Journal of Organometallic Chemistry, 322 (1987) 221–228
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

PREPARATION AND REACTIVITY OF THE PENTAMETHYLCYCLOPENTADIENYL COMPLEXES $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)(L)Cl]$ (L = CO, Bu^{t}NC) AND $[(\eta^5\text{-}C_5Me_5)Ru(L)_2Cl]$ (L = Bu^{t}NC, norbornadiene)

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(Received October 6th, 1986)

Summary

The chloro complexes $[(\eta^5\text{-}C_5Me_5)Ru(norbornadiene)Cl]$ (**2**), $[(\eta^5\text{-}C_5Me_5)Ru(Bu^tNC)_2Cl]$ (**3**), $[(\eta^5\text{-}C_5Me_5)Ru\text{-}(PPh_3)(Bu^tNC)Cl]$ (**4**) and $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)(CO)Cl]$ (**5**) have been prepared from $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)_2Cl]$ (**1**). Reaction of **3–5** with sodium methoxide gave the corresponding hydrides **7–9**. All the chloro complexes **1–5** ionise readily in methanol containing NH_4PF_6 and a donor ligand to give a range of new cations as hexafluorophosphate salts. Treatment of **1** and **4** with $NOBF_4$ gave the dicationic nitrosyls, $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)_2NO](BF_4)_2$ (**12**) and $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)(Bu^tNC)NO](BF_4)_2$ (**17**), respectively.

Introduction

We recently reported the isolation of a molecular hydrogen complex, $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(Bu^tNC)(\eta^2\text{-}H_2)]PF_6$, from the protonation of the neutral monohydride precursor [1]. In order to further study this unusual reactivity we needed a series of related complexes, $[(\eta^5\text{-}C_5R_5)RuLL'(H)]$, where R = H, Me and L,L' = PPh_3, PMe_3, CO, Bu^{t}NC etc. The cyclopentadienyl series of complexes is known for most of the required ligand combinations but for the pentamethylcyclopentadienyl series most of the required compounds are unreported to date. Examples of the classes $[(\eta^5\text{-}C_5Me_5)Ru(CO)_2X]$ [2], $[(\eta^5\text{-}C_5Me_5)Ru(PR_3)_2X]$ [3,4] $[(\eta^5\text{-}C_5Me_5)\text{-}Ru(NO)X_2]$ [5] and $[(\eta^5\text{-}C_5Me_5)Ru(allyl)X_2]$ [6] have all been reported. We now report convenient syntheses of the classes $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)(L)Cl]$, $[(\eta^5\text{-}C_5Me_5)Ru(L)_2Cl]$, related monohydrides and cationic derivatives.

Results and discussion

Reaction of $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)_2Cl]$ (**1**) with excess norbornadiene in refluxing toluene gave $[(\eta^5\text{-}C_5Me_5)Ru(\eta^4\text{-}C_7H_8)Cl]$ (**2**) in 86% yield. Bercaw has reported the

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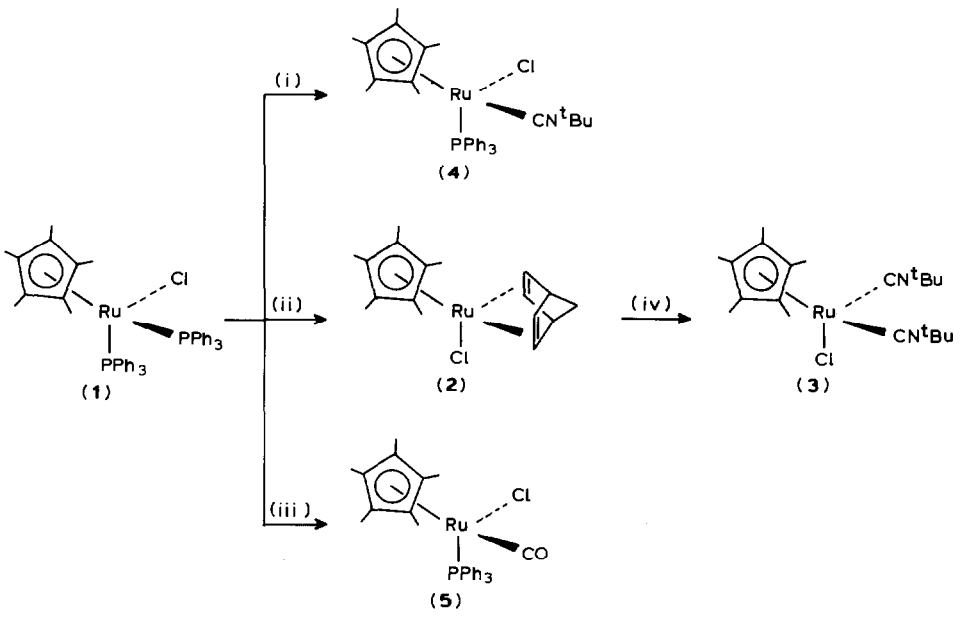
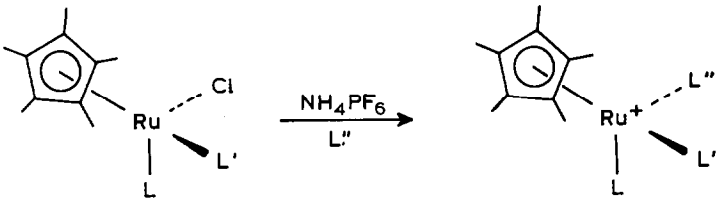


