J) in Hz, $^{31}P\{^1H\}$ NMR spectra (36.2 MHz, 101.3 or 162.0 MHz) were recorded either on a Jeol FX90Q, Bruker AC250 or DPX-400 FT spectrometer with chemical shifts (δ) in ppm to high frequency of external 85% H_3PO_4. All $^{195}Pt\{^1H\}$ NMR spectra (53.7 MHz) were recorded on a Bruker AC250 FT NMR spectrometer with δ referenced to external H_2PtCl_6 (in D_2O/HCl). NMR spectra were measured in $CDCl_3$ unless otherwise stated. Elemental analyses (Perkin–Elmer 2400 CHN Elemental Analyzer) were performed by the Loughborough University Analytical Service within the Department of Chemistry.

2.3. Syntheses

2.3.1. $Ph_2PN\{C_6H_4(3\text{-}CO_2Me)\}PPh_2$ **1a** and bis(phosphino)amines **1b**, **1c**

To a stirred suspension of $H_2N\{C_6H_4(3\text{-}CO_2Me)\}$ (0.840 g, 5.56 mmol) in NEt_3 (2.559 g, 25.3 mmol) and Et_2O (100 mL) was added Ph_2PCl (2.800 g, 12.7 mmol) in Et_2O (20 mL) dropwise over 20 min whilst the temperature was maintained at approx. 0 °C. The mixture was stirred at ambient temperature for ~7 d and the solvent evaporated to dryness under reduced pressure. After addition of degassed distilled water (70 mL), the solid was collected by suction filtration and washed with hexane (50 mL) and absolute EtOH (50 mL) to afford **1a**. Yield: 2.493 g, 85%. Selected data for **1a**: $^{31}P\{^1H\}$ NMR ($CDCl_3$): 69.0 ppm. ^1H NMR: δ 7.64–6.83 (m, 24H, arom. H), 3.74 (s, 3H, CO_2Me). FT–IR: ν_{CO} 1722 cm^{-1}. FAB–MS: *m/z* 519 [M^+]. Found C, 72.57; H, 5.27; N, 2.62. $C_{32}H_{27}NO_2P_2\cdot0.5H_2O$ (528.5) requires C, 72.71; H, 5.35; N, 2.65%. In a similar manner $Ph_2PN\{C_6H_3(3,5\text{-}CO_2Me)_2\}PPh_2$ (**1b**) and $Ph_2PN\{C_6H_4(4\text{-}CO_2Me)\}PPh_2$ (**1c**) were prepared in 82% and 58% isolated yields respectively. Selected data for **1b**: $^{31}P\{^1H\}$ NMR ($CDCl_3$): 69.0 ppm. ^1H NMR: δ 7.89–7.24 (m, 23H, arom. H), 3.74 (s, 3H, CO_2Me). FT–IR: ν_{CO} 1727 cm^{-1}. FAB–MS: *m/z* 578 [M^+]. Found C, 69.63; H, 5.06; N, 2.53. $C_{34}H_{29}NO_4P_2\cdot0.5H_2O$ (586.6) requires C, 69.62; H, 5.17; N, 2.39%. Selected data for **1c**: $^{31}P\{^1H\}$ NMR ($CDCl_3$): 68.5 ppm. ^1H NMR: δ 7.66–6.77 (m, 24H, arom. H), 3.83 (s, 3H, CO_2Me). FT–IR: ν_{CO} 1717 cm^{-1}. FAB–MS: *m/z* 536 [M + O]. Found C, 72.65; H, 5.41; N, 2.63. $C_{32}H_{27}NO_2P_2\cdot0.5H_2O$ (528.5) requires C, 72.71; H, 5.35; N, 2.65%.

