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Ruthenium piano-stool complexes containing mono- or bidentate pyrrolidinylalkylphosphines and their reactions with small molecules

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ABSTRACT

Ruthenium piano-stool complexes incorporating the new bidentate aminoalkylphosphine ligand 1,2-bis(dipyrrolidin-1-ylphosphino)ethane (dpyrpe, **I**) or its monodentate counterpart bis(pyrrolidin-1-yl) methylphosphine (pyr_2PMe, **II**) have been prepared, [(C_5R_5)RuCl(PP)] (R = Me and PP = dpyrpe, **1**; R = Me and PP = $(pyr_2PMe)_2$, **2**; R = H and PP = dpyrpe, **3**). Complexes **2** and **3** have been characterized by X-ray crystallography. Complexes **1** and **2** react with $NaBAr^f_4$ in the presence of ligand L to yield [Cp^*Ru(L)(dpyrpe-κ^2P)][BAr^f_4] (L = MeCN, **4a**; CO, **4b**; N_2, **4c**) and [Cp^*Ru(L)(pyr_2PMe)$_2$][BAr^f_4] (L = MeCN, **5a**; CO, **5b**; N_2, **5c**). Complex **4a** was crystallographically characterized. The CO complexes **4b** and **5b** were examined using IR spectroscopy in an attempt to establish the electron-donating capabilities of **I** and **II**. Complex **1** oxidatively adds H_2 in the presence of $NaBAr^f_4$ to yield the Ru(IV) dihydride [Cp^*RuH_2(dpyrpe-κ^2P)][BAr^f_4], **7**.

1. Introduction

The long-standing interest in modifying the reactivity, selectivity and/or stability of homogeneous metal-based catalysts has led to the development of a multitude of unique and innovative ligand systems displaying diverse structures and properties. Undoubtedly, phosphorus-based ligands have likely received the greatest attention [1] since one of the most attractive features of the phosphine ligand within the context of rational ligand design is the relative ease with which both the steric and electronic properties of the phosphine may be tailored simply by modifying the substituents on the phosphorus atom(s).

In recent years, we have developed an interest in exploring the use of novel phosphine ligands which possess exceptional electron-donating properties [2]. In general, many of the more conventional strongly-donating phosphines typically incorporate substituents that make them rather bulky (*e.g.*, $^tBu_3P$ or Cy_3P). Alternatively, bis(pyrrolidin-1-yl)alkylphosphines [3] represent a unique class of hybrid aminoalkylphosphine ligand that possesses significantly strong donor properties maximized through a specific combination of hydrocarbyl and pyrrolidinyl substituents on the phosphorus atom. They are especially attractive since the pyrrolidinyl group is not particularly large, yet π-donation of the lone pair on the nitrogen of the pyrrolidine ring towards the phosphorus atom, together with the inductive donor properties of the alkyl substituent, lead to an overall enhancement of the donor power of the phosphine ligand [3b–e]. Thus, they deliver a unique combination of steric and electronic effects compared to their more conventional counterparts. Indeed, bis(pyrrolidin-1-yl)*tert*-butylphosphine is proposed to be one of the most strongly-donating tertiary phosphines known [3c], yet it is not especially large.

We were intrigued by this rather novel class of phosphine, which is capable of delivering the donor strength normally reserved for the bulkiest of phosphines, yet remains moderately sized. We were particularly interested in pairing these phosphines with Cp^* – itself a good donor auxiliary – in ruthenium chemistry in an effort to produce an exceptionally reactive metal centre. We report herein some of our preliminary results.

2. Experimental

All experiments and manipulations were conducted under an inert atmosphere of prepurified nitrogen or argon using standard Schlenk techniques. Hexanes, toluene and CH_2Cl_2 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]. Diethyl ether and THF were freshly distilled from sodium metal under argon. Acetonitrile was dried and stored over activated 4A molecular sieves in a bulb with

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a Teflon tap, and purged with N_2 before use. 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: $CDCl_3$ (anhydrous $CaCl_2$); CD_2Cl_2 (CaH_2); C_6D_6 (sodium metal); CD_3CN (P_2O_5). NMR spectra (^1H and $^{31}P\{^1H\}$) were obtained using a Varian Unity INOVA 500 MHz spectrometer, with chemical shifts (in ppm) referenced to residual protio solvent peaks (^1H) or external 85% H_3PO_4 (^{31}P). Infrared spectra were acquired using a Nicolet 380 FT-IR spectrometer. Elemental analyses were performed on a CEC 240XA analyzer by the Lakehead University Instrumentation Laboratory. The ligand bis(pyrrolidin-1-yl)methylphosphine was prepared using a modification of a literature procedure [3c]. The ruthenium precursors (Cp^*RuCl_2), $(Cp^*RuCl)_4$ and $CpRuCl(PPh_3)_2$ were prepared as reported [5].

2.1. Synthesis of 1,2-bis(dipyrrolidin-1-ylphosphino)ethane (dpyrpe), **I**

Ligand **I** was prepared using a modified literature procedure [3c]. $Cl_2PCH_2CH_2PCl_2$ (2.00 g, 8.64 mmol) was added to a flame-dried Schlenk tube/dropping funnel assembly, followed by dry diethyl ether (40 mL). The solution was then cooled in an ice-water bath. Next, pyrrolidine (7.1 mL, 86.4 mmol) in dry diethyl ether (20 mL) was added dropwise to the cooled solution over *ca.* 5 min with vigorous stirring yielding copious amounts of white solid. The bath was removed and the mixture was allowed to stir for 4 h. The mixture was then filtered through Celite into a flame-dried flask. Removal of the volatiles under reduced pressure yielded a free-flowing, extremely air-sensitive white solid. Yield: 2.72 g (85%). ^1H NMR (499.9 MHz, C_6D_6, 22 °C): 3.15 (m, 16H, $-CH_2NCH_2-$), 2.06 (m, 4H, $-PCH_2CH_2P-$), 1.52 (m, 16H, $-NCH_2CH_2CH_2CH_2-$). $^{31}P\{^1H\}$ NMR (202.3 MHz, C_6D_6, 22 °C): 72.8 (s, $-PCH_2CH_2P-$).

2.2. Synthesis of [$Cp^*RuCl(dpyrpe-\kappa^2P)$], **1**

2.2.1. Method A

$(Cp^*RuCl)_4$ (0.175 g, 0.161 mmol) was dissolved in hexanes (10 mL). Next, ligand **I** (0.262 g, 0.708 mmol) in diethyl ether was added via syringe to the hexanes solution, and the mixture was allowed to stir for 1 h. Next, the mixture was evaporated to dryness under reduced pressure, and then the orange product was washed with a small volume of hexanes (~2–3 mL). Yield: 0.372 g (90%). Anal. Calcd. for $C_{28}H_{51}ClN_4P_2Ru$: C, 52.4; H, 8.00; N, 8.72. Found: C, 52.7; H, 7.80; N, 8.61. ^1H NMR (499.9 MHz, C_6D_6, 22 °C): 3.18 (m, 8H, $-CH_2NCH_2-$), 3.11 (m, 4H, $-PCH_2CH_2P-$), 2.92 (m, 8H, $-CH_2NCH_2-$), 1.77–1.71 (m, 16H, $-NCH_2CH_2CH_2CH_2-$), 1.66 (s, 15H, Cp^*). $^{31}P\{^1H\}$ NMR (202.3 MHz, C_6D_6, 22 °C): 144.4 (s, $-PCH_2CH_2P-$).

