π-Facial selectivities in the coordination of an optically pure fused cyclopentadienyl ligand to arene ruthenium moieties. NMR spectral and structural characterization of a single diastereomer of $[(PCp)Ru(Me_6C_6)]PF_6$

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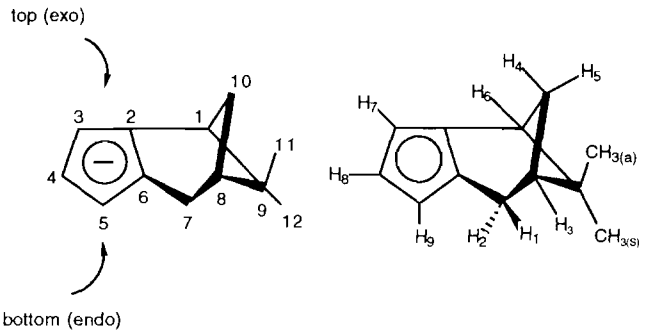
Abstract

Optically pure thallium (1*R*)-(−)-9,9-dimethyltricyclo[6.1.1.$0^{2,6}$]deca-2,5-dienide (TlPCp) reacts with $[(\eta^6\text{-arene})RuCl_2]_2$ (arene = C_6H_6, MeC_6H_5, *p*-$MeC_6H_4CHMe_2$, Me_6C_6) and NH_4PF_6 to form two isomers of the complexes $[(\eta^5\text{-PCp})Ru(\eta^6\text{-arene})]PF_6$. The π-facial stereoselectivity for coordination of PCp is a function of the steric bulk of the arene increasing from a 1:1 (C_6H_6) to a 14:1 (Me_6C_6) *exo*/*endo* isomer ratio. New complexes were characterized by elemental analyses, physical properties, differential pulse voltammetry and ^1H and $^{13}C\{^1H\}$ one- and two-dimensional NMR spectroscopy. The structure of $[(\eta^5\text{-PCp})Ru(\eta^6\text{-}Me_6C_6)]PF_6$ was confirmed by X-ray crystallography. This compound crystallized in the acentric space group $C222_1$ in a unit cell with the following dimensions: $a = 11.451(4)$, $b = 13.426(5)$, $c = 31.249(3)$ Å, $V = 4804(3)$ Å^3, $Z = 8$. Refinement converged to $R(F) = 0.056$ for 1723 independent observed ($I > 3\sigma(I)$) reflections. Ruthenium coordinates to the less sterically hindered *exo* face of the PCp ligand, *anti* to the *gem*-dimethyl group, and is closer to the arene (Ru–ring centroid = 1.73 Å) than to the PCp ligand (Ru–ring centroid = 1.79 Å).

Key words: Crystal structures; Ruthenium complexes; Arene complexes; Cyclopentadienyl complexes

Introduction

Metal complexation of enantiometrically pure chiral cyclopentadienides [1–7] is of considerable current interest in large part, because of the potential utility of such metal complexes in asymmetric synthesis [8]. Paquette *et al.* have studied the complexation of the chiral cyclopentadienide (1*R*)-(−)-9,9-dimethyltricyclo[6.1.1.$0^{2,6}$]deca-2,5-dienide (PCp, **1**, Scheme 1) to Ti(IV) and Fe(0) reagents. They have observed that Ti(IV) reagents react with LiPCp [2] and Me_3SiPCp [7] with high and inverted π-facial selectivities. With LiPCp, coordination of Ti(IV) occurs preferentially to the top (*exo*) face, opposite the *gem*-dimethyl group, while with Me_3SiPCp Ti(IV) preferentially coordinates to the bottom (*endo*) face. They also found [9] that $Fe(CO)_5$ reacts with HPCp to produce *cis*-$[(\eta^5\text{-PCp})Fe(CO_2)]_2$, containing Fe(0) coordinated only to the top (*exo*) face of PCp proximal to the methano bridge.



Scheme 1. PCp (1) and its ^{13}C and ^1H numbering schemes.

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The versatile reagent $[(\eta^5\text{-}C_5H_5)Ru(CH_3CN)_3]PF_6$ is readily prepared by the sequence of reactions [10–12] illustrated in Scheme 2.

$$2RuCl_3 \cdot 3H_2O + 2\ 1,3\text{-cyclohexadiene} \xrightarrow[\Delta]{EtOH}$$

$$[(\eta^6\text{-}C_6H_6)RuCl_2]_2 + 2HCl + 6H_2O \quad (1)$$

$$[(\eta^6\text{-}C_6H_6)RuCl_2]_2 \xrightarrow[(ii)\ NH_4PF_6]{(i)\ LiC_5H_5}$$

$$[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-}C_6H_6)]PF_6 + LiCl + NH_4Cl \quad (2)$$

$$[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-}C_6H_6)]PF_6 \xrightarrow[CH_3CN]{h\nu}$$

$$[(\eta^5\text{-}C_5H_5)Ru(CH_3CN)_3]PF_3 + C_6H_6 \quad (3)$$

Scheme 2.

In an attempt to prepare a similar chiral ruthenium complex we have studied the reactions of $[(\eta^6\text{-arene})RuCl_2]_2$ (arene = C_6H_6, MeC_6H_5, *p*-$MeC_6H_4CHMe_2$, Me_6C_6) with $HNEt_3PCp$, LiPCp and TiPCp and report the results herein.

Experimental

Reagents and physical measurements

Hydrated ruthenium trichloride (43.02% Ru, Johnson Matthey Bishop), TlOEt, 1,3-cyclohexadiene, NH_4PF_6 (Aldrich), α-phellandrene (5-isopropyl-2-methyl-1,3-cyclohexadiene, Technical grade, Fluka), hexamethylbenzene (Lancaster) and 1-methyl-1,4-cyclohexadiene (Pfaltz and Bauer, Inc.) were used as received. $[(\eta^6\text{-arene})RuCl_2]_2$ (arene = C_6H_6 [10], MeC_6H_5 [13], *p*-$MeC_6H_4CHMe_2$ [14], Me_6C_6 [14]) were prepared by literature procedures. (1*R*)-(−)-9,9-dimethyltricyclo-[6.1.1.$0^{2,6}$]deca-2,5-diene was prepared by the Salzer and Schmalle [15] modification of the Paquette and McLaughlin procedure [16]. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 21.60 (C_{12}), 26.41 (C_{11}), 28.12 (C_{10}), 32.21 (C_7), 40.36 (C_1), 40.99 (C_9), 41.08 (C_4), 43.57 (C_8), 119.82 (C_5), 124.93 (C_3), 141.84 (C_6), 152.37 (C_2). Melting points were determined on a Mel-Temp apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. Differential pulse voltammograms were recorded as previously described [17]. NMR spectra were recorded at 7.1, 11.7 and 14.1 tesla using General Electric GN-300 and Varian Unity −500 and −600 spectrometers. All spectra were recorded at 300 K in $CDCl_3$ and all chemical shifts are relative to internal tetramethylsilane (downfield, high frequency shifts are positive). Two dimensional spectra were obtained as previously described [18].

Synthesis

The $[(\eta^5\text{-PCp})Ru(\eta^6\text{-arene})]PF_6$ complexes were all prepared by the following general method. Under a heavy nitrogen flow commercial TlOEt (1.77 mmol) in ethanol was added to HPCp (1.77 mmol). A viscous yellow oil formed. To this mixture was added a solution, or suspension, of 0.59 mmol $[(\eta^6\text{-arene})RuCl_2]_2$ in 100 ml of dry acetonitrile (freshly distilled from CaH_2 under N_2). A white precipitate formed immediately. The mixture was stirred at ambient temperature for 9 h and filtered through a layer of Celite. The clear yellow filtrate was evaporated to dryness on a rotary evaporator and the solid residue was extracted with distilled water (4×50 ml). To the combined aqueous extracts was slowly added an aqueous solution containing 2.65 mmol of NH_4PF_6. The light brown precipitate that formed was isolated by filtration, air dried, dissolved in CH_2Cl_2, dried over anhydrous magnesium sulfate and filtered through a 2 inch plug of neutral alumina. The filtrate was reduced in volume on a rotary evaporator. A ten-fold quantity of anhydrous diethyl ether was added and the mixture was stored in a freezer at −10 °C overnight. The colorless crystals that formed were isolated by filtration and dried under vacuum.