SCHEME 1. (i) Bu^{t}NC, CH_2Cl_2, 20°C; (ii) norbornadiene, C_7H_8, 100°C; (iii) HCO_2H, C_7H_8, 140°C; (iv) Bu^{t}NC, C_7H_8, 100°C.

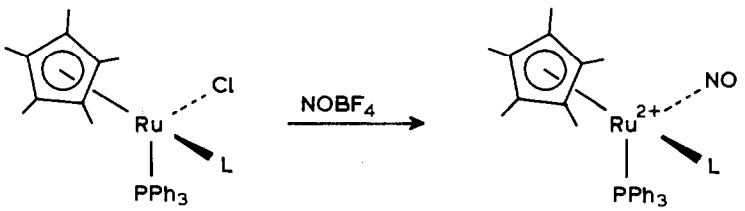
preparation of **2** from $[(\eta^4\text{-}C_7H_8)RuCl_2]_x$ and lithium pentamethylcyclopentadienide in low yield [4]. The bis-isonitrile complex **3** was cleanly prepared from **2** in high yield as an orange crystalline complex which exhibited two bands at 2110 and 2046 cm^{-1} in the infrared spectrum, assignable to $\nu(C{\equiv}N)$. Attempts to prepare **3** directly from **1** gave only poor isolated yields owing to the instability of **3** to the chromatography required to remove triphenylphosphine. Recently the preparation of the bromo analogue of **3** has been reported [7]. The mono-isonitrile complex, $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)(Bu^tNC)Cl]$ (**4**) was prepared free of **3** by treatment of **1** with Bu^{t}NC in dichloromethane at room temperature (see Scheme 1). Carbonylation of **1** with formic acid in toluene at 120°C for 8 h gave $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)(CO)Cl]$ (**5**) as pale yellow crystals. Reaction of **1** with carbon monoxide at 140°C for 16 h gave a mixture of both **5** and $[(\eta^5\text{-}C_5Me_5)Ru(CO)_2Cl]$ in a 5/2 ratio. The corresponding cyclopentadienyl complex, $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl]$ is carbonylated only under extreme conditions, (150 atm., 70°C) and only as far as the monocarbonyl complex [8]. However the use of a trap for dissociated triphenylphosphine such as sulphur or hydrochloric acid allows carbonylation at lower pressures [9]. Reaction of **1** with sodium methoxide gave the hydride $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)_2H]$ (**6**), whose ^1H NMR spectrum contained a high field triplet at $\delta - 11.9$, $J(PH)$ 34 Hz. Similar treatment of **4** and **5** gave the hydrides $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)(Bu^tNC)H]$ (**8**) and $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)(CO)H]$ (**9**) respectively. These complexes could be crystallised from light petroleum ether as analytically pure materials. Preparation of $[(\eta^5\text{-}C_5Me_5)Ru(Bu^tNC)_2H]$ (**7**) by reaction of **3** with sodium methoxide gave impure samples and the best route to pure samples of **7** was by use of $LiAlH_4$ on **3** followed by sublimation of the crude product. The high solubility of **7** in common solvents made crystallisation of impure samples difficult. Reaction of $[(\eta^5\text{-}C_5Me_5)Ru(\eta^4\text{-}$

C_7H_8)Cl] (**2**) with NaOMe gave on work-up an impure oil, which gave inter alia singlets in the H NMR spectrum at δ 1.74 and −5.14 ppm. Attempts to purify this crude product were unsuccessful. The related olefin hydride [(η^5-C_5H_5)Ru(η^4-C_8H_{12})H] has recently been reported [10].