2.2.2. Method B

$(Cp^*RuCl_2)_2$ (0.200 g, 0.325 mmol) was dissolved in THF (15 mL). Next, ligand **I** (0.241 g, 0.650 mmol) in diethyl ether was added via syringe, followed by excess zinc powder (0.200 g). The mixture was stirred for 30 min, and slowly became orange. The volatiles were then removed under reduced pressure, and the product was extracted with CH_2Cl_2 (2 × 10 mL) and filtered through Celite. Removal of the volatiles under reduced pressure yielded an orange solid. Yield: 0.381 g (91%). The NMR spectroscopic data of the orange solid were identical to the product isolated using Method A.

2.3. Synthesis of [$Cp^*RuCl(pyr_2PMe)_2$], **2**

2.3.1. Method A

To a hexanes (10 mL) suspension of $(Cp^*RuCl)_4$ (0.040 g, 0.037 mmol) was added a diethyl ether solution of ligand **II** (0.055 g, 0.294 mmol) via syringe. The mixture was allowed to stir for 1 h, at which time the volatiles were removed *in vacuo* yielding a bright orange, oily solid. The solid was redissolved in diethyl ether (4 mL) and placed into a cold bath (~−60 °C) to facilitate precipitation. After standing for several minutes, a microcrystalline bright orange solid had deposited. The supernatant was cannulated off, and the product was dried under reduced pressure. Yield: 0.072 g (76%). Anal. Calcd. for $C_{28}H_{53}N_4P_2ClRu$: C, 52.2; H, 8.29; N, 8.70. Found: C, 52.2; H, 8.40; N, 8.45. ^1H NMR (499.9 MHz, C_6D_6, 22 °C): 3.20, 3.07, 2.90 (3 × m, 16H, $-CH_2NCH_2-$), 1.67 (s, 15H, Cp^*), 1.60 (m, 22H, $-NCH_2CH_2CH_2CH_2-$ and PCH_3). $^{31}P\{^1H\}$ NMR (202.3 MHz, C_6D_6, 22 °C): 106.5 (br, pyr_2PMe). $^{31}P\{^1H\}$ NMR (202.3 MHz; CD_2Cl_2, −50 °C): 101.1, 111.0 (dd, $^2J_{PP}$ = 69 Hz, pyr_2PMe).

2.3.2. Method B

To a THF (10 mL) solution of $(Cp^*RuCl_2)_2$ (0.050 g, 0.0814 mmol) was added a diethyl ether solution of ligand **II** (0.061 g, 0.326 mmol) via syringe, followed by an excess of zinc powder (0.053 g, 0.814 mmol) against a positive flow of nitrogen. The mixture was allowed to stir for 30 min, at which time the volatiles were removed *in vacuo* yielding a yellow-green oily solid. The solid was dissolved in CH_2Cl_2 (7 mL) and filtered through Celite. Upon removing the volatiles under reduced pressure, a bright orange, oily solid was obtained. The solid was redissolved in diethyl ether (4 mL) and placed into a cold bath (−60 °C) to facilitate precipitation. After standing for several minutes, a microcrystalline bright orange solid had deposited. The supernatant was cannulated off, and the product was dried under reduced pressure. Yield: 0.156 g (74%). The NMR spectroscopic data of the orange solid were identical to the product isolated using Method A.

2.4. Synthesis of [$CpRuCl(dpyrpe-\kappa^2P)$], **3**

$CpRuCl(PPh_3)_2$ (0.095 g, 0.131 mmol) was dissolved in toluene (5 mL). Ligand **I** (0.049 g, 0.131 mmol) in diethyl ether was added via syringe, and the solution was refluxed for 2 h. The yellow-orange solution was allowed to cool to room temperature, and then it was cannulae transferred to a second flask in order to separate it from a small amount of dark brown material that had deposited. The volatiles were removed under reduced pressure, and then the orange residue was redissolved in diethyl ether (4 mL). The solution was cooled to −78 °C for several hours, after which time small orange microcrystals had deposited. The supernatant was cannulated off, and the crystals were dried under reduced pressure. Yield: 0.042 g (56%). Anal. Calcd. for $C_{23}H_{41}ClN_4P_2Ru$: C, 48.3; H, 7.22; N, 9.79. Found: C, 48.8; H, 6.95; N, 10.0. ^1H NMR (499.9 MHz, C_6D_6, 22 °C): 4.85 (s, 5H, Cp), 3.51, 3.34, 2.84, 2.74 (4 × m, 16H, $-CH_2NCH_2-$), 2.28 (m, 4H, $-PCH_2CH_2P-$), 1.79, 1.50 (2 × m, 16H, $-NCH_2CH_2CH_2CH_2-$). $^{31}P\{^1H\}$ NMR (202.3 MHz, C_6D_6, 22 °C): 149.8 (s, $-PCH_2CH_2P-$).

2.5. Synthesis of [$Cp^*Ru(NCMe)(dpyrpe-\kappa^2P)$][$BAr^f_4$], **4a**

Complex **1** (0.103 g, 0.160 mmol) and $NaBAr^f_4$ (0.142 g, 0.160 mmol) were combined and dissolved in a mixture of CH_2Cl_2 (5 mL) and MeCN (5 mL). The mixture was allowed to stir for 2 h. After this time, the cloudy, pale yellow mixture was filtered through Celite. Upon removing the volatiles under reduced pressure, a pale yellow solid was produced. The solid was redissolved in CH_2Cl_2 (~2 mL) and excess hexanes (20 mL) were added. After standing for several minutes, a microcrystalline yellow solid had deposited. The supernatant was cannulated off, and the product was dried under reduced pressure. Yield: 0.196 g (81%). Anal. Calcd. for $C_{62}H_{66}BF_{24}N_5P_2Ru\cdot 2CH_2Cl_2$: C, 45.7; H, 4.20; N, 4.17. Found: C, 45.5; H, 3.92; N, 4.10. ^1H NMR (499.9 MHz, $CDCl_3$, 22 °C): 7.72 (s, 8H, *o*-H

of Ar^f), 7.55 (s, 4H, *p*-H of Ar^f), 3.14 (br, 4H, $-PCH_2CH_2P-$), 3.09, 3.00, 2.87 (3 × m, 16H, $-CH_2NCH_2-$), 2.11 (s, 3H, CH_3CN), 1.78 (m, 16H, $-NCH_2CH_2CH_2CH_2-$), 1.66 (s, 15H, Cp^*). $^{31}P\{^1H\}$ NMR (202.3 MHz, $CDCl_3$, 22 °C): 136.4 (s, $-PCH_2CH_2P-$).