$[(\eta^5\text{-PCp})Ru(\eta^6\text{-}C_6H_6)]PF_6$ (2)

388 mg (65%), m.p. 150 °C dec. (1:1 mixture of *exo* and *endo* isomers). ^1H NMR (300 MHz, $CDCl_3$) *exo* isomer: δ 0.56 (s, 3H, CH_3(s)), 1.36 (s, 3H, CH_3(a)), 1.51 (d, $^3J_{H_4H_5} = 10.22$ Hz, 1H, H_4), 2.21 (apparent ddt, $^3J_{H_3H_5} = 7.81$ Hz, $^4J_{H_3H_6} = 5.11$ Hz, $^3J_{H_1H_3} = {}^2J_{H_2H_3} = 2.70$ Hz, 1H, H_3), 2.55 (dd, $^2J_{H_1H_2} = 17.43$ Hz, $^3J_{H_1H_3} = 2.70$ Hz, 1H, H_1), 2.57 (apparent t, $^3J_{H_5H_6} = {}^4J_{H_3H_6} = 5.11$ Hz, 1H, H_6), 2.77 (dd, $^2J_{H_1H_2} = 17.43$ Hz, $^3J_{H_2H_3} = 2.70$ Hz, 1H, H_2), 2.79 (apparent dt, $^2J_{H_4H_5} = 10.22$ Hz, $^3J_{H_3H_5} = {}^3J_{H_5H_6} = 7.81$ Hz, 1H, H_5), 5.18 (apparent t, $^3J_{H_7H_8} = {}^3J_{H_8H_9} = 2.10$ Hz, 1H, H_8), 5.28 (d, $^3J_{H_7H_8} = 2.10$ Hz, 1H, H_7), 5.30 (d, $^3J_{H_8H_9} = 2.10$ Hz, 1H, H_9), 6.12 (s, 6H, η^6-C_6H_6); *endo* isomer: δ 0.87 (d, $^2J_{H_4H_5} = 9.92$ Hz, 1H, H_4), 1.19 (s, 3H, CH_3(s)), 1.34 (s, 3H, CH_3(a)), 2.20 (apparent, ddt, $^3J_{H_3H_5} = 7.81$ Hz, $^4J_{H_3H_6} = 5.11$ Hz, $^3J_{H_1H_3} = {}^3J_{H_2H_3} = 2.70$ Hz, 1H, H_3), 2.53 (dd, $^2J_{H_1H_2} = 16.83$ Hz, $^3J_{H_1H_3} = 2.70$ Hz, 1H, H_1), 2.60 (apparent t, $^3J_{H_5H_6} = {}^4J_{H_3H_6} = 5.11$ Hz, 1H, H_6), 2.69 (apparent dt, $^2J_{H_4H_5} = 9.92$ Hz, $^3J_{H_3H_5} = {}^3J_{H_5H_6} = 5.11$ Hz, 1H, H_5), 2.71 (dd, $^2J_{H_1H_2} = 16.83$ Hz, $^3J_{H_2H_3} = 2.70$ Hz, 1H, H_2), 5.05 (d, $^3J_{H_7H_8} = 2.10$ Hz, 1H, H_7), 5.19 (apparent t, $^3J_{H_7H_8} = {}^3J_{H_8H_9} = 2.10$ Hz, 1H, H_8), 5.26 (d, $^3J_{H_8H_9} = 2.10$ Hz, 1H, H_9), 6.11 (s, 6H, η^6-C_6H_6). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) *exo* isomer: δ 21.54 (C_{12}), 25.93 (C_7), 26.30 (C_{11}), 35.76 (C_{10}), 39.84 (C_1), 41.01 (C_8), 41.15 (C_9), 77.04 (C_5), 77.85 (C_3), 77.98 (C_4), 86.84 (η^6-C_6H_6), 98.79 (C_6), 114.87 (C_2); *endo* isomer: δ 26.30

(C_7), 26.58 (C_{12}), 27.71 (C_{11}), 36.52 (C_{10}), 39.46 (C_9), 40.41 (C_1), 40.68 (C_8), 74.22 (C_5), 76.27 (C_3), 76.50 (C_4), 86.32 (η^6-C_6H_6), 99.73 (C_6), 115.41 (C_2). *Anal.* Calc. for $C_{18}H_{21}F_6RuP$: C, 44.74; H, 4.35. Found: C, 45.24; H, 4.49%.

[(η^5-PCp)Ru(η^6-MeC$_6$H$_5$)]PF$_6$ (3)

418 mg (68%), m.p. 270 °C dec. (2:3 mixture of *exo* and *endo* isomers). ^{1}H NMR (300 MHz, $CDCl_3$) *exo* isomer: δ 0.57 (s, 3H, CH_3(s)), 1.37 (s, 3H, CH_3(a)), 1.47 (d, $^2J_{H_4H_5}$ = 10.06 Hz, 1H, H_4), 2.24 (apparent tt, $^3J_{H_3H_5}$ = $^4J_{H_3H_6}$ = 5.40 Hz, $^3J_{H_1H_3}$ = $^3J_{H_2H_3}$ = 2.70 Hz, 1H, H_3), 2.33 (s, 3H, *Me*C$_6$H$_5$), 2.50 (apparent t, $^4J_{H_3H_6}$ = $^3J_{H_5H_6}$ = 5.40 Hz, 1H, H_6), 2.60 (dd, $^2J_{H_1H_2}$ = 18.03 Hz, $^3J_{H_1H_3}$ = 2.70 Hz, 1H, H_1), 2.66 (dd, $^2J_{H_1H_2}$ = 18.03 Hz, $^3J_{H_2H_3}$ = 2.70 Hz, 1H, H_2), 2.81 (apparent dt, $^2J_{H_4H_5}$ = 10.06 Hz, $^3J_{H_3H_5}$ = $^3J_{H_5H_6}$ = 5.40 Hz, 1H, H_5), 5.12 (apparent t, $^3J_{H_7H_8}$ = $^3J_{H_8H_9}$ = 2.10 Hz, 1H, H_8), 5.20 (d, $^3J_{H_7H_8}$ = 2.10 Hz, 1H, H_7), 5.22 (d, $^3J_{H_8H_9}$ = 2.10 Hz, 1H, H_9), 6.0–6.1 (m, 5H, MeC$_6$*H*$_5$); *endo* isomer: δ 0.87 (d, $^2J_{H_4H_5}$ = 10.36 Hz, 1H, H_4), 1.19 (s, 3H, CH_3(s)), 1.35 (s, 3H, CH_3(a)), 2.20 (apparent tt, $^3J_{H_3H_5}$ = $^4J_{H_3H_6}$ = 5.40 Hz, $^3J_{H_1H_3}$ = $^3J_{H_2H_3}$ = 2.70 Hz, 1H, H_3), 2.36 (s, 3H, *Me*C$_6$H$_5$), 2.56 (dd, $^2J_{H_1H_2}$ = 18.03 Hz, $^3J_{H_1H_3}$ = 2.70 Hz, 1H, H_1), 2.58 (apparent t, $^3J_{H_5H_6}$ = $^4J_{H_3H_6}$ = 5.40 Hz, 1H, H_6), 2.61 (dd, $^2J_{H_1H_2}$ = 18.03 Hz, $^3J_{H_2H_3}$ = 2.70 Hz, 1H, H_2), 2.70 (apparent dt, $^2J_{H_4H_5}$ = 10.36 Hz, $^3J_{H_3H_5}$ = $^3J_{H_5H_6}$ = 5.40 Hz, 1H, H_5), 4.97 (d, $^3J_{H_7H_8}$ = 2.10 Hz, 1H, H_7), 5.13 (apparent t, $^3J_{H_7H_8}$ = $^3J_{H_8H_9}$ = 2.10 Hz, 1H, H_8), 5.18 (d, $^3J_{H_8H_9}$ = 2.10 Hz, 1H, H_9), 6.0–6.1 (m, 5H, MeC$_6$*H*$_5$). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) *exo* isomer: δ 20.19 (*Me*C$_6$H$_5$), 21.43 (C_{12}), 25.63 (C_7), 26.21 (C_{11}), 35.57 (C_{10}), 39.26 (C_1), 40.50 (C_8), 40.92 (C_9), 77.36 (C_5), 77.94 (C_3), 78.29 (C_4), 85.00 (C_{12}), 85.63 (C_{16} or C_{18}), 85.85 (C_{18} or C_{16}), 87.30 (C_{15} or C_{19}), 87.66 (C_{19} or C_{15}), 97.95 (C_6), 101.15 (C_{13}), 114.28 (C_2); C_{13}, C_{15}, C_{19}, C_{16}, C_{18} and C_{17} are the *i*, *o*, *o'*, *m*, *m'* and *p* carbons of MeC$_6$H$_5$, respectively; *endo* isomer: δ 19.75 (*Me*C$_6$H$_5$), 22.61 (C_{12}), 25.81 (C_7), 26.46 (C_{11}), 36.35 (C_{10}), 39.52 (C_1 and C_9), 40.29 (C_8), 74.51 (C_5), 76.61 (C_3), 77.06 (C_4), 86.43 (C_{17}), 86.55 (C_{16} or C_{18}), 86.83 (C_{18} or C_{16}), 87.14 (C_{15} or C_{19}), 88.25 (C_{19} or C_{15}), 99.01 (C_6), 101.42 (C_{13}), 114.71 (C_2); C_{13}, C_{15}, C_{19}, C_{16}, C_{18} and C_{17} are the *i*, *o*, *o'*, *m*, *m'* and *p* carbons of MeC$_6$H$_5$, respectively. *Anal.* Calc. for $C_{19}H_{23}F_6Ru \cdot 0.25MeC_6H_5$: C, 47.90; H, 4.81. Found: C, 47.84; H, 4.94%.

