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ELECTRON-RICH η^1-CYANO COMPLEXES OF IRON AND RUTHENIUM: PREPARATION AND NUCLEOPHILIC PROPERTIES

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Summary

The cyano complexes $(\eta^5\text{-}C_5H_5)M(Ph_2PCH_2CH_2PPh_2)CN$ (**4**, M = Fe; **6**, M = Ru) and $(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2CN$ (**5**) have been prepared by treatment of the corresponding chlorides with methanolic potassium cyanide. The nucleophilicity of the cyano ligand has been demonstrated by the reactions of **5** with a variety of mild electrophiles (MeI, EtI, allyl bromide, $PhCH_2Br$, ICH_2CH_2OH and cyclohexene oxide) to form the corresponding isonitrile cations.

Introduction

Isonitrile complexes generally have to be prepared via ligand exchange reactions from the free isonitrile [1]. In order to develop more versatile routes to monoisonitrile complexes we were interested in investigating the nucleophilic properties of the cyano ligand in neutral iron and ruthenium complexes. We have recently reported the high nucleophilicity exhibited by the neutral η^1-acetylide complexes $(\eta^5\text{-}C_5H_5)M(PR_3)_2C{\equiv}CR$ (M = Fe, Ru) [2] and by analogy we anticipated that the corresponding neutral cyano complexes $(\eta^5\text{-}C_5H_5)M(PR_3)_2C{\equiv}N$ would also react with mild electrophiles. It has already been reported [3] that $(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2CN$ (**5**) is converted to the corresponding isonitrile cations **8** and **9** on treatment with the strong electrophiles trimethyloxonium and triethyloxonium tetrafluoroborate. During the course of this work the methylation of $(\eta^5\text{-}C_5H_5)Ru(PPh_3)(L)CN$ (L = CO, MeNC) with methyl iodide has been described [4].

Results

Treatment of the η^5-cyclopentadienyl bisphosphine iron and ruthenium halides **1**, **2** and **3** with potassium cyanide in methanol generated the cyano complexes **4**, **5** and **6** respectively.

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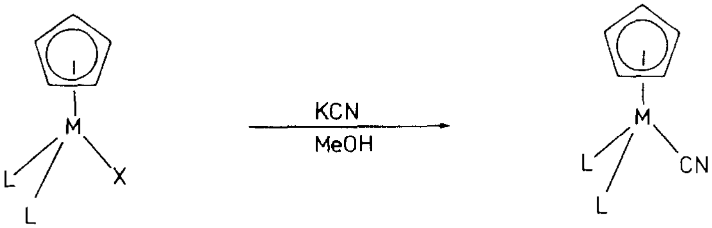
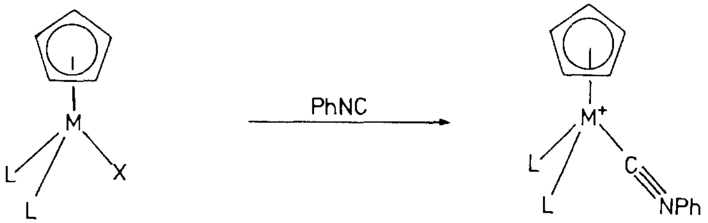


(**1**: X = Br, Cl; M = Fe; $L_2 = Ph_2PCH_2CH_2PPh_2$; **4**
2: X = Cl; M = Ru; L = Ph_3P; **5**
3: X = Cl; M = Ru; $L_2 = Ph_2PCH_2CH_2PPh_2$) **6**

Methylation of the cyano complexes **4** and **5** can be readily achieved by reaction with trimethyloxonium tetrafluoroborate to give the corresponding methylisonitrile cations **7** and **8**. Treatment of the cyano complex **5** with methyl iodide also generates the cation **8**. Although **5** is unreactive towards ethyl bromide, the ethylisonitrile cation **9** is produced in the presence of the more electrophilic ethyl iodide. Similar reactivities are observed with allyl bromide, benzyl bromide and 2-iodoethanol which generate the cations **10**, **11** and **12**, respectively. Reaction of the cyano complex **5** with cyclohexene oxide in the presence of acid produces the 2-hydroxycyclohexylisonitrile cation **13**.