2.6. Synthesis of [Cp*Ru(CO)(dpyrpe-κ²P)][BArᶠ₄], 4b

Complex **1** (0.154 g, 0.240 mmol) and $NaBAr^f_4$ (0.213 g, 0.240 mmol) were combined and dissolved in diethyl ether (10 mL) under CO. The mixture was allowed to stir for 1 h under CO, and then it was filtered through Celite. Removal of the volatiles under reduced pressure yielded a pale yellow solid. Yield: 0.289 g (80%). Analytically pure samples were prepared by recrystallizing the solid from diethyl ether/hexanes via slow diffusion. Anal. Calcd. for $C_{61}H_{63}BF_{24}N_4OP_2Ru$: C, 48.9; H, 4.24; N, 3.74. Found: C, 48.9; H, 4.31; N, 3.59. IR (Nujol, NaCl): ν(CO) = 1960 cm^{-1}. ^1H NMR (499.9 MHz, $CDCl_3$, 22 °C): 7.63 (s, 8H, *o*-H of Ar^f), 7.45 (s, 4H, *p*-H of Ar^f), 3.20 (br m, 4H, $-PCH_2CH_2P-$), 3.01, 2.94, 2.82 (3 × m, 16H, $-CH_2NCH_2-$), 1.90 (m, 8H, $-NCH_2CH_2CH_2CH_2-$), 1.81 (s, 15H, Cp^*), 1.73 (m, 8H, $-NCH_2CH_2CH_2CH_2-$). $^{31}P\{^1H\}$ NMR (202.3 MHz, $CDCl_3$, 22 °C): 130.4 (s, $-PCH_2CH_2P-$).

2.7. Synthesis of [Cp*Ru(N₂)(dpyrpe-κ²P)][BArᶠ₄], 4c

Complex **1** (0.085 g, 0.132 mmol) and $NaBAr^f_4$ (0.117 g, 0.132 mmol) were combined, dissolved in diethyl ether (10 mL) and stirred under N_2 for 30 min. The mixture was then filtered through Celite, and the volatiles were removed under reduced pressure to yield a yellow-orange solid. Yield: 0.144 g (73%). All attempts to recrystallize the product resulted in dinitrogen loss. IR (Nujol, NaCl): ν(N_2) = 2148 cm^{-1}. ^1H NMR (499.9 MHz, CD_2Cl_2, 22 °C): 7.64 (s, 8H, *o*-H of Ar^f), 7.48 (s, 4H, *p*-H of Ar^f), 3.03 (m, 8H, $-CH_2NCH_2-$), 2.90 (m, 4H, $-PCH_2CH_2P-$), 2.79 (m, 8H, $-CH_2NCH_2-$), 1.80 (m, 8H, $-NCH_2CH_2CH_2CH_2-$), 1.73 (m, 8H, $-NCH_2CH_2CH_2CH_2-$), 1.68 (s, 15H, Cp^*). $^{31}P\{^1H\}$ NMR (202.3 MHz, $CDCl_3$, 22 °C): 131.2 (s, $-PCH_2CH_2P-$).

2.8. Synthesis of [Cp*Ru(NCMe)(pyr₂PMe)₂][BArᶠ₄], 5a

Complex **2** (0.100 g, 0.155 mmol) and $NaBAr^f_4$ (0.138 g, 0.155 mmol) were combined and dissolved in a mixture of diethyl ether (5 mL) and MeCN (5 mL). The mixture was allowed to stir for 1 h, at which time the volatiles were removed *in vacuo* yielding a pale yellow solid. The solid was redissolved in CH_2Cl_2 (7 mL) and filtered through Celite. Upon removing the volatiles under reduced pressure, a light yellow solid was produced. The solid was triturated in hexanes (15 mL) for 1 h. After standing for several minutes, a microcrystalline pale yellow solid had deposited. The supernatant was cannulated off, and the product was dried under reduced pressure. Yield: 0.202 g (86%). Anal. Calcd. for $C_{62}H_{68}BF_{24}N_5P_2Ru\cdot CH_2Cl_2$: C, 47.4; H, 4.42; N, 4.38. Found: C, 47.1; H, 4.23; N, 3.94. ^1H NMR (499.9 MHz, CD_3CN, 22 °C): 7.64 (s, 8H, *o*-H of Ar^f), 7.48 (s, 4H, *p*-H of Ar^f), 3.08, 3.00, 2.78 (3 × m, 16H, $-CH_2NCH_2-$), 2.35 (3H, s, CH_3CN), 1.86, 1.77, 1.70 (3 × m, 16H, $-NCH_2CH_2CH_2CH_2-$), 1.50 (s, 15H, Cp^*), 1.42 (6H, PCH_3). $^{31}P\{^1H\}$ NMR (202.3 MHz, CD_3CN, 22 °C): 103.5 (s, pyr_2PMe).

2.9. Synthesis of [Cp*Ru(CO)(pyr₂PMe)₂][BArᶠ₄], 5b

Complex **2** (0.100 g, 0.155 mmol) and $NaBAr^f_4$ (0.138 g, 0.155 mmol) were combined and then suspended in hexanes (10 mL). The mixture was allowed to stir for 1 h under CO, at which time the volatiles were removed *in vacuo* yielding an off-white solid. The solid was redissolved in CH_2Cl_2 (7 mL) and the solution was filtered through Celite. Upon removing the volatiles under reduced pressure, an off-white solid was produced. The solid was triturated in hexanes (15 mL) for 1 h. After standing for several minutes, a microcrystalline solid had deposited. The supernatant was cannulated off, and the product was dried under reduced pressure. Yield: 0.200 g (86%). Anal. Calcd. for $C_{61}H_{65}BF_{24}N_4OP_2Ru$: C, 48.8; H, 4.37; N, 3.74. Found: C, 48.6; H, 4.38; N, 3.62. IR (Nujol, NaCl): ν(CO) = 1957 cm^{-1}. ^1H NMR (499.9 MHz, $CDCl_3$, 22 °C): 7.62 (s, 8H, *o*-H of Ar^f), 7.45 (s, 4H, *p*-H of Ar^f), 2.98–2.86 (m, 16H, $-CH_2NCH_2-$), 1.79 (m, 16H, $-NCH_2CH_2CH_2CH_2-$), 1.69 (s, 15H, Cp^*), 1.59 (s, 6H, PCH_3). $^{31}P\{^1H\}$ NMR (202.3 MHz, C_6D_6, 22 °C): 100.3 (s, pyr_2PMe).

