The (phosphino)tetraphenylborate ligand in ruthenium-arene chemistry

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ABSTRACT

The synthesis of a series of anionic half-sandwich ruthenium-arene complexes $[E][RuCl_2(\eta^6\text{-}p\text{-cyme-ne})\{PR_2(p\text{-}Ph_3BC_6H_4)\}]$ (E = Bu_4N^+: R = Ph, **1a**, ^iPr, **1b** or Cy, **1c**; E = bis(triphenylphosphine)iminium or PNP^+: R = Ph, **1a′**, ^iPr, **1b′** or Cy, **1c′**) are reported. X-ray crystallographic studies of **1a′** and **1b′** confirmed the three-legged piano-stool coordination geometry. In solution, complexes **1a–c** and **1a′–c′** are proposed to form monomer–dimer equilibria as a result of chloride ligand dissociation. Complexes **1a–c** and **1a′–c′** also form the formally neutral zwitterionic complexes $[RuCl(L)(\eta^6\text{-}p\text{-cymene})\{PR_2(p\text{-}Ph_3BC_6H_4)\}]$ (L = pyridine: R = Ph, **2a**, ^iPr, **2b** or Cy, **2c**; L = MeCN: R = Ph, **3a**, ^iPr, **3b** or Cy, **3c**) via chloride ligand abstraction using $AgNO_3$ or MeOTf.

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1. Introduction

Phosphorus-based ligands continue to play a dominating role as co-ligands in organometallic chemistry. Indeed, tertiary phosphines are especially important and have been studied quite extensively, with considerable attention being directed towards developing novel structural variants possessing unique electronic, steric and coordination behaviours [1]. Recent reports describing the synthesis, properties and coordination chemistry of several new classes of *anionic* phosphines [2], in particular the monodentate (phosphino)tetraphenylborate ligands $[PR_2(p\text{-}Ph_3BC_6H_4)]^-$ [3] (Structure I), are quite intriguing. Conceptually, they may be regarded as a tertiary phosphine ligand tethered to a tetraphenylborate anion. The strategic positioning of the triphenylborane group on the phenyl substituent, which projects away from the phosphorus donor atom, might suggest these phosphines are essentially isosteric with their neutral counterparts, and thus only their electronic profile has been altered. In fact, it has been suggested that anionic phosphines exhibit enhanced electron-donor properties vs. their neutral counterparts [2a,2b]. Equally intriguing, anionic phosphine ligands have also proven to be useful in developing new catalytically active zwitterionic complexes [2b]. While many *cationic* complexes are effective in catalyzing a variety of organic transformations, their charge-neutral zwitterionic analogues

might offer several advantages, including enhanced solubilities in low polarity solvents, an increase in tolerance towards coordinating solvents and substrate functional groups, and eliminating competition for the active site between the substrate and a counterion.

We found it surprising that the coordination chemistry of this novel class of phosphine ligand remains underdeveloped, particularly for catalytically important ruthenium. We report here some of our preliminary investigations involving the synthesis of ruthenium-arene complexes containing these anionic phosphine ligands.

2. Experimental

Unless otherwise stated, all experiments and manipulations were conducted under an inert atmosphere of prepurified N_2 using standard Schlenk techniques. Distilled, deionized water was stored in a bulb with a Teflon tap, and purged with N_2 prior to use. Methanol, acetonitrile and pyridine were each stored over activated 4A molecular sieves in a bulb with a Teflon tap, and purged with N_2 before use. All other bulk solvents used in large-scale preparations were pre-dried over activated 4A molecular sieves, passed through a column of alumina, purged with N_2 and stored over 4A molecular sieves in bulbs with Teflon taps [4]. NMR solvents used in solution structure elucidations were dried with appropriate drying agents, vacuum distilled, freeze-pump-thaw degassed three times, and stored in bulbs with Teflon taps: $CDCl_3$ and $C_2D_4Cl_2$ (anhydrous $CaCl_2$); CD_2Cl_2 (CaH_2); acetone-d_6 (activated 4A sieves). NMR

Structure I
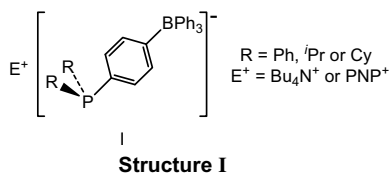
spectra (^{1}H and ^{31}P{^{1}H}) were obtained using a Varian Unity INOVA 500 MHz spectrometer, with chemical shifts (in ppm) referenced to residual protio solvent peaks (^{1}H) or external 85% H_3PO_4 (^{31}P). Elemental analyses were performed on a CEC 240XA analyzer by the Lakehead University Instrumentation Laboratory. The ruthenium precursor [RuCl$_2$(η^6-p-cymene)]$_2$ [5] and the ligands [E][PR$_2$(p-Ph$_3$BC$_6$H$_4$)] (E = Bu$_4$N$^+$ or PNP$^+$; R = Ph or ^{i}Pr) [3] were prepared according to the literature procedures; the ligands were recrystallized from THF/hexanes.

2.1. Synthesis of [E][PCy$_2$(p-Ph$_3$BC$_6$H$_4$)] (E = Bu$_4$N$^+$ or PNP$^+$)

The ligands [E][PCy$_2$(p-Ph$_3$BC$_6$H$_4$)] were prepared in a manner analogous to the literature procedure [3] except using ClPCy$_2$ as a precursor, and isolated either as the Bu$_4$N$^+$ salt (using [Bu$_4$N]Br) or PNP$^+$ salt (using [PNP]Cl) in 84% and 78% yield, respectively. NMR spectroscopic data for the Bu$_4$N$^+$ salt follows. ^{1}H NMR (499.9 MHz, acetone-d_6, 22 °C): 7.38–6.78 (m, 19 H, Ph and PC$_6$H$_4$B), 3.44 (m, 8H, Bu), 2.05 (m, 8H, Bu), 1.86–1.60, 1.33–1.08 (m, 22H, Cy), 1.43 (m, 8H, Bu), 0.97 (t, 12H, Bu). ^{31}P{^{1}H} (202.3 MHz, acetone-d_6, 22 °C): 6.70 (PCy$_2$). The ^{1}H and ^{31}P{^{1}H} NMR spectroscopic data (acetone-d_6, 22 °C) of the anion of the PNP$^+$ salt were identical to the Bu$_4$N$^+$ salt.