[(η^5-PCp)Ru(η^6-p-MeC$_6$H$_4$CHMe$_2$)]PF$_6$ (4)

414 mg (65%), m.p. 290 °C dec. (1:1 mixture of *exo* and *endo* isomers). ^{1}H NMR (300 MHz, $CDCl_3$) *exo* isomer: δ 0.58 (s, 3H, CH_3(s)), 1.24 (d, $^3J_{HH}$ = 6.01 Hz, 3H, CH*CH*$_3$), 1.26 (d, $^3J_{HH}$ = 6.01 Hz, 3H, CH*CH*$_3$), 1.38 (s, 3H, CH_3(a)), 1.49 (d, $^2J_{H_4H_5}$ = 9.91 Hz, 1H, H_4), 2.24 (apparent tt, $^3J_{H_3H_5}$ = $^4J_{H_3H_6}$ = 5.10 Hz, $^3J_{H_1H_3}$ = $^3J_{H_2H_3}$ = 2.10 Hz, 1H, H_3), 2.31 (s, 3H, C$_6$H$_4$*CH*$_3$), 2.47 (apparent t, $^3J_{H_5H_6}$ = $^4J_{H_3H_6}$ = 5.10 Hz, 1H, H_6), 2.58 (dd, $^2J_{H_1H_2}$ = 13.60 Hz, $^3J_{H_1H_3}$ = 2.10 Hz, 1H, H_1), 2.70 (sept, $^3J_{HH}$ = 6.01 Hz, 1H, C*H*Me$_2$), 2.74 (dd, $^2J_{H_1H_2}$ = 13.60 Hz, $^3J_{H_2H_3}$ = 2.10 Hz, 1H, H_2), 2.83 (apparent dt, $^2J_{H_4H_5}$ = 9.91 Hz, $^3J_{H_3H_5}$ = $^3J_{H_5H_6}$ = 5.10 Hz, 1H, H_5), 5.01 (d, $^3J_{H_7H_8}$ = 2.40 Hz, 1H, H_7), 5.06 (d, $^3J_{H_8H_9}$ = 2.40 Hz, 1H, H_9), 5.22 (apparent t, $^3J_{H_7H_8}$ = $^3J_{H_8H_9}$ = 2.40 Hz, 1H, H_8), 5.86–6.06 (m, 4H, *p*-MeC$_6$*H*$_4$CHMe$_2$); *endo* isomer: δ 0.90 (d, $^2J_{H_4H_5}$ = 9.91 Hz, 1H, H_4), 1.23 (s, 3H, CH_3(s)), 1.26 (d, 6H, $^3J_{HH}$ = 6.01 Hz, CH(*CH*$_3$)$_2$), 1.37 (s, 3H, CH_3(a)), 2.23 (apparent tt, $^3J_{H_3H_5}$ = $^4J_{H_3H_6}$ = 5.10 Hz, $^3J_{H_1H_3}$ = $^3J_{H_2H_3}$ = 2.10 Hz, 1H, H_3), 2.37 (s, 3H, C$_6$H$_4$*CH*$_3$), 2.54 (apparent t, $^3J_{H_5H_6}$ = $^4J_{H_3H_6}$ = 5.10 Hz, 1H, H_6), 2.56 (dd, $^2J_{H_1H_2}$ = 13.60 Hz, $^3J_{H_1H_2}$ = 2.10 Hz, 1H, H_1), 2.67 (apparent dt, $^2J_{H_4H_5}$ = 9.91 Hz, $^3J_{H_3H_5}$ = $^3J_{H_5H_6}$ = 5.10 Hz, 1H, H_5), 2.70 (sept, $^3J_{HH}$ = 6.01 Hz, 1H, C*H*Me$_2$), 2.72 (dd, $^2J_{H_1H_2}$ = 13.60 Hz, $^3J_{H_2H_3}$ = 2.10 Hz, 1H, H_2), 4.72 (d, $^3J_{H_7H_8}$ = 2.40 Hz, 1H, H_7), 5.02 (d, $^3J_{H_8H_9}$ = 2.40 Hz, 1H, H_9), 5.35 (apparent t, $^3J_{H_7H_8}$ = $^3J_{H_8H_9}$ = 2.40 Hz, 1H, H_8), 5.86–6.06 (m, 4H, *p*-MeC$_6$*H*$_4$CHMe$_2$). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), *exo* isomer: δ 19.80 (*Me*C$_6$H$_4$), 21.48 (C_{12}), 23.29 (C$_6$H$_4$CH*Me*$_2$), 23.60 (C$_6$H$_4$CH*Me*$_2$), 25.67 (C_7), 25.78 (C_{11}), 31.81 (C$_6$H$_4$*C*H), 35.63 (C_{10}), 39.61 (C_1), 40.93 (C_9), 40.98 (C_8), 77.42 (C_5), 78.01 (C_3), 78.66 (C_4), 85.58 (C_{16} or C_{18}), 86.90 (C_{19} or C_{15}), 85.96 (C_{18} or C_{16}), 88.23 (C_{15} or C_{19}), 97.51 (C_6), 100.61 (C_{13}), 111.77 (C_{17}), 113.86 (C_2); C_{13}, C_{17}, C_{15}, C_{16}, C_{18} and C_{19} are the *i*, *i'*, *o*, *o*, *o'* and *o'* carbons of *p*-MeC$_6$H$_4$CHMe$_2$, respectively; *endo* isomer: δ 19.30 (C_1), 22.75 (C_{12}), 23.08 (C$_6$H$_4$CH*Me*$_2$), 23.45 (C$_6$H$_4$CH*Me*$_2$), 26.27 (C_7), 26.53 (C_{11}), 31.86 (C$_6$H$_4$*C*H), 36.29 (C_{10}), 39.38 (C_9), 40.37 (C_1), 40.60 (C_8), 75.01 (C_5), 76.37 (C_3), 76.86 (C_4), 84.39 (C_{16} or C_{18}), 84.73 (C_{18} or C_{16}), 86.90 (C_{15} or C_{19}), 87.58 (C_{19} or C_{15}), 98.41 (C_6), 100.87 (C_{13}), 112.37 (C_{17}), 114.71 (C_2); C_{13}, C_{17}, C_{15}, C_{16}, C_{18} and C_{19} are the *i*, *i'*, *o*, *o*, *o'* and *o'* carbons of *p*-MeC$_6$H$_4$CHMe$_2$, respectively. *Anal.* Calc. for $C_{22}H_{29}F_6RuP$: C, 49.00; H, 5.38. Found: C, 48.87; H, 5.29%.