2.10. Synthesis of [Cp*Ru(N₂)(pyr₂PMe)₂][BArᶠ₄], 5c

Complex **2** (0.015 g, 0.0233 mmol) and $NaBAr^f_4$ (0.020 g, 0.0233 mmol) were combined in a sealable NMR tube and dissolved in C_6D_6 (0.5 mL) under N_2. The mixture was agitated for about 1 min, after which the contents were analyzed via ^{31}P and ^1H NMR spectroscopy. ^1H NMR (499.9 MHz, C_6D_6, 22 °C): 7.58 (s, 8H, *o*-H of Ar^f), 7.42 (s, 4H, *p*-H of Ar^f), 2.94, 2.76 (2 × m, 16H, $-CH_2NCH_2-$), 1.72,1.67 (2 × m, 16H, $-NCH_2CH_2CH_2CH_2-$), 1.50 (s, 15H, Cp^*), 1.44 (m, 6H, PCH_3). $^{31}P\{^1H\}$ NMR (202.3 MHz, C_6D_6, 22 °C): 98.5 (s, pyr_2PMe).

2.11. Synthesis of [Cp*Ru(CO)(dppe-κ²P)][BArᶠ₄], 6a

$Cp^*RuCl(PPh_3)_2$ (0.100 g, 0.125 mmol) and dppe (0.050 g, 0.125 mmol) were combined and stirred in C_6H_6 (10 mL) for 1.5 h. After this time, the volatiles were stripped away under reduced pressure, $NaBAr^f_4$ (0.111 g, 0.125 mmol) was added, and then the flask was evacuated/purged with CO. Next, diethyl ether (10 mL) was added and the mixture was allowed to stir under CO for 1 h. The murky, pale yellow mixture was then filtered through Celite and then the volatiles were stripped from the filtrate under reduced pressure. The product was triturated with hexanes (10 mL) for ~5 min yielding a pale yellow solid. Yield: 0.149 g (78%). An analytically pure sample was prepared by recrystallizing the product from diethyl ether/hexanes. Anal. Calcd. for $C_{69}H_{51}BF_{24}OP_2Ru$: C, 54.3; H, 3.37. Found: C, 54.5; H, 3.34. IR (Nujol, NaCl): ν(CO) = 1961 cm^{-1}. ^1H NMR (499.9 MHz, $CDCl_3$, 22 °C): 7.73 (s, 8H, *o*-H of Ar^f), 7.56–747 (m, 20H, *p*-H of Ar^f and Ph), 7.18–7.15 (m, 4H, Ph), 2.57 (m, 4H, $-PCH_2CH_2P-$), 1.59 (s, 15H, Cp^*). $^{31}P\{^1H\}$ NMR (202.3 MHz, $CDCl_3$, 22 °C): 71.8 (s, $-PCH_2CH_2P-$).

2.12. Synthesis of [Cp*Ru(CO)(Ph₂PMe)₂][BArᶠ₄], 6b

$Cp^*RuCl(PPh_3)_2$ (0.100 g, 0.125 mmol) was dissolved in C_6H_6 (10 mL). To this solution, Ph_2PMe (47 μL, 0.250 mmol) was added via syringe. The mixture was then stirred for 1.5 h. After this time, the volatiles were stripped away under reduced pressure, $NaBAr^f_4$ (0.111 g, 0.125 mmol) was added, and then the flask was evacuated/purged with CO. Next, diethyl ether (10 mL) was added and the mixture was allowed to stir under CO for 1 h. The murky, pale yellow mixture was then filtered through Celite and then the volatiles were stripped from the filtrate under reduced pressure. The product was triturated with hexanes (10 mL) for ~5 min yielding a pale yellow solid. Yield: 0.132 g (69%). An analytically pure sample was prepared by recrystallizing the product from diethyl ether/hexanes. Anal. Calcd. for $C_{69}H_{53}BF_{24}OP_2Ru\cdot Et_2O$: C, 54.7; H, 3.96. Found: C, 54.7; H, 3.53. IR (Nujol, NaCl): ν(CO) = 1951 cm^{-1}. ^1H NMR (499.9 MHz, $CDCl_3$, 22 °C): 7.75 (s, 8H, *o*-H of Ar^f), 7.61–7.25 (m, 16H, Ph), 7.54 (s, 4H, *p*-H of Ar^f), 6.81 (m, 4H, Ph), 1.50 (s, 15H, Cp^*), 1.37 (m, 6H, PCH_3). $^{31}P\{^1H\}$ NMR (202.3 MHz, $CDCl_3$, 22 °C): 26.3 (s, Ph_2PMe).

2.13. Synthesis of [Cp*RuH$_2$(dpyrpe-κ^{2}P)][BAr$^f_4$], 7

Compound **1** (0.020 g, 0.0311 mmol) and NaBAr$^f_4$ (0.028 g, 0.0311 mmol) were combined in an NMR tube fitted with a rubber septum. The contents of the tube were evacuated and purged with H_2, and then Ar-purged CD_2Cl_2 (0.5 mL) was added via syringe. The mixture was allowed to mix (tumbling) for 30 min. NMR spectroscopy revealed clean and quantitative conversion to compound **7**. ^{1}H NMR (499.9 MHz, CD_2Cl_2, 22 °C): 7.72 (s, 8H, *o*-H of Ar^f), 7.55 (s, 4H, *p*-H of Ar^f), 3.15 (br m, 4H, −PCH$_2$CH$_2$P−), 3.02−2.93 (br m, 16H, −CH$_2$NCH$_2$−), 2.03 (s, 15H, Cp*), 1.91−1.83 (br m, 16H, −NCH$_2$CH$_2$CH$_2$CH$_2$−), −9.76 (t, $^2J_{PH}$ = 29 Hz, 2H, Ru−H). ^{31}P{^{1}H} NMR (202.3 MHz, CD_2Cl_2, 22 °C): 135.6 (s, -PCH$_2$CH$_2$P-).

2.14. X-ray crystallographic studies

Diffraction quality crystals were grown over a period of days at room temperature either by slow evaporation of a concentrated diethyl ether solution (**2** and **3**), or by slow diffusion of hexanes into a concentrated CH_2Cl_2 solution (**4a**). 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 K_α radiation (λ = 0.71073 Å), operating at 50 kV and 30 mA over 2θ ranges of 3.46 ∼ 52.00° (**2**), 4.02 ∼ 52.00° (**3**) or 4.28 ∼ 52.00° (**4a**). No significant decay was observed during the data collection in all cases. 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 **4a**, the phosphine ligand and the −CF$_3$ groups of the anion were disordered; the SHELX commands, EADP, DFIX, EXYZ and SUMP were used to resolve the disorder.

2.14.1. X-ray data for 2

$C_{28}H_{53}ClN_4P_2Ru$, M = 644.2 g/mol, monoclinic, P2(1)/c, a = 10.6418(4) Å, b = 15.2543(5) Å, c = 19.1045(7) Å, α = 90°, β = 103.287(2)°, γ = 90°, Z = 4, V = 3018.28(19) Å^3, D(calc) = 1.418 g/cm^3, μ(Mo K_α) = 0.738 mm^{-1}, crystal dimensions 0.15 × 0.10 × 0.06 mm^3. The structure was refined by full matrix least-squares on F^2. Convergence to final R_1 = 0.0228 and wR_2 = 0.0604 for 6315 (I > 2σ(I)) independent reflections, and R_1 = 0.0252 and wR_2 = 0.0622 for all 5922 (R(int) = 0.0225) independent reflections, with 331 parameters and 0 restraints, were achieved.