2.2. Synthesis of [Bu$_4$N][RuCl$_2$(η^6-p-cymene){PR$_2$(p-Ph$_3$BC$_6$H$_4$)}] (R = Ph, 1a, ^{i}Pr, 1b or Cy, 1c)

In a typical procedure, a Schlenk tube was charged with [RuCl$_2$(η^6-p-cymene)]$_2$ (0.95 mmol) and [Bu$_4$N][PR$_2$(p-Ph$_3$BC$_6$H$_4$)] (1.90 mmol). Next, CH$_2$Cl$_2$ (30 mL) was added via syringe and the deep, dark red solution was allowed to stir for 1.5 h. After this time, the volatiles were removed under reduced pressure to yield an orange-red product, which was recrystallized from CH$_2$Cl$_2$/hexanes via slow diffusion. The products were isolated as orange-red powders in yields >90% after drying under reduced pressure. Analytically pure samples could be obtained by cooling saturated MeOH solutions to −78 °C for several hours, filtering the microcrystalline product, and washing with MeOH. Combustion and NMR spectroscopic data for complexes **1a–c** follow. Complex **1a** (R = Ph): Anal. Calc. for C$_{62}$H$_{79}$BCl$_2$NPRu: C, 70.92; H, 7.60; N, 1.33. Found: C, 71.04; H, 7.15; N, 0.94%. ^{1}H NMR (499.9 MHz, CDCl$_3$, 22 °C): 7.81–6.75 (m, Ph and PC$_6$H$_4$B), 5.06 (d, p-cymene), 4.94 (d, p-cymene), 4.91 (d, p-cymene), 4.86 (d, p-cymene) 2.62 (septet, ^{i}Pr of p-cymene), 2.58 (m, 8H, Bu), 1.78 (s, Me of p-cymene), 1.20 (m, 8H, Bu), 1.09 (m, 8H, Bu), 1.03 (d, ^{i}Pr of p-cymene), 0.83 (t, 12H, Bu). ^{31}P{^{1}H} (202.3 MHz, CDCl$_3$, 22 °C): 24.5, 23.1 ($\sim$9:1, both s, PPh$_2$). Complex **1b** (R = ^{i}Pr): Despite numerous attempts, satisfactory carbon, hydrogen and nitrogen analyses could not be obtained for **1b**. ^{1}H NMR (499.9 MHz, CDCl$_3$, 22 °C): 7.49–6.95 (m, Ph and PC$_6$H$_4$B), 5.13–4.87 (m, p-cymene), 3.15 (m, ^{i}Pr of phosphine), 3.04 (m, ^{i}Pr of phosphine), 2.62 (m, 8H, Bu), 2.56 (m, ^{i}Pr of p-cymene), 2.45 (septet, ^{i}Pr of p-cymene), 1.79 (s, Me of p-cymene), 1.75 (s, Me of p-cymene), 1.41 (m, ^{i}Pr of phosphine), 1.30 (m, 16H, Bu), 1.04 (d, ^{i}Pr of p-cymene), 0.98 (t, 12H, Bu). ^{31}P{^{1}H} (202.3 MHz, CDCl$_3$, 22 °C): 29.2, 27.4, 25.9 ($\sim$2:2.5:1, all s, P^iPr$_2$). Complex **1c** (R = Cy): Anal. Calc. for C$_{62}$H$_{91}$BCl$_2$NPRuX$_3$MeOH (the MeOH was confirmed via ^{1}H NMR spectroscopy): C, 66.95; H, 8.84; N, 1.20.

Found: C, 66.32; H, 8.03; N, 1.02%. ^{1}H NMR (499.9 MHz, CDCl$_3$, 22 °C): 7.43–6.93 (m, Ph and PC$_6$H$_4$B), 5.09–4.84 (m, p-cymene), 3.49 (d, Cy of phosphine), 2.84 (m, ^{i}Pr of p-cymene), 2.69 (m, 8H, Bu), 2.58 (m, ^{i}Pr of p-cymene), 2.14–1.24 (m, Bu and Cy of phosphine), 1.81 (s, Me of p-cymene), 1.76 (s, Me of p-cymene), 1.74 (s, Me of p-cymene), 1.09 (br d, ^{i}Pr of p-cymene), 0.99 (t, 12H, Bu). ^{31}P{^{1}H} (202.3 MHz, CDCl$_3$, 22 °C): 21.4, 19.9, 18.6 ($\sim$1.5:2.5:1, all s, PCy$_2$).

2.3. Synthesis of [PNP][RuCl$_2$(η^6-p-cymene){PR$_2$(p-Ph$_3$BC$_6$H$_4$)}] (R = Ph, 1a$'$, ^{i}Pr, 1b$'$ or Cy, 1c$'$)

Complexes **1a$'$–c$'$** were prepared in a manner analogous to that described for the synthesis of **1a–c**, except using [PNP][PR$_2$(p-Ph$_3$BC$_6$H$_4$)]. Yields were typically >75%. Combustion and NMR spectroscopic data for complexes **1a$'$–c$'$** follow. Complex **1a$'$** (R = Ph): Anal. Calc. for C$_{82}$H$_{73}$BCl$_2$NP$_3$Ru: C, 73.00; H, 5.46; N, 1.04. Found: C, 72.96; H, 5.41; N, 0.95%. ^{1}H NMR (499.9 MHz, CDCl$_3$, 22 °C): 7.81–6.81 (m, Ph and PC$_6$H$_4$B), 5.08 (d, p-cymene), 4.96 (d, p-cymene), 4.91 (d, p-cymene), 4.88 (d, p-cymene), 2.76 (septet, ^{i}Pr of p-cymene), 1.80 (s, Me of p-cymene), 1.06 (d, ^{i}Pr of p-cymene). ^{31}P{^{1}H} (202.3 MHz, CDCl$_3$, 22 °C): 25.6, 24.4 ($\sim$7:1, both s, PPh$_2$), 22.1 (PNP$^+$). Complex **1b$'$** (R = ^{i}Pr): Anal. Calc. for C$_{76}$H$_{77}$BCl$_2$NP$_3$RuX$_3$MeOH (the MeOH was confirmed via ^{1}H NMR spectroscopy): C, 68.70; H, 6.51; N, 1.02. Found: C, 68.51; H, 6.04; N, 0.89%. ^{1}H NMR (499.9 MHz, CDCl$_3$, 22 °C): 7.56–6.82 (m, Ph and PC$_6$H$_4$B), 5.06–4.78 (m, p-cymene), 3.08 (m, ^{i}Pr of phosphine), 3.00 (m, ^{i}Pr of phosphine), 2.58 (m, ^{i}Pr of p-cymene), 2.49 (septet, ^{i}Pr of p-cymene), 1.80 (s, Me of p-cymene), 1.76 (s, Me of p-cymene), 1.34 (m, ^{i}Pr of phosphine), 1.22 (m, ^{i}Pr of phosphine), 1.04 (d, ^{i}Pr of p-cymene). ^{31}P{^{1}H} (202.3 MHz, CDCl$_3$, 22 °C): 29.8, 28.2, 26.5 ($\sim$11:7:1, all s, P^iPr$_2$), 22.2 (PNP$^+$). Complex **1c$'$** (R = Cy): Anal. Calc. for C$_{82}$H$_{85}$BCl$_2$NP$_3$Ru: C, 72.24; H, 6.24; N, 1.03. Found: C, 71.98; H, 6.75; N, 0.94%. ^{1}H NMR (499.9 MHz, CDCl$_3$, 22 °C): 7.61–6.85 (m, Ph and PC$_6$H$_4$B), 5.05–4.81 (m, p-cymene), 3.49 (d, Cy of phosphine), 2.75 (m, ^{i}Pr of p-cymene), 2.50 (m, ^{i}Pr of p-cymene), 2.10–1.16 (m, Cy of phosphine), 1.84 (s, Me of p-cymene), 1.79 (s, Me of p-cymene), 1.77 (s, Me of p-cymene), 1.06 (d, ^{i}Pr of p-cymene). ^{31}P{^{1}H} (202.3 MHz, CDCl$_3$, 22 °C): 22.1 (PNP$^+$), 21.9, 20.5, 19.1 ($\sim$6:4:1, all s, PCy$_2$).