	L	L'	L''	
1	PPh_3	PPh_3	CN^tBu	**10**
1	PPh_3	PPh_3	CO	**11**
2	norbornadiene		CO	**13**
2	norbornadiene		PMe_3	**14**
3	CN^tBu	CN^tBu	$P(OPh)_3$	**15**
4	PPh_3	CN^tBu	CO	**16**
5	PPh_3	CO	CN^tBu	**16**

The chloro complexes **1**–**5** all readily ionise at room temperature in methanol containing ammonium hexafluorophosphate. Thus treatment of **1**, **2** and **4** under carbon monoxide atmosphere leads to high yields of the carbonyl cations **11**, **13** and **16**, respectively. Similarly the isonitrile cations **10** and **16** can be prepared by ionisation of **1** and **5** in the presence of t-butylisonitrile. The reaction of the bis-isonitrile complex **3** under ionising conditions in the presence of triphenylphosphite gave **15**. The ^{1}H NMR spectrum of [(η^5-C_5Me_5)Ru(η^4-C_7H_8)(PMe_3)]PF_6 (**14**) exhibited several features of interest, every proton being coupled to the phosphorous atom; the two distinct olefinic resonances at δ 3.71 and 3.49 ppm having widely differing coupling constants (J(PH)) of 11.5 and ca. 1 Hz, respectively, while the equivalent methylene protons exhibit a long range coupling (^4J(PH)) of 0.5 Hz. Nuclear Overhauser Enhancement experiments allowed the signal at δ 3.71 with the larger coupling to phosphorus to be assigned to the olefinic protons pointing towards the trimethylphosphine ligand. The methine proton with this orientation resonates at δ 4.13, while the other methine proton is found at δ 3.43 ppm.



(**1**) L = PPh_3 (**12**)

(**4**) L = CN^tBu (**17**)

Reaction of the chloro compounds **1** and **4** with $NOBF_4$ gave, respectively, pale-purple crystals of [(η^5-C_5Me_5)Ru(PPh_3)$_2$NO](BF_4)$_2$ (**12**) and orange crystals

of $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)(Bu^tNC)NO](BF_4)_2$ (**17**). The infrared spectrum of **12** contained a strong band at 1805 cm^{-1} characteristic of a linear nitrosyl, while that of **17** contained a band at 1859 cm^{-1} in addition to a strong band at 2221 cm^{-1} due to the isonitrile ligand. This shift of +85 cm^{-1} relative to free Bu^tNC (ν(CN) 2136 cm^{-1}) confirms the dicationic nature of **17**, since the monocations **10** and **16** exhibit shifts of −3 and +36 cm^{-1}, respectively.

The preparation of this extensive series of complexes and the general observation that substitution reactions and ionisation reactions of the (η^5-C_5Me_5) series occur more readily than those of the corresponding (η^5-C_5H_5) series opens up a wide range of chemical reactions. We will describe later further details of chemistry specific to the permethylated series.

Experimental

All reactions and preparations were carried out under nitrogen using standard Schlenk-tube techniques. Tetrahydrofuran was dried over sodium benzophenone ketyl and distilled. Diethyl ether and light petroleum (b.p. 40–60°C) were dried over sodium wire and distilled. Dichloromethane was dried over calcium hydride and distilled. All other solvents were used as supplied. Reactions carried out at > 1 atm pressure were performed in Fischer-Porter bottles. Infrared spectra were recorded on Perkin–Elmer 297 or 1710 FTIR instruments and calibrated against polystyrene film. Nuclear magnetic resonance spectra were recorded on Perkin–Elmer R32 (90 MHz, ^{1}H), Bruker WP80/SY (32.4 MHz, ^{31}P) and Bruker WH 360 (360.135 MHz, ^{1}H) spectrometers. Elemental analyses were by Butterworth Laboratories, London. Chromatography was performed on alumina (Grade IV) under nitrogen. The ligands, trimethylphosphine [11], pentamethylcyclopentadiene [12] and t-butylisonitrile [13] were prepared by published procedures.