2.14.2. X-ray data for 3

$C_{23}H_{41}ClN_4P_2Ru$, M = 572.06 g/mol, monoclinic, C2/c, a = 30.637(4) Å, b = 10.7422(15) Å, c = 15.205(2) Å, α = 90°, β = 93.063(2)°, γ = 90°, Z = 8, V = 4996.9(12) Å^3, D (calc) = 1.521 g/cm^3, μ(Mo K_α) = 0.882 mm^{-1}, crystal dimensions 0.25 × 0.15 × 0.08 mm^3. The structure was refined by full matrix least-squares on F^2. Convergence to final R_1 = 0.0240 and wR_2 = 0.0594 for 4495 (I > 2σ(I)) independent reflections, and R_1 = 0.0269 and wR_2 = 0.0616 for all 4895 (R(int) = 0.0178) independent reflections, with 280 parameters and 0 restraints, were achieved.

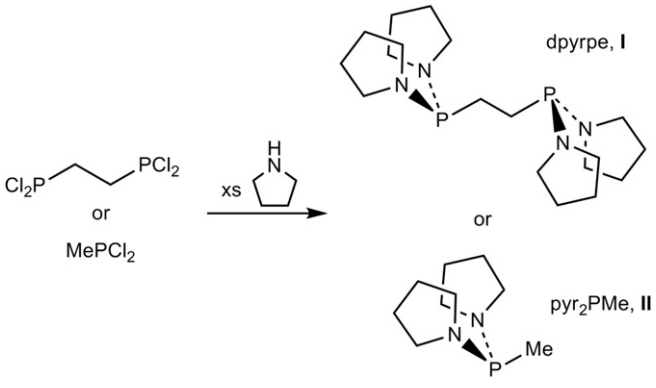
2.14.3. X-ray data for 4a

$C_{62}H_{66}BF_{24}N_5P_2Ru$, M = 1511.02 g/mol, monoclinic, P2(1), a = 12.8983(2) Å, b = 13.5429(2) Å, c = 19.4856(3) Å, α = 90°, β = 103.2460(10)°, γ = 90°, Z = 2, V = 3313.20(9) Å^3, D(calc) = 1.515 g/cm^3, μ(Mo K_α) = 0.396 mm^{-1}, crystal dimensions 0.30 × 0.25 × 0.15 mm^3. The structure was refined by full matrix least-squares on F^2. Convergence to final R_1 = 0.0442 and wR_2 = 0.1147 for 4495 (I > 2σ(I)) independent reflections, and R_1 = 0.0482 and wR_2 = 0.1189 for all 12798 (R(int) = 0.0190) independent reflections, with 870 parameters and 22 restraints, were achieved.

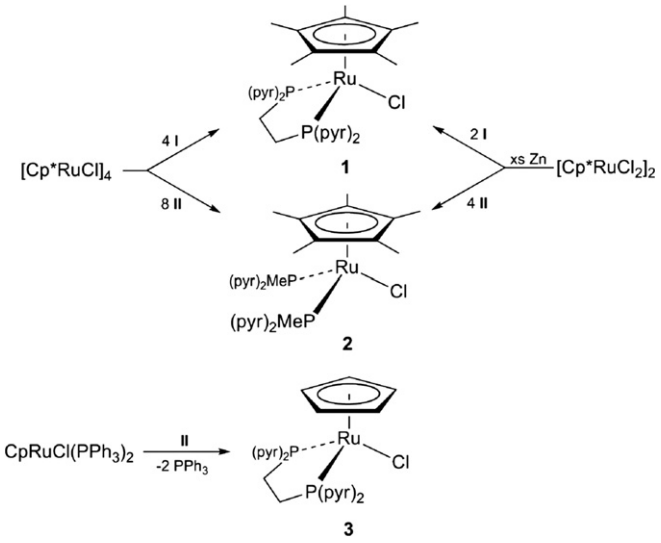
3. Results and discussion

The new ligand 1,2-bis(dipyrrolidin-1-ylphosphino)ethane (dpyrpe, **I**) and its monodentate analogue bis(pyrrolidin-1-yl) methylphosphine (pyr$_2$PMe, **II**) were prepared in good yields using a modification of an established procedure [3c] (Scheme 1). The pyrrolidinylalkylphosphine ligands proved to be extremely air- and moisture-sensitive, but are stable indefinitely under an inert atmosphere. The ^{31}P{^{1}H} NMR spectrum of **I** reveals a sharp singlet at δ = 72.8 ppm, which is similar to that observed for **II** (δ = 74.1 ppm) [3c], but slightly further downfield compared to the corresponding pyrrolyl analogue, 1,2-bis(dipyrrol-1-ylphosphino) ethane [8].

The synthetic approaches used to prepare the ruthenium piano-stool complexes examined as part of this work are illustrated in Scheme 2. Complexes **1** and **2** were isolated as orange solids from reactions between (Cp*RuCl)$_4$ and either ligand **I** or **II**, respectively, in good yields upon work-up. Alternatively, they could also be synthesized in comparable yields using a zinc reduction strategy beginning with (Cp*RuCl$_2$)$_2$ [9]. The orange cyclopentadienyl analogue **3** was prepared by thermally displacing the PPh$_3$ ligands in CpRuCl(PPh$_3$)$_2$ with ligand **I**. All three complexes are stable towards the open air, at least for brief periods (hours). Thus, the ligands **I** and **II** become remarkably stable towards atmospheric elements upon coordination to ruthenium, and even withstand prolonged periods of heating (*i.e.*, in the synthesis of **3**). The ^{31}P{^{1}H} NMR spectra of **1** and **3** each reveal a sharp singlet at δ = 144.4 ppm and δ = 149.8 ppm, respectively, at room temperature. In contrast, complex **2** produces a very broad peak centred at δ = 106.5 ppm under the same conditions. When the temperature is raised to 60 °C, this signal narrows into a sharp singlet. Upon lowering the temperature, the signal first broadens significantly, and eventually decoalesces to produce an AB spin pattern consisting of two equally intense sharp doublets at δ = 111.0 ppm and δ = 101.1 ppm ($^2J_{PP}$ = 69 Hz) by −50 °C. These features of the variable temperature ^{31}P{^{1}H} NMR spectrum of **2** likely originate from hindered rotation about the Ru−P bonds on the NMR time scale [10], which produce rotational isomers at low temperatures. Indeed, the solid state

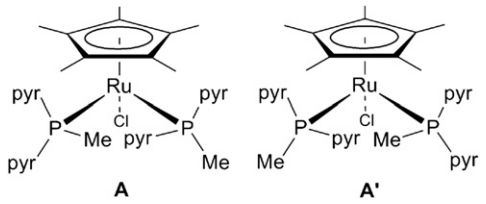


Scheme 1. Synthesis of ligands **I** and **II**.