2.3.2. $PtCl_2$(**1a**) **2a** and complexes **2b**, **2c**, **2ˋb**, **3b**, **4b**

To a CH_2Cl_2 (10 mL) solution of $PtCl_2$(cod) (0.095 g, 0.254 mmol) was added **1a** (0.132 g, 0.254 mmol) as a solid in one portion. The pale yellow solution was stirred for 20 min and the volume concentrated to ~1 mL under reduced pressure. Addition of Et_2O (30 mL) gave a solid which was collected by suction filtration, washed with Et_2O (10 mL) and dried in vacuo. Yield: 0.191 g, 96%. Selected data for **2a**: $^{31}P\{^1H\}$ NMR ($CDCl_3$): 21.4 ppm, $^1J_{PtP}$ 3334 Hz. ^1H NMR: δ 7.90–6.67 (m, 24H, arom. H), 3.75 (s, 3H, CO_2Me). FT–IR: ν_{CO} 1724, ν_{PtCl} 314, 292 cm^{-1}. Found C, 49.19; H, 3.59; N, 1.53%. $C_{32}H_{27}NO_2P_2PtCl_2$ (785.5) requires C, 48.93; H, 3.47; N, 1.78%. In a similar manner the following dihalometal(II) complexes were synthesised using $PtCl_2$(cod) (for **2b**, **2c**), $PdCl_2$(cod) (for **2ˋb**), $PtBr_2$(cod) (for **3b**) or PtI_2(cod) (for **4b**): Selected data for **2b** (99% isolated yield): $^{31}P\{^1H\}$ NMR ($CDCl_3$): 22.5 ppm, $^1J_{PtP}$ 3339 Hz. ^1H NMR: δ 8.39–7.35 (m, 23H, arom. H), 3.78 (s, 6H, CO_2Me). ^{195}Pt NMR: −4056 ppm. FT–IR: ν_{CO} 1733, 1720, ν_{PtCl} 307, 290 cm^{-1}. Found C, 48.16; H, 3.61; N, 1.63%. $C_{34}H_{29}NO_4P_2PtCl_2$ (843.5) requires C, 48.41; H, 3.47 N, 1.66%. Selected data for **2c** (86% isolated yield): $^{31}P\{^1H\}$ NMR ($CDCl_3$): 21.3 ppm, $^1J_{PtP}$ 3330 Hz. ^1H NMR: δ 7.88–6.57 (m, 24H, arom. H), 3.83 (s, 3H, CO_2Me). FT–IR: ν_{CO} 1721, ν_{PtCl} 307, 290 cm^{-1}. Found C, 48.98; H, 3.55; N, 1.92%. $C_{32}H_{27}NO_2P_2PtCl_2$ (785.5) requires C, 48.93; H, 3.47; N, 1.78%. Selected data for **2ˋb** (91% isolated yield): $^{31}P\{^1H\}$ NMR ($CDCl_3$): 36.1 ppm. ^1H NMR: δ 8.38–7.44 (m, 23H, arom. H), 3.79 (s, 6H, CO_2Me). FT–IR: ν_{CO} 1733, 1720, ν_{PdCl} 314, 296 cm^{-1}. Found C, 53.71; H, 4.04; N, 1.83%. $C_{34}H_{29}NO_4P_2PdCl_2$ (754.8) requires C, 54.10; H, 3.88; N, 1.86%. Selected data for **3b** (89% isolated yield): $^{31}P\{^1H\}$ NMR ($CDCl_3$): 21.3 ppm, $^1J_{PtP}$ 3260 Hz. ^1H NMR: δ 8.37–7.37 (m, 23H, arom. H), 3.78 (s, 6H, CO_2Me). FT–IR: ν_{CO} 1733, 1721 cm^{-1}. Found C, 44.01; H, 3.32; N, 1.36%. $C_{34}H_{29}NO_4P_2PtBr_2$ (932.4) requires C, 43.79; H, 3.14; N, 1.50%. Selected data for **4b** (85% isolated yield): $^{31}P\{^1H\}$ NMR ($CDCl_3$): 17.4 ppm, $^1J_{PtP}$ 3066 Hz. ^1H NMR: δ 8.30–7.32 (m, 23H, arom. H), 3.74 (s, 6H, CO_2Me). FT–IR: ν_{CO} 1728 cm^{-1}. Found C, 39.42; H, 2.78; N, 1.30%. $C_{34}H_{29}NO_4P_2PtI_2$ (1026.4) requires C, 39.78; H, 2.85; N, 1.36%.