2.4. Synthesis of [RuCl(py)(η^6-p-cymene){PPh$_2$(p-Ph$_3$BC$_6$H$_4$)}], 2a

In a Schlenk tube, complex **1a** (0.279 g, 0.265 mmol) was dissolved in CH$_2$Cl$_2$ (20 mL). Excess pyridine (1.1 mL, 13.3 mmol) was added via syringe, followed by AgNO$_3$ (0.050 g, 0.292 mmol). Almost immediately an orange mixture was produced, which gradually turned yellow and deposited a white precipitate of AgCl. After stirring for 1.5 h, the mixture was filtered through Celite, and the orange filtrate was extracted with water (6 × 30 mL) with vigorous shaking. The combined organic layers were dried over MgSO$_4$ and filtered through Celite. Removal of the volatiles under reduced pressure yielded an orange-yellow solid. The solid was recrystallized from CH$_2$Cl$_2$/diethyl ether via slow diffusion. Yield: 90%. Anal. Calc. for C$_{51}$H$_{48}$BClNPRu: C, 71.18; H, 5.63; N, 1.63. Found: C, 70.99; H, 5.76; N, 1.56%. ^{1}H NMR (499.9 MHz, acetone-d_6, 22 °C): 8.91 (m, 2H, o-H of py), 7.79–6.82 (m, 32H, py, Ph and PC$_6$H$_4$B), 5.94, 5.70, 5.59, 5.49 (each m, each 1H, p-cymene), 2.36 (septet, 1H, ^{i}Pr of p-cymene), 1.82 (s, 3H, Me of p-cymene), 1.12 (d, 3H, ^{i}Pr of p-cymene), 1.05 (d, 3H, ^{i}Pr of p-cymene). ^{31}P{^{1}H} (202.3 MHz, acetone-d_6, 22 °C): 40.1 (s, PPh$_2$).

2.5. Synthesis of [RuCl(py)(η^6-p-cymene){P^{i}Pr$_2$(p-Ph$_3$BC$_6$H$_4$)}], 2b

Complex **1b** (0.200 g, 0.203 mmol) was dissolved in CH$_2$Cl$_2$ (10 mL) in a Schlenk tube. Next, excess pyridine (1.6 mL, 19.3 mmol)

was added via syringe, followed by a slight excess of MeOTf (25 μL, 0.224 mmol). After stirring for 1 h a yellow solution was obtained. The solution was then filtered through a short plug of silica gel (∼2 cm W × 1 cm H), and then the volatiles were removed under reduced pressure to yield a bright yellow solid. Yield: 86%. Anal. Calc. for $C_{45}H_{52}BClNPRu$: C, 68.82; H, 6.69; N, 1.78. Found: C, 68.94; H, 6.27; N, 1.50%. ^{1}H NMR (499.9 MHz, CDCl$_3$, 22 °C): 8.67 (br, 2H, o-H of py), 7.77–6.92 (m, 22H, py, Ph and PC$_6$H$_4$B), 5.37, 5.28, 5.00, 4.90 (each m, each 1H, p-cymene), 2.90 (m, 1H, ^{i}Pr of phosphine), 2.42 (m, 1H, ^{i}Pr of phosphine), 2.07 (septet, 1H, ^{i}Pr of p-cymene), 1.47 (m, 6H, ^{i}Pr of phosphine), 1.35 (s, 3H, Me of p-cymene), 1.13 (d, 3H, ^{i}Pr of p-cymene), 1.03 (d, 3H, ^{i}Pr of p-cymene), 0.79 (m, 6H, ^{i}Pr of phosphine). ^{31}P{^{1}H} (202.3 MHz, CDCl$_3$, 22 °C): 34.1 (s, P^iPr$_2$).

2.6. Synthesis of [RuCl(py)(η⁶-p-cymene){PCy₂(p-Ph₃BC₆H₄)}], 2c

Complex **2c** was prepared in a manner analogous to that described for **2a** using complex **1c′** as the precursor. Yield: 21%. Anal. Calc. for $C_{51}H_{60}BClNPRu$: C, 70.34; H, 6.89; N, 1.61. Found: C, 69.79; H, 6.79; N, 1.14%. ^{1}H NMR (499.9 MHz, CDCl$_3$, 22 °C): 8.86 (br, 2H, o-H of py), 7.88–6.97 (m, 22H, py, Ph and PC$_6$H$_4$B), 5.33, 5.22, 5.04, 4.96 (each m, each 1H, p-cymene), 2.44 (septet, 1H, ^{i}Pr of p-cymene), 1.38 (s, 3H, Me of p-cymene), 1.17 (d, 3H, ^{i}Pr of p-cymene), 1.16 (d, 3H, ^{i}Pr of p-cymene), 2.26–1.08 (m, 22H, Cy of phosphine). ^{31}P{^{1}H} (202.3 MHz, CDCl$_3$, 22 °C): 27.51 (s, PCy$_2$).

2.7. Synthesis of [RuCl(MeCN)(η⁶-p-cymene){PPh₂(p-Ph₃BC₆H₄)}], 3a

Complex **1a** (0.234 g, 0.222 mmol) in CH$_2$Cl$_2$ (15 mL) was treated with excess MeCN (580 μL, 11.1 mmol) via syringe. Next, a slight excess of MeOTf (30 μL, 0.266 mmol) was then added via syringe. The solution was allowed to stir for 3 h whereupon a colour change from red to orange was observed. The solvent was removed under reduced pressure to yield an orange solid. The product was redissolved in CH$_2$Cl$_2$ (∼75 mL) and filtered through a plug of silica gel (2 cm W × 1 cm H), discarding the first 50 mL. The volatiles were removed under reduced pressure to yield an orange solid. Yield: 89%. Anal. Calc. for $C_{48}H_{46}BClNPRuX1 \cdot 75CH_2Cl_2$ (the CH$_2$Cl$_2$ was confirmed via ^{1}H NMR spectroscopy): C, 61.98; H, 5.18; N, 1.45. Found: C, 62.06; H, 5.90; N, 1.31%. ^{1}H NMR (499.9 MHz, CDCl$_3$, 22 °C): 7.75–6.89 (m, 29H, Ph and PC$_6$H$_4$B), 5.73, 5.25, 4.87, 4.67 (each m, each 1H, p-cymene), 2.54 (septet, 1H, ^{i}Pr of p-cymene), 1.91 (s, 3H, Me of p-cymene), 1.54 (s, 3H, MeCN), 1.19 (d, 3H, ^{i}Pr of p-cymene), 1.13 (d, 3H, ^{i}Pr of p-cymene). ^{31}P{^{1}H} (202.3 MHz, CDCl$_3$, 22 °C): 31.6 (s, PPh$_2$).