Treatment of the halo complexes **1** (X = Br) and **2** with phenylisonitrile in methanol generates the corresponding cations **14** and **15**.

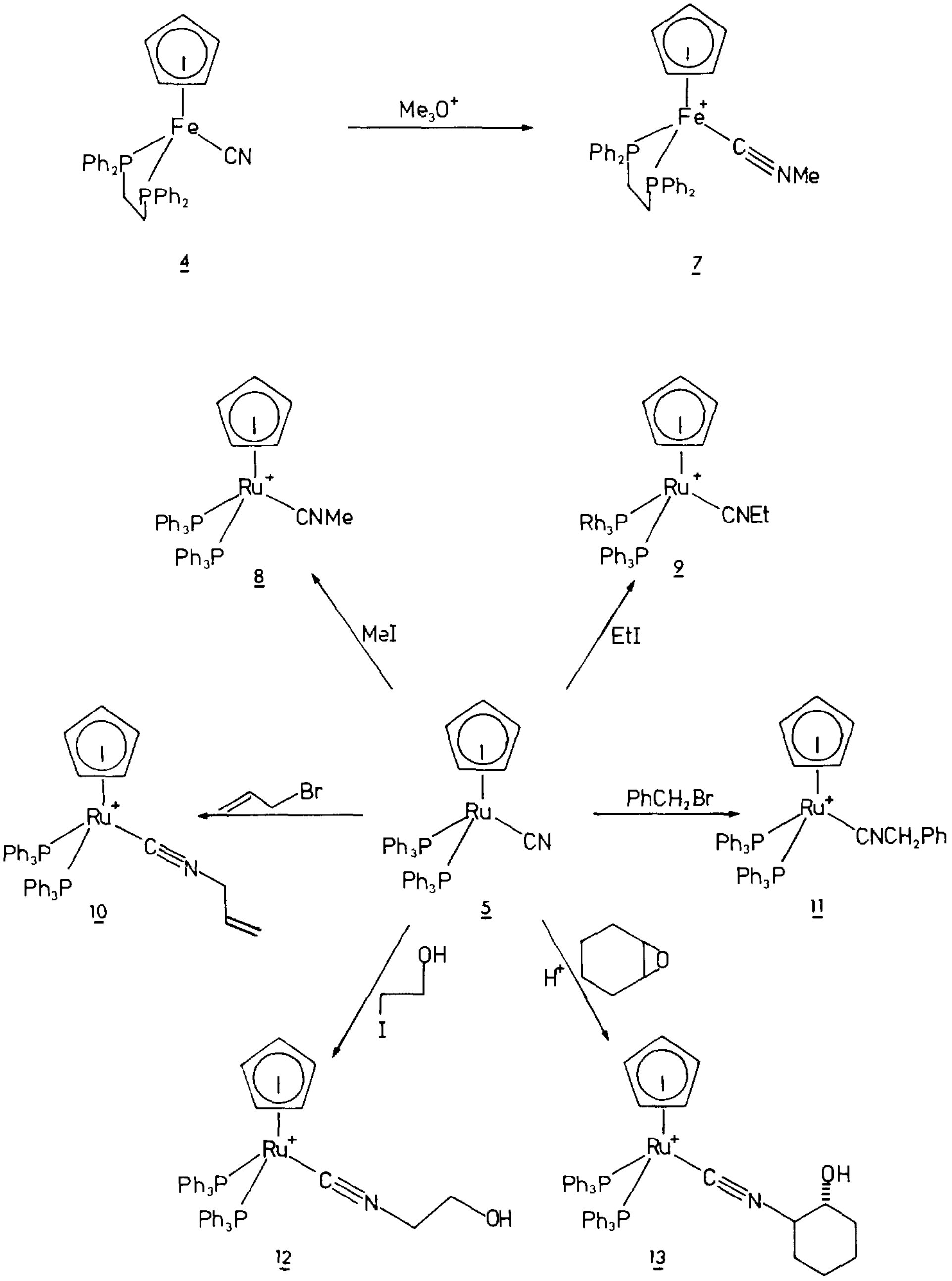


(**1**: M = Fe; X = Br; $L_2 = Ph_2PCH_2CH_2PPh_2$; **14**
2: M = Ru; X = Cl; L = Ph_3P) **15**