2.3.3. *cis*-$PtCl_2[Ph_2PNH\{C_6H_3(3,5\text{-}CO_2Me)_2\}](Ph_2POMe)$ **5a** and complexes **5b**, **5c**, **5d**

A suspension of **2b** (0.218 g, 0.258 mmol) in MeOH (60 mL) was stirred at ambient temperature for approx. 16 h. The solid was filtered under reduced pressure, washed with MeOH (8 mL) and dried in vacuo. Yield: 0.178 g, 79%. Selected data for **5a**: $^{31}P\{^1H\}$ NMR ($CDCl_3$): 81.4 ppm, $^1J_{PtP}$ 4332 Hz; 30.1 ppm, $^1J_{PtP}$ 3960 Hz; $^2J_{PP}$ 16 Hz ^1H NMR: δ 8.33 (d, $^2J_{PH}$ 10.5 Hz, 1H, NH), 8.06–7.33 (m, 23H, arom. H), 3.80 (s, 6H, CO_2Me), and 2.81 (d, $^3J_{PH}$ 11.5 Hz, 3H, OMe). ^{195}Pt NMR: −4315 ppm. FT–IR (KBr): ν_{NH} 3239, ν_{CO} 1732, 1725, ν_{PtCl} 316, 284 cm^{-1}. Found C, 48.00; H, 3.61; N, 1.58. $C_{35}H_{33}NO_5P_2PtCl_2$ (875.6) requires C, 48.01; H, 3.81; N, 1.60%. The platinum(II) complexes **5b** (98% isolated yield) and **5c** (96% isolated yield) were synthesised by metathesis of **5a** with either NaBr or NaI in MeOH/acetone. Selected data for **5b**: $^{31}P\{^1H\}$ NMR ($CDCl_3$): 80.6 ppm, $^1J_{PtP}$ 4268 Hz; 30.6 ppm, $^1J_{PtP}$ 3934 Hz; $^2J_{PP}$ 21 Hz. ^1H NMR: δ 8.15 (d, $^2J_{PH}$ 10.6 Hz, 1H, NH), 8.08–7.32 (m, 23H, arom. H), 3.81 (s, 6H, CO_2Me) and 2.80 (d, $^3J_{PH}$ 11.6 Hz, 3H, OMe). ^{195}Pt NMR: −4556 ppm. FT–IR (KBr): ν_{NH} 3233, ν_{CO} 1726 cm^{-1}. FAB–MS: *m/z* 884 [M–Br]. Found C, 42.73; H, 3.11; N, 1.31. $C_{35}H_{33}NO_5P_2PtBr_2\cdot0.25CH_2Cl_2$ (985.7) requires C, 42.95; H, 3.40; N, 1.42%. Selected data for **5c**: $^{31}P\{^1H\}$ NMR ($CDCl_3$): 80.4 ppm, $^1J_{PtP}$ 4110 Hz; 29.9 ppm, $^1J_{PtP}$ 3789 Hz; $^2J_{PP}$ 9 Hz. ^1H NMR: δ 8.08–7.32 (m, 24H, arom. H and NH), 3.81 (s, 6H, CO_2Me) and 2.79 (d, $^3J_{PH}$ 11.3 Hz, 3H, OMe). ^{195}Pt NMR: −5074 ppm. FT–IR (KBr): ν_{NH} 3194, ν_{CO} 1725 cm^{-1}. FAB–MS: *m/z* 931 [M–I]. Found C, 40.06; H, 3.27; N, 1.25. $C_{35}H_{33}NO_5P_2PtI_2$ (1058.5) requires C, 39.71; H, 3.15; N, 1.32%. Selected data for **5d**: $^{31}P\{^1H\}$ NMR ($CDCl_3$): 108.2,