Scheme 2. Synthesis of complexes **1**–**3**.

X-ray structure of **2** (*vide infra*) is consistent with rotamers **A**/**A**′, both of which possess non-equivalent phosphine ligands:



Complexes **2** and **3** were crystallographically characterized, and each structure reveals a number of interesting features. Views of each complex are presented in Figs. 1 and 2. Selected bond lengths and angles are provided in Tables 1 and 2.

As expected, complex **2** adopts the typical piano-stool structure often observed for Cp and Cp* complexes of ruthenium. The substituents on each phosphine ligand are staggered asymmetrically with respect to one another (as in **A**/**A**′, above). Also, all four pyrrolidinyl ring substituents of the phosphine are staggered

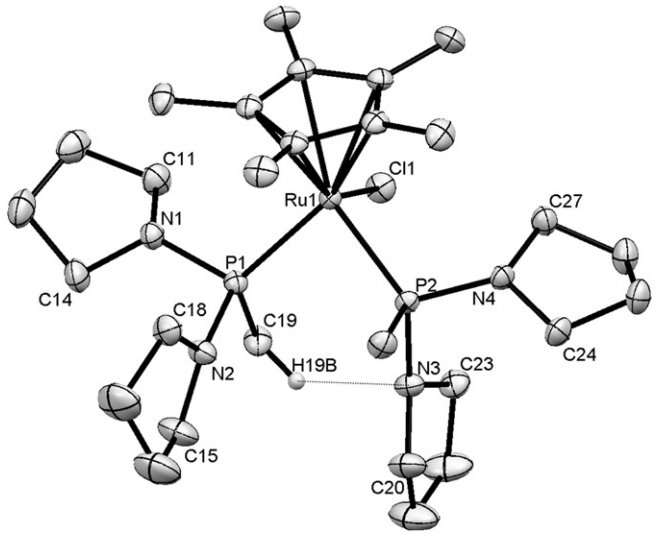


Fig. 1. Molecular structure of complex **2** (hydrogen atoms omitted for clarity).

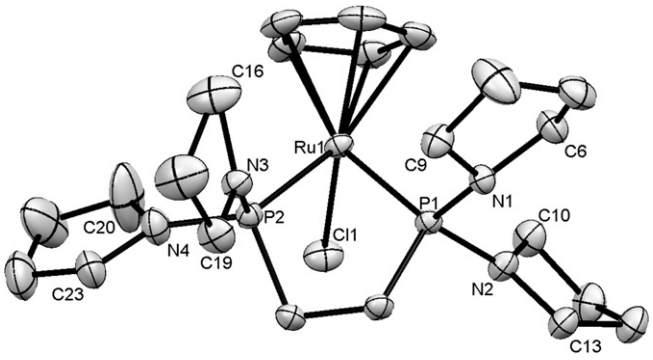
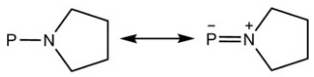


Fig. 2. Molecular structure of complex **3** (hydrogen atoms omitted for clarity).

around their respective P–N bond such that the nitrogen lone pair is positioned away from the phosphorus lone pair (*i.e.*, the Ru–P bond). Three of the four pyrrolidinyl rings possess nitrogen atoms that are approaching planarity (N(2), N(3) and N(4)), with the sum of the angles around each nitrogen ranging between 353 and 357°. A suspiciously short distance between N(3) and the methyl substituent on the adjacent phosphine ligand, specifically the C(19) and H(19B) atoms, might suggest a weak intramolecular hydrogen bond. The N(3)–C(19) distance (3.263(2) Å) and the N(3)–H(19B) distance (calculated 2.510 Å) are both shorter than the sum of the van der Waal radii for nitrogen-carbon (3.41 Å) and nitrogen-hydrogen (2.74 Å) [11]. Strangely, the fourth nitrogen, N(1), is intermediate between tetrahedral and planar (347°). The shortest N···H contact distance (2.81 Å) between this particular nitrogen and the nearest (non-pyrrolidinyl) hydrogen atom is outside of the sum of the van der Waal radii for nitrogen and hydrogen, thus the observed pyramidalization in the solid state is likely not due to an additional inter- or intramolecular N–H interaction. The roughly planar geometries about N(2), N(3) and N(4) of the pyrrolidinyl rings might suggest π-donation of the lone nitrogen pair into a vacant phosphorus-based orbital, as depicted in **B** and **C**:



Indeed, the four P–N distances range between 1.6833(16)–1.7087(16) Å, with the shorter distances being observed for the more planar nitrogen atoms. These phenomena have been noted in a number of other systems bearing similar ligands [3]. Thus, it is anticipated that these ligands (and hybrid aminoalkylphosphine ligands in general) might possess enhanced Lewis basicities compared to their hydrocarbyl counterparts. The Ru–P distances

Table 1
Selected bond distances (Å) and angles (°) for complex **2**.

Ru(1)–P(1)	2.2893(4)	P(1)–Ru(1)–P(2)	89.78(2)
Ru(1)–P(2)	2.2797(5)	P(1)–N(1)–C(11)	118.6(1)
Ru(1)–Cl(1)	2.4530(5)	P(1)–N(1)–C(14)	123.1(1)
P(1)–N(1)	1.707(2)	C(11)–N(1)–C(14)	104.8(2)
P(1)–N(2)	1.683(2)	P(1)–N(2)–C(15)	126.1(1)
P(2)–N(3)	1.709(2)	P(1)–N(2)–C(18)	120.2(1)
P(2)–N(4)	1.691(1)	C(18)–N(2)–C(15)	110.3(2)
N(3)–C(19)	3.263(2)	P(2)–N(4)–C(24)	122.0(1)
N(3)–H(19B)	2.510[a]	P(2)–N(4)–C(27)	122.8(1)
Ru(1)–centroid	1.899[a]	C(24)–N(4)–C(27)	109.8(1)
		P(2)–N(3)–C(20)	126.5(1)
		P(2)–N(3)–C(23)	118.0(1)
		C(20)–N(3)–C(23)	108.5(2)

[a] Calculated distance.

Table 2
Selected bond distances (Å) and angles (°) for complex **3**.