[(η^5-PCp)Ru(Me$_6$C$_6$)]PF$_6$ (5)

475 mg (71%), m.p. 147 °C dec. (14:1 mixture of *exo* and *endo* isomers). ^{1}H NMR (500 MHz, $CDCl_3$) *exo* isomer: δ 0.49 (s, 3H, CH_3(s)), 1.22 (d, $^2J_{H_4H_5}$ = 10.00 Hz, 1H, H_4), 1.32 (s, 3H, CH_3(a)), 2.14 (apparent ddt, $^3J_{H_3H_5}$ = 6.00 Hz, $^4J_{H_3H_6}$ = 5.00 Hz, $^3J_{H_1H_3}$ = $^3J_{H_2H_3}$ = 3.00 Hz, 1H, H_3), 2.28 (dd, $^2J_{H_1H_2}$ = 17.00 Hz, $^3J_{H_1H_3}$ = 3.00 Hz, 1H, H_1), 2.28 (s, 18H, Me$_6$C$_6$), 2.37 (apparent t, $^3J_{H_5H_6}$ = $^4J_{H_3H_6}$ = 6.00 Hz, 1H, H_6), 2.46 (ddd, $^2J_{H_1H_2}$ = 17.00 Hz, $^3J_{H_2H_3}$ = 3.00 Hz, $^4J_{H_2H_5}$ = 1.00 Hz, 1H, H_2), 2.72 (apparent dtd, $^2J_{H_4H_5}$ = 10.00 Hz, $^3J_{H_3H_5}$ = $^3J_{H_5H_6}$ = 6.00 Hz,

$^4J_{H_2H_5}$ = 1.00 Hz, 1H, H_5), 4.60 (apparent t, $^3J_{H_7H_8} = {}^3J_{H_8H_9}$ = 2.00 Hz, 1H, H_8), 4.66 (dd, $^3J_{H_7H_8}$ = 2.00 Hz, $^4J_{H_7H_9}$ = 1.00 Hz, 1H, H_7), 4.67 (dd, $^3J_{H_8H_9}$ = 2.00 Hz, $^4J_{H_7H_9}$ = 1.00 Hz, 1H, H_9); *endo* isomer: δ 0.74 (d, $^2J_{H_4H_5}$ = 10.00 Hz, 1H, H_4), 1.14 (s, 3H, CH_3(s)), 1.29, (s, 3H, CH_3(a)), 2.11 (apparent tt, $^3J_{H_3H_5} = {}^3J_{H_3H_6}$ = 5.00 Hz, $^3J_{H_1H_3} = {}^3J_{H_2H_3}$ = 3.00 Hz, 1H, H_3), 2.22 (s, 18H, Me_6C_6), 2.27 (dd, $^2J_{H_1H_2}$ = 17.00 Hz, $^3J_{H_1H_3}$ = 3.00 Hz, 1H, H_1), 2.44 (dd, $^2J_{H_1H_2}$ = 17.00 Hz, $^3J_{H_1H_3}$ = 3.00 Hz, 1H, H_2), 2.46 (apparent t, $^3J_{H_5H_6} = {}^4J_{H_3H_6}$ = 5.00 Hz, 1H, H_6), 2.60 (apparent dt, $^2J_{H_4H_5}$ = 10.00 Hz, $^3J_{H_3H_5} = {}^3J_{H_5H_6}$ = 5.00 Hz, 1H, H_5), 4.41 (apparent t, $^3J_{H_7H_8} = {}^3J_{H_8H_9}$ = 2.00 Hz, 1H, H_8), 4.46 (d, $^3J_{H_7H_8}$ = 2.00 Hz, 1H, H_7), 4.46 (d, $^3J_{H_8H_9}$ = 2.00 Hz, 1H, H_9). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) *exo* isomer: δ 17.11 (Me_6C_6), 21.40 (C_{12}), 24.98 (C_7), 26.24 (C_{11}), 34.55 (C_{10}), 38.90 (C_1), 40.80 (C_8), 41.29 (C_9), 77.93 (C_5), 79.10 (C_3), 79.72 (C_4), 95.27 (C_6), 99.00 (Me_6C_6), 112.32 (C_2); *endo* isomer: δ 17.24 (Me_6C_6), 21.81 (C_{12}), 24.80 (C_7), 26.24 (C_{11}), 35.20 (C_{10}), 39.03 (C_1), 40.60 (C_8), 76.12 (C_5), 79.43 (C_3), 79.62 (C_4), 96.46 (C_6), 99.30 (Me_6C_6), 114.89 (C_2). *Anal.* Calc. for $C_{24}H_{33}F_6RuP$: C, 50.81; H, 5.82. Found: C, 50.76; H, 5.96%.

X-ray data collection and processing

Colorless crystals of $[(\eta^5\text{-PCp})Ru(\eta^6\text{-}Me_6C_6)]PF_6$ were isolated from a CH_2Cl_2/ether solution. For all samples examined, the crystals seemed to grow in clusters. The crystals used for data collection and refinement were cleaved from the clusters using a razor blade, but it appeared that some diffraction maxima still contained contributions from secondary crystallite fragments. Crystal structure analyses were performed on four different crystals, all showing broad, ill-shaped peaks. The analysis using the best of the data sets is reported. Crystal data and details of data collection

TABLE 1. Crystallographic data for $[(\eta^5\text{-PCp})Ru(\eta^6\text{-}Me_6C_6)]PF_6$

Chemical formula	$C_{24}H_{26}F_6PRu$
Formula weight	560.50
Crystal system	orthorhombic
a (Å)	11.451(4)
b (Å)	13.426(5)
c (Å)	31.249(3)
V (Å^3)	4804(3)
Z	8
Space group	$C222_1$
T (°C)	23 ± 1
λ (Å)	0.71069
ρ_{calc} (g cm^{-3})	1.550
μ (cm^{-1})	7.6
Absorption: min./max.	0.95/1.00
$R(F)$[a]	0.056
$R_w(F)$[b]	0.062

[a] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w(F) = [(\Sigma\omega(|F_o| - |F_c|)^2/\Sigma\omega F_o^2]^{1/2}$.

TABLE 2. Atom coordinates for $[(\eta^5\text{-PCp})Ru(\eta^6\text{-}Me_6C_6)]PF_6$[a]

Atom	x	y	z	B_{eq}
Ru	−0.0038(2)	0.1354(1)	0.12484(4)	3.32(5)
P(1)	−1/2	0.1247(8)	1/4	6.2(4)
P(2)	0.6746(8)	0	1/2	4.8(5)
F(11)	−0.470(1)	0.122(2)	0.2020(4)	14(1)
F(12)	−0.593(1)	0.205(1)	0.243(1)	15(2)
F(13)	−0.590(1)	0.044(2)	0.244(1)	16(2)
F(21)	0.577(1)	0.045(1)	0.5280(6)	13(1)
F(22)	0.678(1)	0.100(1)	0.4752(6)	12(1)
F(23)	0.773(1)	0.040(1)	0.5284(5)	10(1)
C(1)	−0.254(1)	0.241(1)	0.0865(7)	3.1(4)
C(2)	−0.139(2)	0.188(2)	0.0805(7)	4(1)
C(3)	−0.029(2)	0.222(2)	0.0662(6)	4(1)
C(4)	0.039(2)	0.135(2)	0.0593(6)	6(1)
C(5)	−0.031(2)	0.049(2)	0.0685(6)	4(1)
C(6)	−0.143(2)	0.083(2)	0.0818(6)	4(1)
C(7)	−0.252(2)	0.023(2)	0.0897(8)	5(1)
C(8)	−0.350(2)	0.101(2)	0.0916(7)	6(2)
C(9)	−0.347(2)	0.183(2)	0.0587(7)	5(1)
C(10)	−0.318(2)	0.179(2)	0.1209(6)	5(1)
C(11)	−0.041(2)	0.195(2)	0.1924(7)	5(1)
C(12)	−0.043(2)	0.091(2)	0.1933(6)	2(1)
C(13)	0.047(2)	0.026(2)	0.1781(8)	5(1)
C(14)	0.152(2)	0.081(2)	0.1608(6)	4(1)
C(15)	0.154(2)	0.185(2)	0.1575(6)	4(1)
C(16)	0.060(2)	0.242(2)	0.1733(7)	4(1)
C(91)	−0.455(2)	0.251(2)	0.0581(9)	7(2)
C(92)	−0.307(2)	0.162(1)	0.0121(7)	5(1)
C(111)	−0.135(2)	0.259(2)	0.2094(7)	6(1)
C(121)	−0.151(2)	0.041(2)	0.2103(7)	7(1)
C(131)	0.046(2)	−0.086(2)	0.1793(8)	7(2)
C(141)	0.259(2)	0.022(2)	0.1426(7)	5.0(6)
C(151)	0.270(2)	0.235(3)	0.130(1)	13(2)
C(161)	0.066(2)	0.354(2)	0.1713(8)	8(1)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $8\pi^2/3\Sigma_i U_{ii}$.