2.8. Synthesis of [RuCl(MeCN)(η⁶-p-cymene){PⁱPr₂(p-Ph₃BC₆H₄)}], 3b

Complex **1b** (0.201 g, 0.204 mmol) was dissolved in CH$_2$Cl$_2$ (20 mL) and treated with excess MeCN (533 μL, 10.2 mmol) via syringe. Next, a slight excess of AgNO$_3$ (0.042 g, 0.245 mmol) was added and the mixture was allowed to stir for 1 h. During this time, the mixture turned orange and a white precipitate deposited. The mixture was filtered through Celite and the orange filtrate was extracted with water (6 × 30 mL) with vigorous shaking. The combined organic layers were dried over MgSO$_4$ and filtered. Removal of the volatiles under reduced pressure yielded a bright orange solid. Yield: 86%. Anal. Calc. for $C_{42}H_{50}BClNPRu$: C, 67.71; H, 6.78; N, 1.88. Found: C, 67.94; H, 7.05; N, 1.62%. ^{1}H NMR (499.9 MHz, CDCl$_3$, 22 °C): 7.70–6.95 (m, 19H, Ph and PC$_6$H$_4$B), 5.39, 5.34, 4.97, 4.83 (each m, each 1H, p-cymene), 3.01 (m, 1H, ^{i}Pr of phosphine), 2.62 (m, 1H, ^{i}Pr of phosphine), 2.27 (septet, 1H, ^{i}Pr of p-cymene), 2.01 (s, 3H, Me of p-cymene), 1.83 (s, 3H, MeCN), 1.41 (m, 6H, ^{i}Pr of phosphine), 1.32 (m, 6H, ^{i}Pr of phosphine), 1.11 (d, 3H, ^{i}Pr of p-cymene), 1.09 (d, 3H, ^{i}Pr of p-cymene). ^{31}P{^{1}H} (202.3 MHz, CDCl$_3$, 22 °C): 37.0 (s, P^iPr$_2$).

2.9. Synthesis of [RuCl(MeCN)(η⁶-p-cymene){PCy₂(p-Ph₃BC₆H₄)}], 3c

Complex **3c** was prepared in a manner analogous to that described for **3b** using complex **1c′** as the precursor. Yield: 30%. Anal. Calc. for $C_{48}H_{58}BClNPRu$: C, 69.67; H, 7.08; N, 1.69. Found: C, 69.67; H, 7.01; N, 1.39%. ^{1}H NMR (499.9 MHz, CDCl$_3$, 22 °C): 7.70–6.98 (m, 19H, Ph and PC$_6$H$_4$B), 5.41, 5.60, 5.00, 4.82 (each m, each 1H, p-cymene), 2.69 (septet, 1H, ^{i}Pr of p-cymene), 1.84 (s, 3H, Me of p-cymene), 1.54 (s, 3H, MeCN), 1.14 (d, 3H, ^{i}Pr of p-cymene), 1.09 (d, 3H, ^{i}Pr of p-cymene) 2.34–0.88 (m, 22H, Cy of phosphine). ^{31}P{^{1}H} (202.3 MHz, CDCl$_3$, 22 °C): 29.72 (s, PCy$_2$).

2.10. X-ray crystallographic studies

Diffraction quality crystals were grown over a period of days at room temperature via slow diffusion of hexanes into saturated CH$_2$Cl$_2$ solutions of either **1a′** or **1b′**. The crystals were mounted on a glass fibre with grease and cooled to −93 °C in a stream of nitrogen gas controlled with a Cryostream Controller 700. Data collection was performed on a Bruker SMART APEX II X-ray diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å), operating at 50 kV and 30 mA over 22 ranges of 2.50–52.00° (**1a′**) or 2.94–52.00°. No significant decay was observed during the data collection. Data were processed using the Bruker AXS Crystal Structure Analysis Package [6]: Data collection: APEX2; cell refinement: SAINT; data reduction: SAINT; structure solution: XPREP and SHELXTL; structure refinement: SHELXTL. Neutral atom scattering factors were taken from Cromer and Waber [7]. The structures were solved by direct methods. Full-matrix least-square refinements minimizing the function $\sum w(F_{o2} - F_{c2})^2$ were applied to each compound. All non-hydrogen atoms were refined anisotropically. All of the H atoms were placed in geometrically calculated positions. For **1b′**, one of the ^{i}Pr groups and one of the Ph groups are disordered. The SHELX commands EDPA, DFIX and SUMP were applied to resolve the disorder of the structure. Graphical representations of the structures were produced using ORTEP-3 [8].

2.10.1. X-ray data for 1a′
$C_{82}H_{73}BCl_2NP_3Ru$, M = 1348.1 g/mol, monoclinic, $P2(1)/n$, a = 10.0396(3) Å, b = 18.0768(6) Å, c = 38.2871(12) Å, α = 90°, β = 95.773(2)°, γ = 90°, Z = 4, V = 6913.2(4) Å^3, D_{calc} = 1.295 g/cm^3, μ(Mo Kα) = 0.419 mm^{-1}, crystal dimensions 0.10 × 0.08 × 0.08 mm^3. The structure was refined by full matrix least-squares on F^2. Convergence to final R_1 = 0.0657 and wR_2 = 0.0953 for 6315 (I > 2Φ(I)) independent reflections, and R_1 = 0.1721 and wR_2 = 0.1298 for all 13,589 (R(int) = 0.1181) independent reflections, with 808 parameters and 0 restraints, were achieved.

2.10.2. X-ray data for 1b′
$C_{77}H_{78}BCl_4NP_3Ru$, M = 1363.99 g/mol, triclinic, $P\bar{1}$, a = 11.0955(2) Å, b = 14.1779(3) Å, c = 22.9304(4) Å, α = 79.4280(10)°, β = 77.2810(10)°, γ = 80.7990(10)°, Z = 2, V = 3431.99(11) Å^3, D_{calc} = 1.320 g/cm^3, μ(Mo Kα) = 0.498 mm^{-1}, crystal dimensions 0.24 × 0.12 × 0.09 mm^3. Convergence to final R_1 = 0.0652 and wR_2 = 0.1457 for 7964 (I > 2Φ(I)) independent reflections, and R_1 = 0.1276 and wR_2 = 0.1778 for all 13,483 (R(int) = 0.0791) independent reflections, with 779 parameters and 11 restraints, were achieved.

3. Results and discussion

3.1. Synthesis of [E][RuCl₂(η⁶-**p**-cymene){PR₂(**p**-Ph₃BC₆H₄)}] (E = Bu₄N⁺ or PNP⁺; R = Ph, ⁱPr or Cy)

The anionic tertiary phosphines examined as part of this work each contain as a common design element a BPh$_3$ group tethered to a general PR$_2$ framework via an aryl linker (see Structure I). In

this way, they represent structurally similar, yet anionic analogues of their neutral counterparts phenyldiarylphosphines and phenyldialkylphosphines. Accordingly, lithiation of (p-BrC$_6$H$_4$)PR$_2$, followed by addition of electrophilic BPh$_3$ provides the anionic monodentate (phosphino)tetraphenylborate ligands [PR$_2$(p-Ph$_3$BC$_6$H$_4$)]$^-$ [3] in relatively good yields. This convenient synthetic strategy allowed us to expand the series to include the synthesis of the desirable cyclohexyl analogue. Although the general procedure permits the isolation of the tetrabutylammonium salts of these ligands, [Bu$_4$N][PR$_2$(p-Ph$_3$BC$_6$H$_4$)], we found it could easily be adapted to include the bis(triphenylphosphine)iminium (PNP$^+$) analogues, [PNP][PR$_2$(p-Ph$_3$BC$_6$H$_4$)] (R = Ph, ^{i}Pr or Cy), since PNP$^+$ is known to form crystalline salts with anions that are often difficult to crystallize (*vide infra*).