(η^5-C_5Me_5)Ru(PPh_3)$_2$Cl (1)

The published procedure [3] was followed, but a brown solid impurity was formed along with the product. Extraction of the residue with dichloromethane (50 ml) and concentration of the extract gave a dark brown solution, which was put on an alumina column (2 × 20 cm) in light petroleum. The pure product was rapidly eluted with dichloromethane; concentration and crystallisation by addition of light petroleum gave orange crystals, which were identified as **1** by ^{1}H NMR spectroscopy. ^{1}H NMR ($CDCl_3$): δ 7.43 and 7.04 (m, 30H, Ph), 1.02 (t, J(PH) ~ 1 Hz, 15H, C_5Me_5).

(η^5-C_5Me_5)Ru(NBD)Cl (2)

A suspension of **1** (0.95 g, 1.19 mmol) and norbornadiene (4 ml, large excess) in toluene (30 ml) was stirred (100°C) for 16 h. The volume was reduced and the concentrated solution was placed on an alumina column in light petroleum. Triphenylphosphine was eluted with toluene and the product then eluted with diethyl ether. Concentration gave lustrous orange crystals, yield 370 mg (86%), identified by IR and NMR spectroscopy [4].

(η^5-C_5Me_5)Ru(Bu^tNC)$_2$Cl (3)

A solution of **2** (220 mg, 0.56 mmol) and t-butylisonitrile (0.2 ml, 1.91 mmol) in toluene (30 ml) was stirred for 4 h at 100°C. Evaporation gave an orange oil.

Crystallisation from light petroleum gave orange crystals, yield 260 mg (97%) (Found: C, 55.14; H, 7.45; N, 6.47. $C_{20}H_{33}ClN_2Ru$ calc: C, 54.84; H, 7.59; N, 6.40%). IR (Nujol): ν_{max} 2110s and 2046s cm^{-1} (CN); ^1H NMR ($CDCl_3$): δ 1.75 (s, 15H, C_5Me_5), 1.48 (s, 18H, CMe_3).

(η^5-C_5Me_5)Ru(PPh_3)(Bu^tNC)Cl (4)

A solution of **1** (570 mg, 0.72 mmol) and t-butylisonitrile (66 mg, 0.79 mmol) in dichloromethane (30 ml) was stirred (20°C) for 10 min. Evaporation, extraction with hot decane, filtration of the extract and cooling to −20°C gave orange crystals, which were washed with ice-cold light petroleum, yield 380 mg (86%). (Found: C, 64.43; H, 6.19; N, 2.53; $C_{33}H_{39}ClNPRu$ calc: C, 64.22; H, 6.37; N, 2.27%). IR (Nujol): ν_{max} 2102sh, 2059s cm^{-1} (CN); ^1H NMR ($CDCl_3$): δ 7.60 and 7.29 (m, 15H, Ph), 1.43 (d, J(PH) ~ 1.8 Hz, 15H, C_5Me_5), 1.20 (s, 9H, CMe_3).

(η^5-C_5Me_5)Ru(PPh_3)(CO)Cl (5)

A solution of **1** (0.97 g, 1.23 mmol) and formic acid (1 ml, excess) in toluene (25 ml) was stirred (120°C) for 8 h in a Fischer-Porter bottle. Concentration gave a bright orange solution which was put on an alumina column (2 × 20 cm) in light petroleum. Triphenylphosphine was eluted with toluene and the product then rapidly eluted with dichloromethane. Concentration and slow addition of light petroleum gave pale yellow crystals, yield 0.5 g (73%). (Found: C, 61.86; H, 5.38. $C_{29}H_{30}ClOPRu$ calc: C, 61.97; H, 5.38%). IR (Nujol): ν_{max} 1918s cm^{-1} (CO); ^1H NMR (C_6D_6): δ 7.79 and 6.98 (m, 15H, Ph), 1.38 (d, J(PH) ~ 1.7 Hz, 15H, C_5Me_5); $^{31}P\{^1H\}$ NMR (CH_2Cl_2): δ 48.2.

Reaction of a toluene solution of **1** with CO (5 atm) at 140°C for 16 h gave a mixture of **5** and (η^5-C_5Me_5)Ru$(CO)_2$Cl (5/2), which was identified by IR and ^1H NMR spectroscopy [2].