TABLE 3. Selected bond distances (Å) for $[(\eta^5\text{-PCp})Ru(\eta^6\text{-}Me_6C_6)]PF_6$

Ru–C2	2.19(2)	C3–C4	1.42(3)
Ru–C3	2.18(2)	C4–C5	1.43(3)
Ru–C4	2.11(1)	C5–C6	1.42(3)
Ru–C5	2.13(2)	C6–C7	1.50(3)
Ru–C6	2.20(2)	C7–C8	1.53(3)
Ru–C11	2.30(2)	C8–C9	1.50(3)
Ru–C12	2.26(2)	C8–C10	1.43(3)
Ru–C13	2.29(3)	C9–C91	1.53(3)
Ru–C14	2.23(2)	C9–C92	1.55(3)
Ru–C15	2.18(1)	C11–C12	1.39(2)
Ru–C16	2.21(2)	C11–C16	1.45(2)
C1–C2	1.51(2)	C12–C13	1.43(3)
C1–C9	1.58(2)	C13–C14	1.51(3)
C1–C10	1.55(3)	C14–C15	1.40(2)
C2–C3	1.42(3)	C15–C16	1.41(3)
C2–C6	1.41(2)		

TABLE 4. Selected bond angles (°) for [(η^5-PCp)Ru(η^6-Me_6C_6)]PF_6

C1–C2–C3	132(2)	C9–C8–C10	84(2)
C1–C2–C6	116(2)	C2–C1–C9	107(2)
C3–C2–C6	111(2)	C2–C1–C10	104(2)
C2–C3–C4	106(2)	C9–C1–C10	78(1)
C3–C4–C5	109(2)	C1–C9–C8	90(2)
C4–C5–C6	108(2)	C1–C9–C91	105(2)
C2–C6–C5	106(2)	C1–C9–C92	114(2)
C2–C6–C7	124(2)	C8–C9–C91	115(2)
C5–C6–C7	129(3)	C8–C9–C92	121(2)
C6–C7–C8	104(2)	C91–C9–C92	109(2)
C7–C8–C9	117(2)	C1–C10–C8	94(2)
C7–C8–C10	110(2)	Me_6C_6 ccc av.	120(2)

are given in Table 1. Systematic searches in reciprocal space using a Rigaku AFC6R diffractometer on a 12 kW rotating anode generator showed that the crystals belonged to the orthorhombic system. Systematic absences (*hkl*, $h+k\neq 2n$ and 00*l*, $l\neq 2n$) suggested the space group $C222_1$, which was confirmed by successful solution and refinement. Data were obtained using the ω-scan technique. Three standard reflections measured every 150 reflections during the entire data collection period showed no significant trends. Empirical absorption corrections based on azimuthal scans of several reflections, were applied and the data were corrected for Lorentz and polarization effects. The structure was solved by direct methods [19a]. The non-hydrogen atoms were refined anisotropically except for Cl and C141 which were kept isotropic. The hydrogens are in calculated positions. Full-matrix least-squares refinements minimizing $\Sigma w(|F_o|-|F_c|)^2$ with $\sigma^2(F^2)=\sigma^2$ (counts)+$(0.03I)^2$ converged to the values given in Table 1 (all calculations were performed using ref. 19b). The maximum and minimum peaks on the final difference Fourier map corresponded to 0.78 and -0.81 e/Å^3, respectively. The scattering factor coefficients and anomalous dispersion coefficients were taken from ref. 20a and 20b, respectively. Final atom coordinates are given in Table 2 and selected bond lengths and angles are given in Tables 3 and 4, respectively.

Results and discussion

HPCp (see Scheme 1) reacts with TlOEt in ethanol to form TlPCp. Addition of a solution, or suspension, of [(η^6-arene)$RuCl_2$]$_2$ in acetonitrile to the TlPCp solution produces TlCl and [(η^5-PCp)Ru(η^6-arene)]Cl. The latter are converted by addition of an aqueous solution of NH_4PF_6 into the corresponding PF_6 salts (Scheme 3) in good yields.

$$\text{HPCp} + \text{TlOEt} \xrightarrow{\text{EtOH}} \text{TlPCp} + \text{EtOH} \quad (4)$$

$$\text{TlPCp} + [(\eta^6\text{-arene})RuCl_2]_2 \xrightarrow{CH_3CN} [(\eta^5\text{-PCp})Ru(\eta^6\text{-arene})]Cl \quad (5)$$

$$[(\eta^5\text{-PCp})Ru(\eta^6\text{-arene})]Cl + NH_4PF_6 \xrightarrow{H_2O} [(\eta^5\text{-PCp})Ru(\eta^6\text{-arene})]PF_6 + NH_4Cl \quad (6)$$

Scheme 3.

Though the PCp^- anion may be generated by reaction of HPCp with BuLi in ether, with NEt_3 in ether, or with TlOEt in ethanol only TlPCp reacts with the [(η^6-arene)$RuCl_2$]$_2$ to give good yields of [(η^5-PCp)Ru(η^6-arene)]Cl. With either LiPCp or $HNEt_3$PCp the yields were quite meager (5–10%) as compared to 65 –70% with TlPCp. The increased yields with TlPCp are probably, in part, due to the driving force providing by the very low solubility of TlCl.

Coordination of ruthenium can occur to either the top (*exo*) or bottom (*endo*) face (see Scheme 1) of PCp giving rise to two isomeric products. For the arenes benzene, toluene and *p*-cymene, the two isomers were formed in roughly equal amounts. However, for hexamethylbenzene one isomer was greatly favored over the other by a ratio of 14:1. Varying the temperatures of the reaction mixtures from -78 to 35 °C had no perceptible effect on the isomer ratio, in marked contrast to what is reported [4] for the reactions of Ti(IV) or Zr(IV) reagents with LiPCp. These differences may perhaps be attributed to the observation that LiPCp exists in a temperature dependent monomer–dimer equilibrium [21] with the dimer favored at low temperatures, whereas TlPCp might exist only as a monomer. At low temperatures both Ti(IV) and Zr(IV) preferentially coordinate to the *endo* face and at higher temperatures to the *exo* face of PCp. Thus, both monomeric LiPCp and TlPCp appear to favor coordination of a metal to the *exo* face of PCp.

As Paquette and co-workers have distinguished their isomeric products on the basis of differential long range anisotropic influences on the proton chemical shifts of the methano bridge and *gem*-dimethyl protons, we have structurally characterized [(η^5-PCp)Ru(η^6-Me_6C_6)]PF_6 (Fig. 1) and carried out a detailed analysis of its ^{1}H and $^{13}C\{^1H\}$ NMR spectra.