As anticipated, the ligands [Bu$_4$N][PR$_2$(p-Ph$_3$BC$_6$H$_4$)] readily cleave the chloride bridge of [RuCl$_2$(η^6-p-cymene)]$_2$ to provide the monomeric half-sandwich adducts [Bu$_4$N][RuCl$_2$(η^6-p-cymene){PR$_2$(p-Ph$_3$BC$_6$H$_4$)}] (R = Ph, **1a**, ^{i}Pr, **1b** or Cy, **1c**) in good yields as orange-red, air-stable powders (Scheme 1). The corresponding PNP$^+$ analogues (**1a′–c′**) could be isolated in a similar fashion starting from [PNP][PR$_2$(p-Ph$_3$BC$_6$H$_4$)]. Alternatively, they could also be prepared via cation exchange simply by stirring the Bu$_4$N$^+$ salts **1a–c** in methanol in the presence of a twofold excess of [PNP]Cl.

3.2. Solid-state structures of **1a′** and **1b′**

In order to confirm the proposed structures of complexes **1a–c** and **1a′–c′**, and to gain a better insight into the impact these new ligands may have on their solid-state structures, we attempted to grow single crystals for X-ray crystallographic studies. Unfortunately, our attempts involving the Bu$_4$N$^+$ salts were often frustrated by the production of oily products despite investigating a variety of crystal-growing conditions. However, the PNP$^+$ salts proved to be better candidates, and after employing conventional slow-diffusion techniques, we were immediately successful in growing single crystals of **1a′** and **1b′** for crystallographic studies.

The ruthenate(II) anions of **1a′** and **1b′** are displayed in Figs. 1 and 2, respectively, along with selected bond distances and angles in the captions. The ruthenium centres of **1a′** and **1b′** adopt the expected three-legged piano-stool coordination geometry typically observed for these complexes. The phosphine ligand in each complex projects between the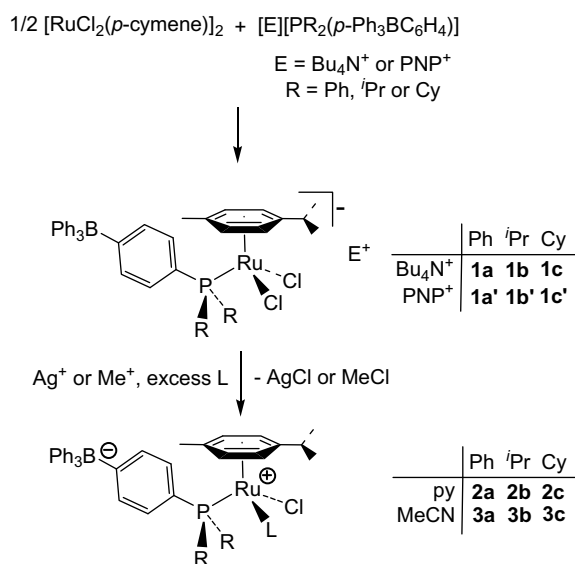 substituents of the arene ligand, approx-imately bisecting C(2)–C(3) in **1a′** and C(5)–C(6) in **1b′** when viewed down the ruthenium-arene centroid axis; this presumably permits minimal steric interactions with the arene methyl and isopropyl substituents. An approximately staggered conformation of the phosphine substituents is observed about the ruthenium–phosphorus axis in each complex. Remarkably, the substituent bearing the bulky BPh$_3$ group is positioned near the arene ligand in both cases. The pseudo-octahedral geometry about the metal in each complex is evidenced by the approximately 90° angles observed for the angles P(1)–Ru(1)–Cl(1), P(1)–Ru(1)–Cl(2) and Cl(1)–Ru(1)–Cl(2), with the η^6-p-cymene ligand occupying three facial coordination sites.

The bond distances and angles observed in the solid-state structures of **1a′** and **1b′** resemble those determined for other structurally characterized analogues. The ruthenium–phosphorus and ruthenium-chloride bond distances (see captions of Figs. 1 and 2) in both complexes compare well with those observed for the neutral complexes [RuCl$_2$(η^6-arene)(PR$_3$)] [9], and for the trichlororuthenate anions in [Ph$_4$P][RuCl$_3$(η^6-p-cymene)] [10], [(dibenzo-18-crown-6)K(μ-Cl)$_3$Ru(η^6-p-cymene)] [11], [RuCl(N-butylimidazole)$_2$(η^6-p-cymene)][RuCl$_3$(η^6-p-cymene)] [12], and [N,N-bis(6-methylpyrid-2-ylium)-(1R,2R)-1,2-diaminocyclohexane][RuCl$_3$(η^6-p-cymene)]$_2$ [13]. However, these same distances in **1a′** are somewhat shorter than those observed in **1b′**, and this may be related to the comparatively smaller size of the phosphine in **1a′**. The longer Ru(1)-centroid distance in **1b′** (1.704 Å) compared to **1a′** (1.683 Å) would also seem to suggest the phosphine [P^{i}Pr$_2$(p-Ph$_3$BC$_6$H$_4$)]$^-$ has a greater steric profile compared to [PPh$_2$(p-Ph$_3$BC$_6$H$_4$)]$^-$. The distances between the metal and the arene carbon atoms are asymmetric in both complexes (2.175(6)–2.251(5) Å for **1a′**; 2.182(6)–2.242(6) Å for **1b′**). In fact, the Ru(1)–C(arene) distances *trans* to the phosphine ligand in each complex are slightly longer than those *trans* to the Ru(1)–Cl(1) or Ru(1)–Cl(2) distances. This is likely linked to the large *trans* influence exerted by the phosphine ligands [9]. Indeed, it has been suggested that the anionic ligands [PR$_2$(p-Ph$_3$BC$_6$H$_4$)]$^-$ in general may exert a greater *trans* influence over their neutral analogues [3].