(η^5-C_5Me_5)Ru(PPh_3)$_2$H (6)

Sodium methoxide (200 mg, 3.7 mmol) was added to a suspension of **1** (280 mg, 0.31 mmol) in methanol (10 ml). The orange suspension was stirred at 20°C for 16 h. The solvent was removed under reduced pressure to give a yellow solid. Extraction with diethyl ether (2 × 20 ml) followed by concentration of the extract and addition of light petroleum gave yellow micro crystals, yield 210 mg. (78%). (Found: C, 72.40; H, 6.20. $C_{46}H_{46}P_2Ru$ calc: C, 72.50; H, 6.09%). IR (Nujol): ν_{max} 1926w cm^{-1} (RuH); ^1H NMR (C_6D_6): δ 7.56 and 6.90 (m, 30H, Ph), 1.43 (t, J(PH) 1 Hz, 15H, C_5Me_5), −11.9 (t, J(PH) 34 Hz, 1H, RuH).

(η^5-C_5Me_5)Ru(Bu^tNC)$_2$H (7)

$LiAlH_4$ (15 mg, 0.39 mmol) was added to a solution of (η^5-C_5Me_5)Ru$(Bu^tNC)_2$Cl (**3**) (130 mg, 0.30 mmol) in thf (30 ml) at 0°C. The suspension was stirred at 20°C for 2 h. Hydrolysis and removal of solvent gave a brown solid. Extraction with light petroleum (2 × 30 ml) and subsequent removal of solvent from the extract left a brown oil, which was sublimed (60°C/10^{-3} Torr) to give pure **7** as a pale yellow solid, yield 78 mg (65%). (Found: C, 58.98; H, 8.51; N, 6.81. $C_{20}H_{34}N_2Ru$ calc: C, 59.52; H, 8.49; N, 6.94%). IR (Nujol): ν_{max} 2048s (CN) and 1927s cm^{-1} (CN + RuH): ^1H NMR (C_6D_6); δ 2.07 (s, 15H, C_5Me_5), 1.16 (s, 18H, CMe_3), −10.8 (s, 1H, RuH).

(η^5-C_5Me_5)Ru(PPh_3)(Bu^{t}NC)H (8)

A suspension of **4** (200 mg, 0.32 mmol) in methanol (10 ml) and sodium methoxide (200 mg, 3.7 mmol) was stirred at 20°C for 1 h. Evaporation, extraction with light petroleum, and concentration of the extract gave yellow crystals, yield 170 mg, (89%) (Found: C, 67.63; H, 6.81; N, 2.42. $C_{33}H_{40}NPRu$ calc: C, 68.02; H, 6.92; N, 2.40%). IR (Nujol): ν_{max} 2011s (CN), 1915s cm^{-1} (RuH): ^1H NMR (C_6D_6): δ 7.75 and 7.09 (m, 15H, Ph), 1.84 (d, J(PH) ~1.3 Hz, 15H, C_5Me_5), 0.94 (s, 9H, CMe_3). −11.3, (d, J(PH) 38 Hz, 1H, RuH).

(η^5-C_5Me_5)Ru(PPh_3)(CO)H (9)

Sodium methoxide (200 mg, 3.7 mmol) was added to a suspension of **5** (220 mg, 0.39 mmol) in methanol (10 ml). The yellow suspension was stirred (50°C) for 6 h. Evaporation, extraction with light petroleum and concentration followed by cooling (−20°C) gave pale yellow microcrystals, yield 150 mg. (73%). (Found: C, 65.93; H, 6.06. $C_{29}H_{31}OPRu$ calc: C, 66.02; H, 5.92%); IR (Nujol): ν_{max} 1901s cm^{-1} (CO + RuH); ^1H NMR (C_6D_6): δ 7.68 and 7.01 (m, 15H, Ph), 1.71 (d, J(PH) ~1.3 Hz, 15H, C_5Me_5), −10.8 (d, J(PH) 35 Hz, 1H, RuH).