As can be seen from Fig. 1, the major isomer involves coordination of ruthenium to the *exo* face of the PCp ligand. The ruthenium atom is not equidistant from the η^5-PCp and η^6-Me_6C_6 ligands. It is closer to the arene (Ru–ring centroid = 1.73 Å) than to the cyclopentadienide (Ru–ring centroid = 1.79 Å). Though both donor rings of these ligands are planar (the mean deviations from the C_2–C_6 and C_{11}–C_{16} planes are only 0.0043 and 0.016 Å, respectively), these two planes are not parallel (the dihedral angle between these two

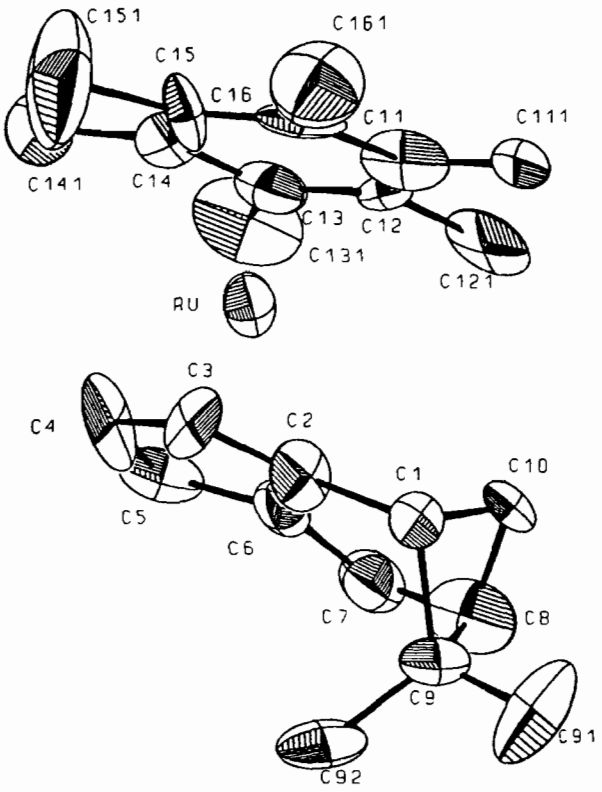

Fig. 1. ORTEP drawing of the cation of $[(\eta^5\text{-PCp})Ru(\eta^6\text{-}Me_6C_6)]PF_6$ showing the atom numbering scheme (50% probability ellipsoids). Hydrogen atoms are omitted.

planes is 6.83°). These data compare with those reported for $[(\eta^5\text{-}C_5Me_5)Ru(\eta^6\text{-}C_5H_5SiMe_3)OTf$ [22] and $[(\eta^5\text{-}C_5Me_5)Ru(\eta^6\text{-}Me_6C_6)](TCNQ)$ [23] where the dihedral angles between the planes are 2.9 and 1.2°, respectively. For both these complexes the arene is closer (1.70 and 1.75 Å, respectively) to the ruthenium than is the cyclopentadienide (1.82 and 1.80 Å, respectively). For $[(\eta^6\text{-}Me_6C_6)_2Ru](TCNQ)$ [24] the ruthenium arene centroid distance is 1.76 Å and the dihedral angle between the two arene planes is only 0.85°. Ring–ring steric repulsions are most likely responsible for these structural changes.

The ^1H and $^{13}C\{^1H\}$ NMR spectral assignments for $[(\eta^5\text{-PCp})Ru(Me_6C_6)]^+$ were made in the following way. A combination of $^{13}C\{^1H\}$, APT and fully coupled ^{13}C NMR spectra established the number of hydrogens attached to each carbon. For example, the fully coupled carbon data: δ 17.11 (q, $^1J_{CH}=129.08$ Hz, Me_6C_6), 21.40 (qq, $^1J_{CH}=124.09$ Hz, $^3J_{CH}=4.53$ Hz, C_{12}), 24.98 (apparent tt, $^1J_{CH}=131.12$ Hz, $^2J_{CH}=^3J_{CH}=4.00$ Hz, C_7), 26.24 (qq, $^1J_{CH}=125.68$ Hz, $^3J_{CH}=4.53$ Hz, C_{11}), 34.55 (tt, $^1J_{CH}=139.44$ Hz, $^2J_{CH}=6.20$ Hz, C_{10}), 38.90 (dt, $^1J_{CH}=148.28$ Hz, $^2J_{CH}=6.20$ Hz, C_1), 40.80 (dt, $^1J_{CH}=147.29$ Hz, $^2J_{CH}=6.20$ Hz, C_8), 41.29 (s, C_9), 77.93 (dtd, $^1J_{CH}=183.04$ Hz, $^2J_{CH}=^3J_{CH}=6.50$ Hz, $^3J_{CH'}=2.87$ Hz, C_5), 79.10 (dtd, $^1J_{CH}=180.17$ Hz, $^2J_{CH}=^3J_{CH}=6.50$ Hz, $^3J_{CH'}=2.87$ Hz, C_3), 79.72 (dt, $^1J_{CH}=180.09$ Hz, $^2J_{CH}=7.10$ Hz, C_4), 95.27 (bs, C_6), 99.00 (q, $^2J_{CH}=4.31$ Hz, Me_6C_6), 112.32 (bs, C_2) suggested the assignments as noted. The carbon–hydrogen coupling constants are in the expected ranges for a structure of this type [25]. An INADEQUATE spectrum (Fig. 2) confirmed these assignments by establishing the carbon–carbon connectivity. To the best of our knowledge, this is the first reported INADEQUATE spectrum of an organometallic compound. Indirect detection $^1H/^{13}C$ heteronuclear correlation (HMQC, Fig. 3), in concert with $^1H/^1H$ COSY, selective $^1H/^1H$ homonuclear decoupling, 2DHOJ (Fig. 4) and NOE difference spectra unambiguously established the proton chemical shifts, coupling constants and assignments. The δ 0.49 ppm CH_3 resonance showed strong NOEs with the $CH_3(a)$, H_6, H_2, H_3, H_7, H_8 and H_9 resonances establishing the *syn* relationship between this methyl group and the Cp ring. Strong NOEs between the δ 1.32 ppm. resonance and the $CH_3(s)$, H_5, H_6 and H_3 resonances established the *anti* relationship between this methyl group and the Cp ring and the *syn* relationship between $CH_3(a)$ and H_5. Strong NOEs between the Me_6C_6 resonance and the H_4 and H_1 resonances showed that H_1 and H_4 are proximate to the Me_6C_6 methyls.

Collectively the NMR data show that the solution and solid-state structures of $[(\eta^5\text{-PCp})Ru(\eta^6\text{-}Me_6C_6)]^+$ are the same. The solid-state structure consists of separated cations and anions with no unusual interactions. The bond distances (Table 3) and bond angles (Table 4) are in the expected ranges. The ^1H and $^{13}C\{^1H\}$ NMR spectra of the other complexes were assigned by comparison with those of the Me_6C_6 analog. Diagnostic data are given in Table 5.

One notes in particular that the *exo* isomers are readily distinguished from the *endo* isomers on the basis that the $CH_3(s)$ and H_4 proton resonances occur near 0.5 and 1.5 ppm, respectively, for the *exo* isomers and near 1.2 and 0.9 ppm, respectively, for the *endo* isomers as a result of differential diamagnetic anisotropy effects of the Cp ring current. The $CH_3(a)$ and H_5 chemical shifts are much less diagnostic but the chemical shift differences, $\Delta\delta$, for the $CH_3(a)$, $CH_3(s)$; H_4, H_5 and C_{11}, C_{12} pairs of resonances are quite diagnostic. These chemical shift differences are always larger for the *exo* isomers except for $\Delta\delta$ H_4, H_5 where the situation is reversed.