3.3. Solution NMR spectroscopic studies

In contrast to their neutral counterparts, the solution NMR spectra of complexes **1a–c** and **1a′–c′** unexpectedly proved to be somewhat more complex. For example, multiple sets of *ortho* and *meta* arene hydrogen signals of varying intensities were observed in the ^{1}H NMR spectra of these complexes, rather than the single pair of doublets typically observed for (ideal C_s-symmetric) [RuCl$_2$(η^6-p-cymene)(PR$_3$)] [5a]. Perhaps more revealing, the ^{31}P{^{1}H} NMR spectrum of each complex displays several signals attributed to the single phosphine ligand, compared to the lone singlet observed for the neutral complexes bearing more conventional phosphines [9,14]. Moreover, the number and the relative intensities of the signals vary with the R group on the phosphine, and to a certain extent, the identity of the counterion. Thus, the room temperature ^{31}P{^{1}H} NMR spectra of the R = Ph complexes each reveal *two* closely spaced singlets with substantially different intensities (**1a**: δ = 24.5 and 23.1 ppm, ~9:1; **1a′**: δ = 25.6 and 24.4 ppm, ~7:1; for comparison, the PPh$_3$ ligand of [RuCl$_2$(η^6-p-cymene)(PPh$_3$)] appears at δ = 25.3 ppm [14a]), while under the same conditions, the R = ^{i}Pr and Cy analogues (for example, see Fig. 3) each yield *three* closely spaced singlets (**1b**: δ = 29.2, 27.4 and 25.9 ppm, ~2:2.5:1; **1b′**: δ = 29.8, 28.2 and 26.5 ppm, ~11:7:1; **1c**: δ = 21.4, 19.9 and 18.6 ppm, ~1.5:2.5:1; **1c′**: δ = 21.9, 20.5 and 19.1 ppm, ~6:4:1).

The accumulated NMR evidence seemed to suggest several distinct ruthenium species exist in solution for each complex, despite only one structure being observed in the solid state (at least for **1a′** and **1b′**). There are two possible scenarios we might propose to ex-

1/2 [RuCl$_2$(p-cymene)]$_2$ + [E][PR$_2$(p-Ph$_3$BC$_6$H$_4$)]

E = Bu$_4$N$^+$ or PNP$^+$
R = Ph, ^{i}Pr or Cy

	Ph	^{i}Pr	Cy
Bu$_4$N$^+$	**1a**	**1b**	**1c**
PNP$^+$	**1a′**	**1b′**	**1c′**

Ag$^+$ or Me$^+$, excess L | - AgCl or MeCl

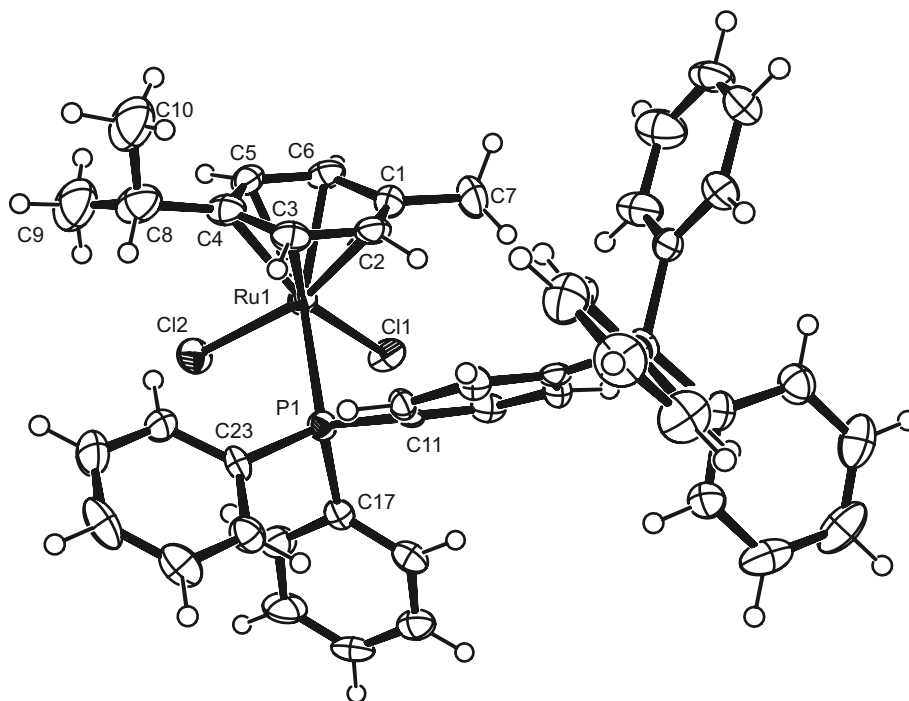|	Ph	^{i}Pr	Cy
py	**2a**	**2b**	**2c**
MeCN	**3a**	**3b**	**3c**

Scheme 1.

Fig. 1. ORTEP representation of the ruthenate anion of **1a**′. Selected bond lengths (Å) and angles (°): Ru(1)–P(1), 2.3534(16); Ru(1)–Cl(1), 2.4149(15); Ru(1)–Cl(2), 2.4149(14); Ru(1)–C(1), 2.212(6); Ru(1)–C(2), 2.201(5); Ru(1)–C(3), 2.175(6); Ru(1)–C(4), 2.231(6); Ru(1)–C(5), 2.228(6); Ru(1)–C(6), 2.251(5); P(1)–Ru(1)–Cl(1), 83.86(5); P(1)–Ru(1)–Cl(2), 89.48(5); Cl(1)–Ru(1)–Cl(2), 87.58(5).
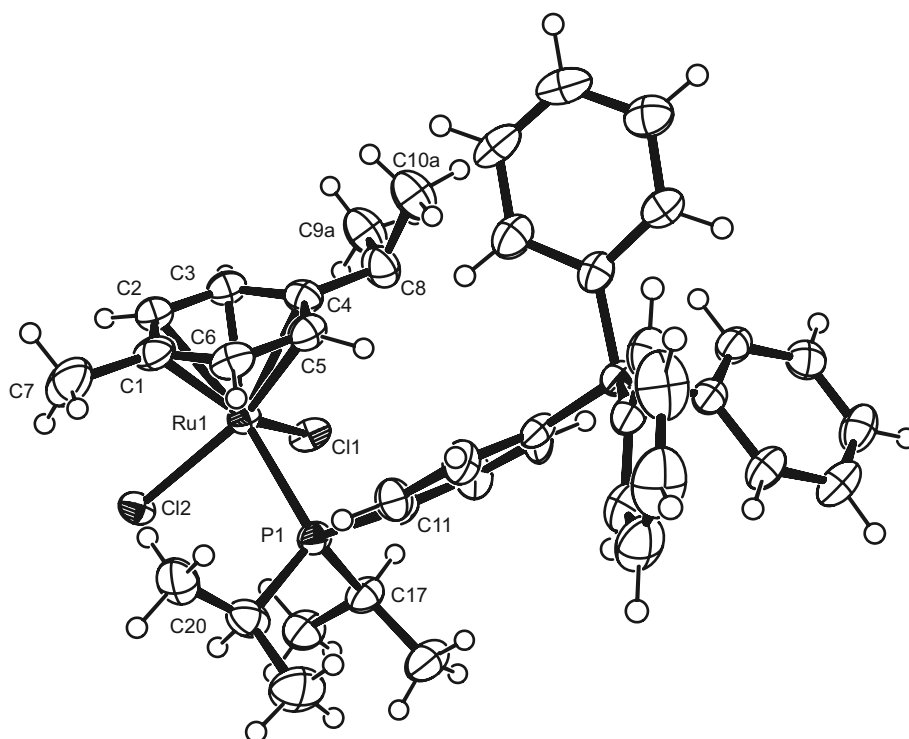