Discussion

Electron-rich ruthenium chloro complexes such as **2** and **3** show considerable ionic properties when dissolved in methanol [5]. This can be exploited for the conversion of the halo complexes **1**, **2** and **3** into the corresponding cyano complexes **4**, **5** and **6** with methanolic potassium cyanide. In each case the reaction is presumably proceeding via initial formation of the solvated cations $[(\eta^5\text{-}C_5H_5)ML_2(MeOH)]^+$.

The cyano complexes **4** and **5** are methylated on nitrogen by the strong electrophile trimethyloxonium tetrafluoroborate to give the methylisonitrile cations **7** and **8**. These cyano complexes, however, are much more nucleophilic than this suggests. Thus cyano complex **5** can be alkylated with a variety of mild electrophiles such as methyl iodide, ethyl iodide, allyl bromide, benzyl bromide and 2-iodoethanol. Although not nucleophilic enough to react with cyclohexene oxide alone, in the



SCHEME 1

presence of acid to facilitate epoxide ring opening, **5** produces the *β*-hydroxyisonitrile complex **13** (Scheme 1).

Experimental

All reactions and purifications were performed under nitrogen atmosphere using standard vacuum line and Schlenk tube techniques [6]. ^{1}H NMR spectra were recorded on Perkin–Elmer R32B (90 MHz) and Bruker WH300 instruments. (η^5-C_5H_5)Fe($Ph_2PCH_2CH_2PPh_2$)Br (**1**) [7], (η^5-C_5H_5)Fe($Ph_2PCH_2CH_2PPh_2$)Cl (**1**) [8], (η^5-C_5H_5)Ru(PPh_3)$_2$Cl (**2**) [9] (η^5-C_5H_5)Ru($Ph_2PCH_2CH_2PPh_2$)Cl (**3**) [9], and phenylisonitrile [10] were prepared by literature procedures.

Preparation of (η^5-C_5H_5)Fe($Ph_2PCH_2CH_2PPh_2$)CN (4)

Potassium cyanide (0.3 g, 4.5 mmol) was added to a solution of (η^5-C_5H_5)Fe($Ph_2PCH_2CH_2PPh_2$)Br (**1**, 1.0 g, 1.7 mmol) in distilled methanol (20 ml) and the resulting solution stirred for 3 h at 20°C. The solvent was evaporated under reduced pressure and the resulting solid extracted with dichloromethane (2 × 10 ml). Chromatography (Al_2O_3; eluant dichloromethane) gave a yellow solution which after concentration (10 ml) and addition of diethyl ether gave yellow-brown crystals of **4** (0.54 g, 51%); ν_{max} 2060s (CN) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ7.8–7.0 (m, 20 H, aryl-H), 5.25 (s, 2 H, CH_2Cl_2), 4.3 (t, J 1.5 Hz, 5H, C_5H_5), 2.8–2.2 (m, 4 H, CH_2) (lit. [11] δ 8–7(m), 4.28(s), 2.8–2.0(m)) ppm.

Cyano complex **4** could also be prepared in a similar fashion from (η^5-C_5H_5)Fe($Ph_2PCH_2CH_2PPh_2$)Cl (**1**).