The *exo* and *endo* isomers of the C_6H_6, MeC_6H_5 and *p*-$MeC_6H_4CHMe_2$ complexes could not be separated by column chromatography on silica, Sephadex or alumina with a wide variety of eluants, or by fractional crystallization. The isomer ratios were determined by integration of the aforementioned resonances. Except for the most bulky arene, Me_6C_6, the isomer ratios are

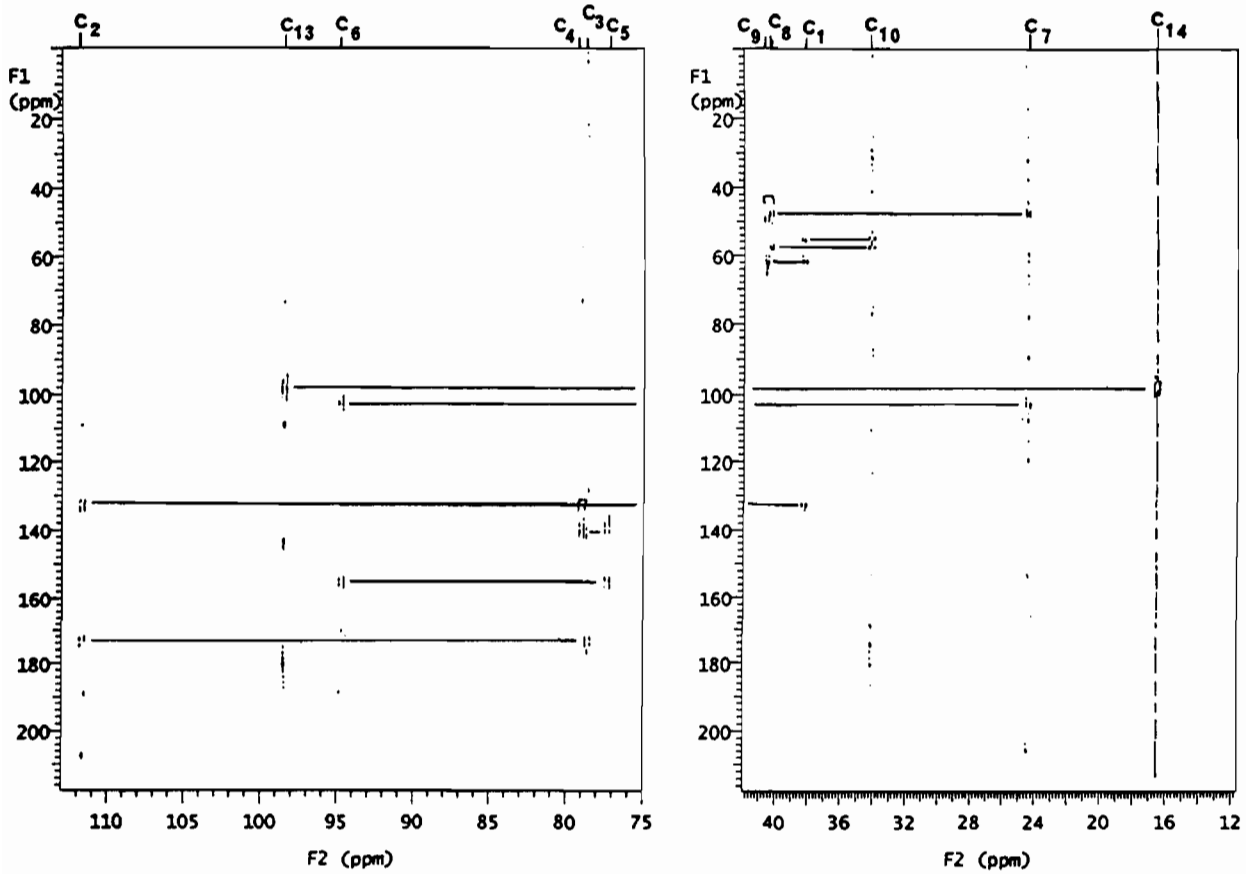

Fig. 2. 150 MHz ^{13}C INADEQUATE NMR spectrum of $[(\eta^5\text{-PCp})Ru(Me_6C_6)]PF_6$ (approximately 300 mg in 0.5 ml $CDCl_3$). The C–C connectivities are denoted by horizontal lines. The C_{11} and C_{12} connectivity was not observed.

TABLE 5. Comparative ^1H and $^{13}C\{^1H\}$ NMR data for isomeric $[(\eta^5\text{-PCp})Ru(\eta^6\text{-arene})]PF_6$ complexes ($CDCl_3$, δ (ppm))

Arene/isomer	δ^1H						$\delta^{13}C$		
	$CH_3(a)$	$CH_3(s)$	$\Delta\delta$	H_4	H_5	$\Delta\delta$	C_{11}	C_{12}	$\Delta\delta$
C_6H_6/*exo*	1.36	0.56	0.80	1.51	2.79	1.28	26.30	21.54	4.76
C_6H_6/*endo*	1.34	1.19	0.15	0.87	2.69	1.82	27.71	26.58	1.13
MeC_6H_5/*exo*	1.37	0.57	0.80	1.47	2.81	1.34	26.21	21.43	4.78
MeC_6H_5/*endo*	1.35	1.19	0.16	0.87	2.70	1.83	26.46	22.61	3.85
p-$MeC_6H_4CHMe_2$/*exo*	1.38	0.58	0.80	1.49	2.83	1.34	25.78	21.48	4.30
p-$MeC_6H_4CHMe_2$/*endo*	1.37	1.23	0.14	0.90	2.67	1.77	26.53	22.75	3.78
Me_6C_6/*exo*	1.32	0.49	0.83	1.22	2.72	1.50	26.24	21.50	4.74
Me_6C_6/*endo*	1.29	1.14	0.15	0.74	2.60	1.86	26.24	21.81	4.43

all near 1:1 showing that the π-facial selectivity of coordination of the PCp ligand to an (arene)Ru^{2+} moiety is very low.

Because $[(\eta^5\text{-PCp})Ru(\eta^6\text{-}Me_6C_6)]PF_6$ was obtained highly isomerically enriched, we have investigated its substitution chemistry. Thermal or photochemical reaction with CO or CH_3CN does not result in displacement of the Me_6C_6 ligand. In both cases the starting complex was recovered in high yield. This is somewhat surprising in that photochemical liberation of arenes from $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-arene})]^+$ in CH_3CN does occur for C_6H_6, MeC_6H_5, *p*-xylene, mesitylene, pentamethylbenzene and hexamethylbenzene, though the quantum yield for the hexamethylbenzene liberation is an order of magnitude less than that found for C_6H_6 liberation [26]. By extrapolation from the enthalpies of reaction of $[(\eta^5\text{-}C_5Me_5)Ru(CH_3CN)_3]^+$ with arenes [22] one would expect the Ru–C_6Me_6 interactions to be rather strong in keeping with the above observations. Indeed, the Ru–Me_6C_6 distance is 0.02 Å shorter in $[(\eta^5\text{-PCp})Ru(\eta^6\text{-}Me_6C_6)]PF_6$ than in $[(\eta^5\text{-}Me_5C_5)Ru(\eta^6\text{-}Me_6C_6)](TCNQ)$.