Fig. 2. ORTEP representation of the ruthenate anion of **1b**′. Selected bond lengths (Å) and angles (°): Ru(1)–P(1), 2.3897(15); Ru(1)–Cl(1), 2.4380(13); Ru(1)–Cl(2), 2.4382(13); Ru(1)–C(1), 2.217(5); Ru(1)–C(2), 2.242(6); Ru(1)–C(3), 2.231(6); Ru(1)–C(4), 2.214(6); Ru(1)–C(5), 2.188(5); Ru(1)–C(6), 2.182(6); P(1)–Ru(1)–Cl(1), 88.95(5); P(1)–Ru(1)–Cl(2), 87.11(5); Cl(1)–Ru(1)–Cl(2), 89.75(5).

plain these observations. The first involves the formation of rotational isomers in solution, a result of hindered rotation about the ruthenium–phosphorus bond. The origin of these rotamers in solution would likely be linked to the bulky BPh_3 group tethered to the phosphine. Indeed, hindered rotation about metal–phosphorus bonds has been observed in the arene-metal complexes $[Os(\eta^6\text{-}C_6H_6)(\eta^2\text{-}ON=CMe_2)(PMe^tBu_2)]PF_6$ and $[OsX_2(\eta^6\text{-}C_6R_3H_3)(PH^tBu_2)]$ (R = H or Me; X = Cl or I) [15]. However, no signal coalescence or

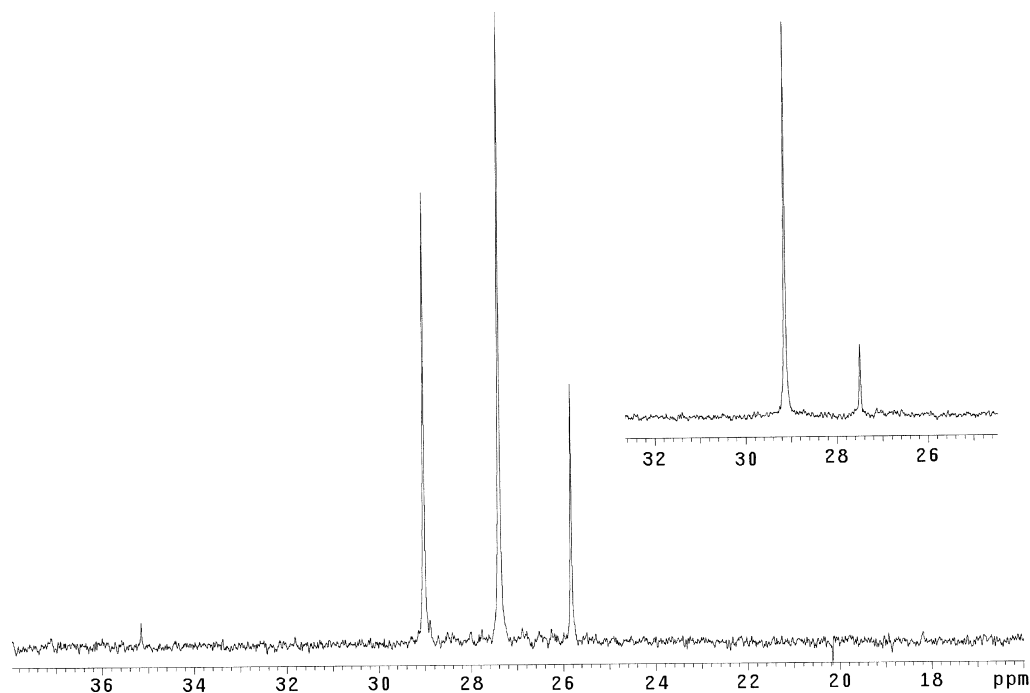**Fig. 3.** ^{31}P{^{1}H} NMR spectra (CDCl$_3$) of complex **1b**, and **1b** in the presence of excess chloride ion (inset).

even signal broadening was observed in the ^{31}P{^{1}H} NMR spectra of complexes **1a–c** up to 80 °C in C$_2$D$_4$Cl$_2$, suggesting these different ruthenium species in solution do not originate from the formation of rotational isomers.

A second plausible, and perhaps more likely scenario which could account for the unusual NMR spectroscopic behaviour in solution is the formation of monomer–dimer equilibria. We see no evidence of phosphine dissociation in the ^{31}P{^{1}H} NMR spectra of **1a–c** and **1a′–c′**. However, dynamic equilibria involving halide dissociation have been observed for other anionic (*p*-cymene)ruthenate(II) complexes [10,11]. Accordingly, we examined the effects of added chloride ion to CDCl$_3$ solutions (~0.04 M) of **1a–c**. In all cases, the reactions proceeded very cleanly, and we noticed (in some instances a dramatic) change in the ^{31}P{^{1}H} NMR spectrum of each complex, with generally only one main peak observed in the presence of excess chloride. When a threefold excess of [Et$_4$N]Cl was added to **1a**, we observed only a marginal change in the intensities of the two ^{31}P signals, and the peak downfield at $\delta = 24.5$ ppm remained dominant. In contrast, complexes **1b** and **1c** responded more dramatically towards adding excess [Et$_4$N]Cl. Thus, with complex **1b** (inset, Fig. 3) one dominant signal at $\delta = 29.2$ ppm was observed; of the other two original upfield signals, one ($\delta = 27.4$ ppm) substantially decreased in intensity, while the other ($\delta = 25.9$ ppm) disappeared completely. An almost identical response was also witnessed for complex **1c**: a single dominant peak at $\delta = 21.4$ ppm was observed, while the remaining two signals upfield became considerably less intense ($\delta = 19.9$ ppm) or completely disappeared ($\delta = 18.6$ ppm). The ^{1}H NMR spectra of **1a–c**, particularly in the coordinated arene region, also became dramatically simplified upon adding excess chloride ion, with each now revealing a prominent pair of doublets corresponding to the *ortho* and *meta* hydrogens of the arene ring (**1a**, $\delta = 5.11$ and 4.97 ppm; **1b**, $\delta = 4.94$ and 4.89; **1c**, $\delta = 4.89$ and 4.83), consistent with that observed for [RuCl$_2$(η^6-*p*-cymene)(PR$_3$)] [9a].

We also explored how the equilibria responded to the addition of an excess of a chloride scavenger. Unfortunately, the NMR spectra were not as clean (e.g., reactions involving **1a** yielded unappealing mixtures of products). Nonetheless, when solutions of complex **1b** in CD$_2$Cl$_2$ were treated with a twofold excess of MeOTf, the

^{31}P{^{1}H} spectra revealed the complete consumption of the complexes with downfield signals at $\delta = 29.2$ ppm and $\delta = 27.4$ ppm, and a single albeit broad signal at δ 26 ppm dominated the spectrum (~75%). Similarly, for **1c**, the complexes with signals downfield at $\delta = 21.4$ and $\delta = 19.9$ ppm disappeared completely, with the main product now appearing at δ 19 ppm (~80%). In both cases, a sharp resonance at $\delta = 3.03$ ppm in the ^{1}H NMR spectrum revealed the evolution of chloromethane [16].