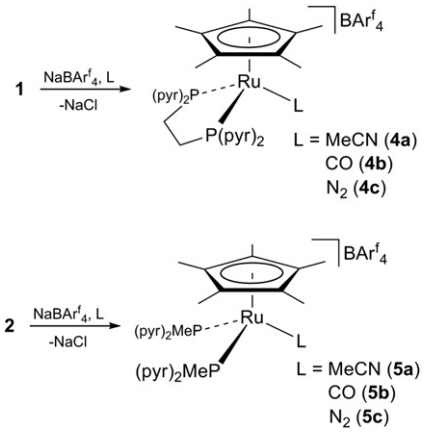
Ru(1)–P(1)	2.2626(6)	P(1)–Ru(1)–P(2)	81.45(2)
Ru(1)–P(2)	2.2654(6)	P(1)–N(1)–C(6)	118.8(1)
Ru(1)–Cl(1)	2.4334(6)	P(1)–N(1)–C(9)	119.0(1)
P(1)–N(1)	1.715(2)	C(6)–N(1)–C(9)	107.5(2)
P(1)–N(2)	1.671(2)	P(1)–N(2)–C(10)	123.5(1)
P(2)–N(3)	1.682(2)	P(1)–N(2)–C(13)	124.3(1)
P(2)–N(4)	1.669(2)	C(10)–N(2)–C(13)	110.6(2)
Ru(1)–centroid	1.879[a]	P(2)–N(3)–C(16)	120.6(1)
		P(2)–N(3)–C(19)	126.4(1)
		C(16)–N(3)–C(19)	110.0(2)
		P(2)–N(4)–C(20)	126.7(2)
		P(2)–N(4)–C(23)	122.7(2)
		C(20)–N(4)–C(23)	110.6(2)

[a] Calculated distance.

(2.2893(4) Å and 2.2797(5) Å) and P–Ru–P bond angle in **2** (89.78(2)°) are similar to those determined for [Cp*RuCl(Ph_2PH)$_2$] (2.282(1) Å and 2.277(1) Å), 90.68(4)° [12]. It has been suggested that the pyrrolidinyl group exerts a steric effect similar to that of a phenyl group [8]. Accordingly, the cone angle of **II** has been estimated to be similar to that of Ph_2PMe, specifically 136° [3c]. The cone angle of Ph_2PH has been estimated to be 128° [13], thus it is likely then that the cone angle of ligand **II** falls within this range.

Similar structural features were also observed for complex **3**. Once again, three pyrrolidinyl ring substituents on the phosphine ligand have nitrogen atoms (*i.e.*, N(2), N(3) and N(4)) that are nearly planar (the sum of the angles around each nitrogen range between 357 and 360°), while the fourth (N(1)) is more intermediate (345°) with no reasonably short N–H contact distances observed. The P–N distances within the phosphine ligand (1.669(2)–1.715(2) Å) again follow a pattern where an increase in planarity about the nitrogen atoms leads to a shortening of the P–N bond. The complex [CpRuCl(dppe-κ^2P)], a structural analogue of **3**, has Ru–P distances (2.275(2) Å and 2.282(2) Å) and a P–Ru–P bond angle (83.49(4)°) [14] that are only slightly larger than those observed for **3** (2.2654(6) Å and 2.2626(6) Å, 81.45(2)°), suggesting the dipyrrolidinylphosphino group in **I** is perhaps close in size to the corresponding diphenylphosphino group in dppe. The cone angle for dppe has been estimated to be 125° [13], and so we might then expect the cone angle for ligand **I** to be about the same.

We explored the substitution chemistry of complexes **1** and **2**, which was found to resemble in a number of ways what is typically observed for ruthenium piano-stool complexes (Scheme 3). All of the complexes were characterized using NMR spectroscopy and microanalytical data. The chloride ligand in either complex is readily removed using $NaBAr^f_4$ (Ar^f = 3,5-bis(trifluoromethyl) phenyl) and replaced, for example, with MeCN to give [Cp*Ru(NCMe)(dpyrpe-κ^2P)][BAr^f_4], **4a**, and [Cp*Ru(NCMe)(pyr_2PMe)$_2$][BAr^f_4], **5a**. The $^{31}P\{^1H\}$ NMR resonance for **4a** appears as a sharp singlet at δ = 136.4 ppm, a position further upfield of the parent chloride. Similarly, complex **5a** also yields a sharp upfield signal at δ = 103.5 ppm, which contrasts the broad resonance observed for **2** at room temperature. Complex **4a** was also characterized by X-ray crystallography. A view of the cation of **4a** is provided in Fig. 3; selected bond lengths and angles are listed in Table 3. Unlike what is observed in the solid state structures of **2** and **3**, all four pyrrolidinyl nitrogens are essentially planar (sum of the angles around each nitrogen ranging between 357 and 359°). The P–N distances are short (1.672(4)–1.680(5) Å). The acetonitrile ligand is linear (173.3(4)°). The Ru–P distances (2.2967(9) Å and 2.304(1) Å) are shorter than those observed in [Cp*RuCl(dippe-κ^2P)] (2.336(2) Å and 2.331(2) Å) [15] and [Cp*Ru(dippe-κ^2P)][BAr^f_4] (2.331(1) Å and 2.356(1) Å) [16] (dippe = 1,2-bis(diisopropylphosphino)ethane), likely reflecting the smaller size of ligand **I** compared to dippe.



Scheme 3. Synthesis of complexes **4a**–**c** and **5a**–**c**.

Using a similar synthetic approach, the corresponding CO complexes [Cp*Ru(CO)(dpyrpe-κ^2P)][BAr^f_4], **4b**, and [Cp*Ru(CO)(pyr_2PMe)$_2$][BAr^f_4], **5b** (δ ($^{31}P\{^1H\}$) = 130.4 and 100.3 ppm, respectively) were also prepared. For complex **4b**, ν(CO) = 1960 cm^{-1}, while for **5b**, ν(CO) = 1957 cm^{-1}. Infrared spectroscopy of metal-CO derivatives has been used extensively as a method of gauging the donor abilities of pyrrolidinylalkylphosphine ligands [3b–d]. In general, these studies have revealed that tertiary phosphines bearing two *N*-bound pyrrolidinyl substituents are stronger electron donor ligands compared to their trialkyl- or triarylphosphine counterparts. In order to establish the relative donor strengths of ligands **I** and **II** as part of [Cp*Ru(CO)(PP)]$^+$ (PP = bidentate or 2 × monodentate phosphines), we also prepared the complexes [Cp*Ru(CO)(dppe-κ^2P)][BAr^f_4], **6a**, and [Cp*Ru(CO)(Ph_2PMe)$_2$][BAr^f_4], **6b**, for the purposes of drawing comparisons with **4b** and **5b**, respectively, since they contain conventional phosphine ligands which perhaps, at least sterically, resemble the phosphine ligands studied as part of this work. Surprisingly, our results were less definitive when compared to what has been observed in other studies [3b–d]. The infrared absorption of the CO ligand in complex **6a** appears at ν(CO) = 1961 cm^{-1}, suggesting that ligand **I** and dppe have very similar donor properties, despite the very different substituents on each phosphine. For complex **6b**, ν(CO) = 1951 cm^{-1}, which again suggests the Ph_2PMe ligand is at least similar, and perhaps is even a slightly *stronger* phosphine donor ligand compared to **II**. We also note that the infrared absorption of the

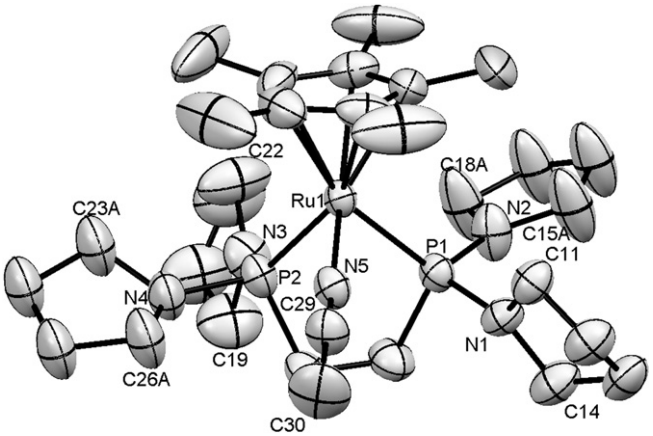


Fig. 3. Molecular structure of the cation of complex **4a** (hydrogen atoms omitted for clarity).