[η^5-C_5Me_5)Ru(PPh_3)$_2$(Bu^{t}NC)][PF_6] (10)

A suspension of (η^5-C_5Me_5)Ru(PPh_3)$_2$Cl (**1**) (150 mg, 0.19 mmol), NH_4PF_6 (60 mg, 0.38 mmol) and t-butylisonitrile (0.1 ml, 0.96 mmol) in methanol (30 ml) was stirred at reflux for 8 h. Evaporation and recrystallisation from dichloromethane diethyl ether gave pale yellow microcrystals, yield 160 mg (86%) (Found: C, 61.61; H, 5.61; N, 1.56. $C_{51}H_{54}F_6NP_3Ru$ calc: C, 61.94; H, 5.50; N, 1.42%). IR (Nujol): ν_{max} 2133s cm^{-1} (CN): ^1H NMR [(CD_3)CO]: δ 7.36 (m, 30H, Ph), 1.79 (s, 9H, CMe_3), 1.33 (t, J(PH) ~1.7 Hz, 15H, C_5Me_5); $^{31}P\{^1H\}$ NMR (CH_2Cl_2): δ 50.1.

[(η^5-C_5Me_5)Ru(PPh_3)$_2$CO][PF_6] (11)

A suspension of **1** (500 mg, 0.63 mmol) and NH_4PF_6 (310 mg, 1.88 mmol) in methanol (30 ml) was stirred (20°C) for 16 h in the presence of carbon monoxide (1 atm.). Evaporation and recrystallisation from dichloromethane diethyl ether gave pale yellow microcrystals, yield 450 mg (79%). (Found: C, 60.41; H, 5.08. $C_{47}H_{45}F_6OP_3Ru$ calc: C, 60.45; H, 4.86%). IR (Nujol): ν_{max} 1959s, cm^{-1} (CO); ^1H NMR ((CD_3)$_2$CO): δ 7.39 (m, 30H, Ph), 1.40 (t, J(PH) ~1.7 Hz, 15H, C_5Me_5); $^{31}P\{^1H\}$NMR (CH_2Cl_2): δ 48.8.

[(η^5-C_5Me_5)Ru(PPh_3)$_2$NO][BF_4]$_2$ (12)

A suspension of **1** (490 mg, 0.63 mmol) and $NOBF_4$ (100 mg, 0.85 mmol) in dichloromethane (30 ml) was stirred (20°C) for 1 h. Filtration and addition of diethyl ether gave pale purple microcrystals, yield (430 mg (72%). (Found: C, 57.13; H, 4.63; N, 1.56. $C_{46}H_{45}B_2F_8NOP_2Ru$ calc: C, 57.23; H, 4.70; N, 1.45%). IR (Nujol): ν_{max}, 1805s cm^{-1} (NO); ^1H NMR [(CD_3)$_2$CO]: δ 7.90 (m, 30H, Ph), 1.84 (t, J(PH) ~2 Hz, 15H, C_5Me_5).

[(η^5-C_5Me_5)Ru(NBD)CO][PF_6] (13)

A red suspension of **2** (80 mg, 0.22 mmol), NH_4PF_6 (72 mg, 0. 44 mmol) and methanol (25 ml) was stirred (20°C) under an atmosphere of carbon monoxide for

16 h. Evaporation of the solvent gave a yellow solid. Recrystallisation from dichloromethane/diethyl ether gave pale yellow crystals, yield 91 mg (83%). (Found: C, 43.30; H, 4.71. $C_{18}H_{23}F_6OPRu$ calc: C, 43.13; H, 4.62%). IR (Nujol): ν_{max} 2005s cm^{-1} (CO); ^1H NMR [$(CD_3)_2CO$]: δ 5.11 (m, 2H, =CH), 4.42 (m, 2H, =CH), 4.27 (m, 1H, -CH), 3.62 (m, 1H, -CH), 1.93 (s, 15H, C_5Me_5), 1.42 (t, 2H, CH_2).

[(η^5-C_5Me_5)Ru(NBD)(PMe_3)][PF_6] (14)

A suspension of **2** (60 mg, 0.16 mmol), NH_4PF_6 (55 mg, 0.32 mmol) and trimethylphosphine (0.2 ml, 2.0 mmol) in methanol (30 ml) was stirred (20°C) for 8 h. Evaporation of the solvent gave a pale yellow solid. Recrystallisation from dichloromethane/diethyl ether gave bright yellow crystals, yield 80 mg, (86%).