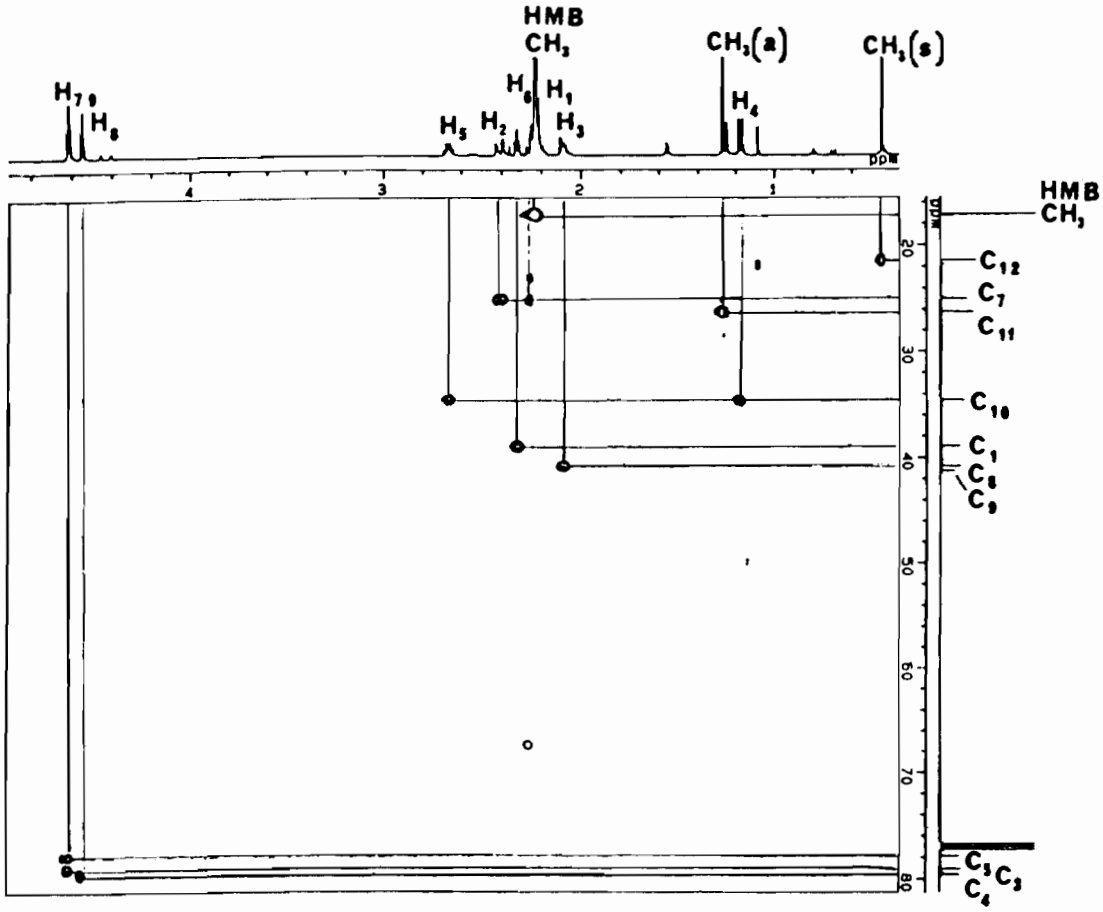

Fig. 3. 500 MHz indirect detection (HMQC) heteronuclear $^{1}H/^{13}C$ correlation NMR spectrum of $[(\eta^5\text{-PCp})Ru(\eta^6\text{-}Me_6C_6)]PF_6$ (approximately 20 mg in 0.5 ml $CDCl_3$). The high resolution 1-D ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra are shown on the top and to the right, respectively (see Scheme 1 for atom numbering). The $^{1}H/^{13}C$ chemical shift correlations are noted by the vertical/horizontal line intersections.

TABLE 6. Redox characteristics of some arene and cyclopentadienyl ruthenium(II) complexes[a]

Complex	E_{pa} Ru(II)/Ru(III)	E_{pc} Ru(II)/Ru(I)
$[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-}C_6H_6)]PF_6$	1.69	−2.33
$[(\eta^5\text{-}MeC_5H_4)Ru(\eta^6\text{-}C_6H_6)]PF_6$	1.66	−2.40
$[(\eta^5\text{-PCp})Ru(\eta^6\text{-}C_6H_6)]PF_6$	1.50	−2.42
$[(\eta^5\text{-PCp})Ru(\eta^6\text{-}MeC_6H_5)]PF_6$	1.45	−2.46
$[(\eta^5\text{-PCp})Ru(\eta^6\text{-}MeC_6H_4CHMe_2)]PF_6$	1.43	−2.51
$[(\eta^5\text{-PCp})Ru(\eta^6\text{-}Me_6C_6)]PF_6$	1.33	−2.63
$[(\eta^5\text{-}C_5H_5)_2Ru]$	0.49[b]	−2.55
$[(\eta^5\text{-}Me_5C_5)Ru(\eta^5\text{-}C_5H_5)]$	0.27[b]	−2.57
$[(\eta^5\text{-}Me_5C_5)_2Ru$	0.09[b]	−2.69

[a]In CH_2Cl_2 containing 0.1 M TBAP at 25 °C; E values were determined by differential pulse voltammetry and are given vs. Fc^+/Fc. [b]See ref. 28 for comparative values and discussion.

$[(\eta^5\text{-PCp})Ru(\eta^6\text{-}Me_6C_6)]PF_6$ also is not converted into an η^4-cyclohexadiene complex by reaction with $NaBH_4$, as is $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-}C_6H_6)]PF_6$ [27]. $[(\eta^5\text{-PCp})Ru(\eta^6\text{-}Me_6C_6)]PF_6$ reacts with phosphines both thermally and photochemically to liberate the arene, but an inseparable mixture of products is formed independent of the phosphine to ruthenium ratio.

Because the redox properties of transition metal complexes provide a measure of the donor abilities of the coordinated ligands, we have determined the po-

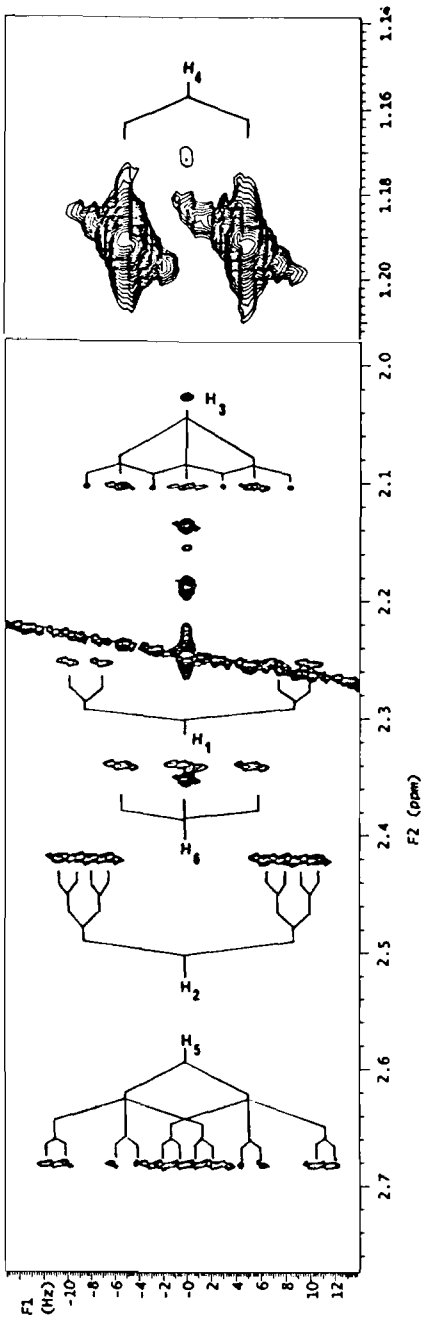

Fig. 4. 600 MHz Homonuclear 2DHOJ NMR spectrum of $[(\eta^5\text{-PCp})Ru(\eta^6\text{-}Me_6C_6)]PF_6$ (approximately 20 mg in 0.5 ml $CDCl_3$). This spectrum was obtained with presaturation of the $Me_6C_6CH_3$ resonance. The coupling trees are indicated.

tentials for the one-electron oxidations and reductions of several ruthenium complexes (Table 6) by differential pulse voltammetry. These data were obtained on mixtures of the *exo* and *endo* isomers. Since single oxidation and reduction peaks were observed in each case for these quasi-reversible processes there is no measurable difference in the redox properties of the two isomers under these conditions. One notes, from the potentials, that the ease of oxidation and reduction are inversely related as expected for metal centered redox processes. The more electron rich the metal center the less positive is the oxidation potential and the more negative is the reduction potential. Since $[(\eta^5\text{-PCp})Ru(\eta^6\text{-}C_6H_6)]^+$ is easier to oxidize and harder to reduce than $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-}C_6H_6)]^+$ this implies that the PCp ligand is a better donor toward ruthenium(II) than is C_5H_5. On the same basis PCp is a better donor than $\eta^5\text{-}MeC_5H_4$. By comparing the redox properties of the $[(\eta^5\text{-PCp})ru(\eta^6\text{-arene})]^+$ species we conclude that the arene donor abilities decrease in the order: $Me_6C_6 > p\text{-}MeC_6H_4CHMe_2 > MeC_6H_5 > C_6H_6$, as might be anticipated considering alkyl substituents on the arene ring to be electron releasing.

Supplementary material

For the crystal structure, listings of crystal and refinement data, bond distances and angles, H atom coordinates, and thermal parameters (*U*) (13 pages) and structure factors (12 pages) are available from the authors.

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