Table 3
Selected bond distances (Å) and angles (°) for complex **4a**.

Ru(1)–P(1)	2.304(1)	P(1)–Ru(1)–P(2)	81.34(4)
Ru(1)–P(2)	2.2967(9)	N(5)–C(29)–C(30)	178.5(6)
Ru(1)–N(5)	2.024(4)	P(1)–N(1)–C(11)	124.4(3)
P(1)–N(1)	1.672(4)	P(1)–N(1)–C(14)	123.9(3)
P(1)–N(2)	1.680(5)	C(11)–N(1)–C(14)	109.4(4)
P(2)–N(3)	1.674(5)	P(1)–N(2)–C(15A)	124.9(7)
P(2)–N(4)	1.677(4)	P(1)–N(2)–C(18A)	126.2(7)
Ru(1)–centroid	1.899[a]	C(15A)N(2)–C(18A)	107.7(9)
		P(2)–N(3)–C(19)	122.8(4)
		P(2)–N(3)–C(22)	124.0(4)
		C(19)–N(3)–C(22)	111.6(5)
		P(2)–N(4)–C(23A)	122.5(6)
		P(2)–N(4)–C(26A)	127.0(7)
		C(23A)–N(4)–C(26A)	107.0(9)

[a] Calculated distance.

carbonyl ligand in the complex $[Cp^*Ru(CO)(PMe_3)_2][PF_6]$ occurs at $\nu(CO) = 1935\ cm^{-1}$ [17], which is lower than that observed for complex **5b**, and thus indicates PMe_3 is a better donor than ligand **II**. Interestingly, this contrasts a separate study where ligand **II** was revealed to be a better donor phosphine compared to PMe_3, based on ν(CO) absorption data. [3c].

During the course of our efforts to explore the substitution chemistry of complexes **1** and **2**, we also attempted to synthesize coordinatively unsaturated, 16-electron complexes of the type $[Cp^*Ru(PP)]^+$ (PP = dpyrpe or $(pyr_2PMe)_2$). We were motivated by the expectation that such complexes might possess exceptional catalytic potential. Clearly, such species could at least be trapped using a suitable ligand (*i.e.*, complexes **4a,b** and **5a,b**), which provided indirect evidence for their production. Interestingly, when complex **1** is treated with $NaBAr^f_4$ in either CH_2Cl_2 or diethyl ether, rather than preparing the corresponding coordinatively unsaturated, 16-electron complex, the 18-electron complex $[Cp^*Ru(N_2)(dpyrpe\text{-}\kappa^2P)][BAr^f_4]$, **4c**, was observed to form when the reaction was performed under dinitrogen. Complex **4c** is stable under dinitrogen even in solution, but proved to be difficult to purify as a solid, likely due to the lability of the dinitrogen ligand. This issue has been noted before in similar complexes [18]. Consistent with the observations made for the other cationic complexes prepared as part of this work, the $^{31}P\{^1H\}$ NMR spectrum of **4c** reveals a sharp singlet at $\delta = 131.2$ ppm. The infrared absorption of the dinitrogen ligand in **4c** appears at $\nu(N_2) = 2148\ cm^{-1}$, which is similar to what has been reported for other ruthenium–dinitrogen complexes [18]. The analogous complex containing ligand **II**, $[Cp^*Ru(N_2)(pyr_2PMe)_2][BAr^f_4]$, **5c** ($\delta$ ($^{31}P\{^1H\}$) = 98.5 ppm), proved to be exceptionally labile, and could only be characterized *in situ* in solution. Unfortunately, the same reactions were unselective when they were repeated under argon rather than dinitrogen. For example, reacting complex **1** with $NaBAr^f_4$ under argon using argon-purged solvents rapidly yields at least four different products (based on ^{31}P NMR spectroscopy), none of which we could confidently characterize.

Coordinatively unsaturated complexes $[Cp^*Ru(PP)]^+$ generally promote oxidative addition of dihydrogen to form the corresponding Ru(IV) dihydride complexes $[Cp^*RuH_2(PP)]^+$ [9c,16,18,19]. Indeed, when complex **1** is treated with $NaBAr^f_4$ under an H_2 atmosphere, the Ru(IV) dihydride $[Cp^*RuH_2(dpyrpe\text{-}\kappa^2P)][BAr^f_4]$, **7**, forms. Complex **7** produces a sharp singlet at $\delta = 135.6$ ppm in its $^{31}P\{^1H\}$ NMR spectrum. The most diagnostic feature of the ^1H NMR spectrum of **7** is a triplet centred at $\delta = -9.76$ ppm ($^2J_{PH} = 29$ Hz), which is assigned to the hydride ligands. Other complexes of the type $[(C_5R_5)MH_2(PP)]^+$ (R = H or Me; M = Fe or Ru) possess a transoid arrangement of the hydride ligands [9c,18,20], and thus this is likely the case for **7** as well. Surprisingly, extending these reactions to include complex **2** only yielded unappealing mixtures as evidenced by the ^{31}P NMR spectra of the products of these reactions.

4. Summary

We report here a number of new ruthenium complexes with structures based on the common piano-stool $[(C_5R_5)RuL_n]$ (R = H or Me) architecture, and containing the pyrrolidinylalkylphosphine ligands **I** and **II**. These particular ligands appear to share the same steric properties as the more conventional phosphines dppe and Ph_2PMe, respectively, based on solid state structural studies. Quite unexpectedly, the IR studies involving the CO derivatives were not as definitive in establishing the donor properties of these phosphines when bound to the Ru(II) fragment $\{Cp^*Ru(CO)\}^+$, and thus their effect on the metal remains unclear at the moment. We hope to expand this investigation to include a broader range of pyrrolidinylalkylphosphines and ruthenium complexes in our pursuit for better insight into their impact on ruthenium chemistry.

Acknowledgements

We are very grateful for the financial support provided by the Natural Sciences and Engineering Research Council (NSERC) of Canada.

Appendix A. Supplementary data

CCDC 823355, 823356 and 823357 contain the supplementary crystallographic data for complexes **2**, **3** and **4a**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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