^1H NMR (CD_2Cl_2, 360 MHz): δ 4.13 (m, 1H, CH), 3.71 (dtd, ^3J(PH) 11.5, J(HH) 4.0, 1 Hz, 2H, =CH), 3.49 (tdd, J(HH) 4.0, 1 Hz, ^3J(PH) ~ 1.0 Hz, 2H, =CH), 3.43 (m, 1H, CH), 1.90 (d, ^1J(PH) 9.0 Hz, 9H, PMe_3), 1.73 (d, J(PH) 1.7 Hz, 15H, C_5Me_5), 1.32 (td, J(HH) 1.7 Hz, J(PH) 0.5 Hz, 2H, CH_2). J(HH) coupling constants were confirmed from the $^1H\{^{31}P\}$ spectrum.

[(η^5-C_5Me_5)Ru(Bu^tNC)$_2${$P(OPh)_3$}][PF_6] (15)

A suspension of **3** (75 mg, 0.17 mmol), NH_4PF_6 (55 mg, 0.32 mmol) and triphenylphosphite (0.5 ml, 1.90 mmol) was stirred (20°C) for 30 min. Evaporation of solvent and recrystallisation from dichloromethane/diethyl ether gave a white microcrystalline solid, yield 117 mg (80%). (Found: C, 52.01; H, 5.35; N, 3.16. $C_{38}H_{48}F_6N_2O_3P_2Ru$ calc: C, 53.20; H, 5.64; N, 3.27%). IR (Nujol): ν_{max} 2167s, 2131s cm^{-1} (CN); ^1H NMR ($(CD_3)_2CO$): δ 7.31 (m, 15H, Ph), 1.75 (d, J(PH) 3.0 Hz, 15H, C_5Me_5), 1.55 (s, 18H, CMe_3).

[(η^5-C_5Me_5)Ru(PPh_3)(Bu^tNC)CO][PF_6] (16)

A suspension of **4** (130 mg, 0.21 mmol) and NH_4PF_6 (100 mg, 0.61 mmol) in methanol (30 ml) was stirred under carbon monoxide (1 atm.) at 20°C for 6 h. Evaporation of the pale yellow suspension, extraction with dichloromethane and addition of diethyl ether gave white microcrystals, yield 70 mg. (44%) (Found: C, 53.94; H, 5.26; N, 1.77. $C_{34}H_{44}F_6NOP_2Ru$ calc: C, 53.75; H, 5.84; N, 1.84%). IR (Nujol): ν_{max} 2172s (CN), 1967s cm^{-1} (CO); ^1H NMR ($(CD_3)_2CO$): δ 7.58 and 7.30 (m, 15H, Ph), 1.76 (d, J(PH) 1.8 Hz, 15H, C_5Me_5), 1.32 (s, 9H, CMe_3).

Similarly, reaction of **5** (150 mg, 0.27 mmol) with t-butylisonitrile (0.2 ml, 1.91 mmol) in the presence of NH_4PF_6 (100 mg, 0.63 mmol) for 3 h at 50°C gave **16**, yield 145 mg (71%).

[(η^5-C_5Me_5)Ru(PPh_3)(Bu^tNC)NO][BF_4]$_2$ (17)

A solution of **4** (150 mg, 0.24 mmol) and $NOBF_4$ (86 mg, 0.74 mmol) in acetone (30 ml) was stirred for 15 min at 20°C. Removal and solvent under reduced pressure and recrystallisation from dichloromethane/diethyl ether (2/1) gave orange crystals, yield 90 mg. (47%) (Found: C, 50.60; H, 4.96; N, 3.50. $C_{33}H_{39}B_2F_8N_2OPRu$ calc: C, 50.47; H, 5.01; N, 3.57%) IR (Nujol): ν_{max} 2221s cm^{-1} (CN), 1859 br.s. cm^{-1} (NO). ^1H NMR [CD_3NO_2]: δ 7.77 and 7.49 (m, 15H, Ph), 2.04 (d, J(PH) 2.2 Hz, 15H, C_5Me_5), 1.43 (s, 9H, CMe_3).

Acknowledgements

We thank the SERC for a studentship [F.M.C.-L.], Johnson-Matthey Chemicals Ltd. for a generous loan of $RuCl_3$, Dr F.G.N. Cloke (Sussex) for ^{31}P spectra, and Dr I. Sadler and his staff for high field NMR spectra at the SERC facility (Edinburgh).

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