Although we cannot unequivocally assign structures to all of the species observed in solution for **1a–c** and **1a′–c′**, we might propose the equilibrium structures depicted in Scheme 2. Thus, complex **1a**, and presumably **1a′**, appear to favour monomeric species **A** in solution, since little response was observed to the addition of excess chloride ion. In contrast, complexes **1b/b′** and **1c/c′** appear to show a greater tendency towards chloride dissociation yielding bridged species, **B** and **C**, and only favour monomeric species **A** in the presence of excess chloride ion. Interestingly, the ^{31}P peak ratios remained essentially unchanged in CDCl$_3$, CD$_2$Cl$_2$ or C$_2$D$_4$Cl$_2$, suggesting the equilibria at least were not strongly dependent on the identity of the chlorinated solvent. Unfortunately, we were unsuccessful in isolating any bridged species from solutions of **1a–c** or **1a′–c′**. Nonetheless, similar complexes have been identified or isolated for other ruthenium(II)-arene complexes [9d,17]. The *extent* of unassisted spontaneous chloride loss from complexes **1a–c** and **1a′–c′** in solution is intriguing, and perhaps is linked to phosphine basicity here. Indeed, complexes **1a** and **1a′** bearing the comparatively weaker donor phosphine [PPh$_2$(*p*-Ph$_3$BC$_6$H$_4$)]$^-$ appear to show little tendency toward chloride dissociation since species **A** dominates in solution. However, bridged species (**B** and **C**) appear to form more readily in solutions containing complexes **1b/1b′** and **1c/1c′** which bear the stronger donor phosphines [PR$_2$(*p*-Ph$_3$BC$_6$H$_4$)]$^-$ (R = ^{i}Pr or Cy).

3.4. Synthesis of [RuCl(L)(η^6-p-cymene){PR$_2$(p-Ph$_3$BC$_6$H$_4$)}] (R = Ph, ^{i}Pr or Cy; L = MeCN or py)

Intrigued by these results, we next turned our attention towards exploring the possibility of complexes **1a–c** or **1a′–c′** functioning as precursors to formally neutral, zwitterionic complexes
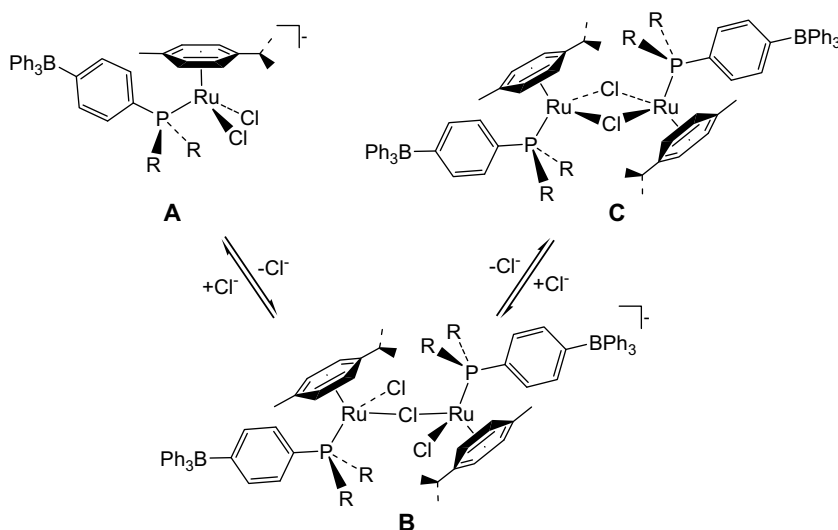
Scheme 2.

by way of chloride ligand removal (Scheme 1). Our initial efforts centred on trapping the zwitterions with suitable ligands with the anticipation of forming stable 18-electron complexes. Interestingly, the choice of Lewis acid was critical in effecting halide removal, however we found AgNO$_3$ or MeOTf were effective in all reactions examined (AgNO$_3$ was usually favoured in order to facilitate aqueous extraction of [Bu$_4$N]NO$_3$). Thus, treating either **1a–c** or **1a′–c′** with AgNO$_3$ or MeOTf in the presence of excess pyridine or acetonitrile yielded the 18-electron zwitterionic complexes [RuCl(py)(η^6-*p*-cymene){PR$_2$(*p*-Ph$_3$BC$_6$H$_4$)}] (R = Ph, **2a**; R = ^{i}Pr, **2b**; R = Cy, **2c**) and [RuCl(MeCN)(η^6-*p*-cymene){PR$_2$(*p*-Ph$_3$BC$_6$H$_4$)}] (R = Ph, **3a**; R = ^{i}Pr, **3b**; R = Cy, **3c**) as air-stable, orange-yellow powders.

Complexes **2a–c** and **3a–c** were characterized in solution using ^{1}H and ^{31}P{^{1}H} NMR spectroscopy, and the proposed formulae were confirmed by microanalytical data. The chirality of the metal centres was clearly demonstrated in their respective ^{1}H NMR spectra, and revealed diastereotopic methyl signals for the arene isopropyl substituent (and, for **2b** and **3b**, the isopropyl substituents of the phosphine ligands), as well as four individual arene hydrogen atom signals [18]. The ^{1}H NMR spectra of the pyridine adducts also revealed signals corresponding to the *ortho*-pyridine hydrogens with chemical shifts diagnostic of coordinated pyridine [19] (for **2a**, δ = 8.91 ppm; for **2b**, δ = 8.67 ppm; for **2c**, δ = 8.86), while the acetonitrile adducts showed signals corresponding to coordinated acetonitrile (for **3a**, δ = 1.54 ppm; for **3b**, δ = 1.83 ppm; for **3c**, δ = 1.54 ppm). We note that *neutral* complexes **2a–c** and **3a–c** produce only one sharp signal in their ^{31}P{^{1}H} NMR spectra, possibly suggesting the importance of complex charge on chloride dissociation in solution for **1a–c** and **1a′–c′**.

4. Summary

Some interesting observations have emerged from this preliminary work. The coordination chemistry of the anionic phosphines [PR$_2$(*p*-Ph$_3$BC$_6$H$_4$)]$^-$ appears to mimic their neutral analogues in ruthenium-arene chemistry to some extent. However, our results suggest that the anionic properties of these phosphines encourage chloride dissociation in [RuCl$_2$(η^6-*p*-cymene){PR$_2$(*p*-Ph$_3$BC$_6$H$_4$)}]$^-$, with the extent of dissociation possibly dictated by their electron-releasing characteristics. This behaviour, to the best of our knowledge, is unique in [RuCl$_2$(η^6-*p*-cymene)(PR$_3$)] chemistry. These complexes also function as convenient precursors to formally neutral zwitterionic complexes via chloride ligand removal, which are readily trapped as their solvated adducts. We are currently exploring further the role of these novel phosphine ligands in ruthenium half-sandwich chemistry, and hope to report these results at a later date.

Appendix A. Supplementary material

CCDC 687100 and 687101 contain the supplementary crystallographic data for complexes **1a′** and **1b′**. 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.2008.06.013.

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