Preparation of (η^5-C_5H_5)Ru(PPh_3)$_2$CN (5) [12]

Potassium cyanide (0.2 g, 3.0 mmol) was added to a solution of (η^5-C_5H_5)Ru(PPh_3)$_2$Cl (**2**, 1.0 g, 1.4 mmol) in distilled methanol (40 ml). The solution was heated for 2 h under reflux and the solvent removed under reduced pressure to give a pale yellow solid. Crystallisation from dichloromethane-methanol gave yellow crystals of **5** (890 mg, 80%) (Found: C, 64.4; H, 4.8; N, 1.6; P, 7.5. $C_{43}H_{37}Cl_2NP_2Ru$ calcd.: C, 64.3; H, 4.6; N, 1.7; P, 7.7%); ν_{max} (Nujol): 2070s (CN) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.2 (m, 30 H, aryl-H), 5.3 (s, 2 H, CH_2Cl_2), 4.35 (s, 5 H, C_5H_5), {lit. [12] δ 7.2(m), 5.3 (s), 4.38 (s)} ppm; ^{31}P-{^{1}H} NMR (CH_2Cl_2): δ 49.4 (s) ppm; *m/e* (E.I.) 718 (M^+).

Preparation of (η^5-C_5H_5)Ru($Ph_2PCH_2CH_2PPh_2$)CN (6)

Potassium cyanide (0.45 g, 6.8 mmol) was added to a suspension of (η^5-C_5H_5)Ru($Ph_2PCH_2CH_2PPh_2$)Cl (1.2 g, 2.0 mmol) in methanol (50 ml) and the mixture heated under reflux for 30 min. The solvent was evaporated under reduced pressure and the resulting yellow solid extracted with dichloromethane (2 × 10 ml). Addition of petroleum ether (40–60°C) (50 ml) to the combined extracts gave a yellow precipitate which was recrystallised from dichloromethane/diethyl ether to give yellow crystals of **6** (0.3 g, 25%), m.p. 255°C. (Found: C, 59.0; H, 4.8; N, 2.1; P, 9.2. $C_{33}H_{31}Cl_2NP_2Ru$ calcd.: C, 58.7, H, 4.6; H, 2.1; P, 9.2%); ν_{max} (Nujol) 2060(CN) cm^{-1}; ^{1}H NMR ($CHCl_3$) δ 8.0–7.0(m, 20H, aryl-H), 5.25 (s, 2 H, CH_2Cl_2), 4.75 (s, 5 H, C_5H_5), 2.9–2.1 (m, 4 H, CH_2) ppm; *m/e* (F.D.) 591 (M^+).

Reaction of (η^5-C_5H_5)Fe($Ph_2PCH_2CH_2PPh_2$)CN (4) with [Me_3O]BF_4

Trimethyloxonium tetrafluoroborate (65 mg, 0.43 mmol) was added to a solution of (η^5-C_5H_5)Fe($Ph_2PCH_2CH_2PPh_2$)CN (**4**, 0.2 g, 0.37 mmol) in dichloromethane

(10 ml) and the mixture stirred at 18°C for 1 h. Evaporation of the solvent under reduced pressure followed by crystallisation from chloroform/diethyl ether gave yellow crystals of $[(\eta^5\text{-}C_5H_5)Fe(Ph_2PCH_2CH_2PPh_2)CNMe]BF_4 \cdot 3/2CHCl_3$ (**7**, 90 mg, 38%) (Found: C, 50.4; H, 4.2; N, 1.8; P, 7.6. $C_{34.5}H_{33.5}BCl_{4.5}F_4FeNP_2$ calcd.: C, 50.0; H, 4.0; N, 1.7; P, 7.5%). ν_{max} (Nujol): 2150s (CN), 1050 vs (BF_4) cm^{-1}; ^1H NMR (CD_2Cl_2): δ 7.7–7.2 (m, 20 H, aryl-H), 7.27 (s, 3/2 H, $CHCl_3$), 4.53 (t, J 1.3 Hz, 5 H, C_5H_5), 2.74 (t, J 1.4 Hz, 3 H, Me), 2.64–2.43 (m, 4 H, CH_2CH_2) ppm; *m/e* (F.D.) 560 (M^+).

Preparation of $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2CNMe]BF_4$ *(8)*

The trimethyloxonium tetrafluoroborate (0.24 g, 1.62 mmol) was added to a solution of $(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2CN$ (**5**, 1.0 g, 1.4 mmol) in dichloromethane (20 ml) and the mixture stirred at 18°C for 30 min. Evaporation of the solvent under reduced pressure and crystallisation of the resulting yellow solid from dichloromethane-diethyl ether gave olive-green rhombic crystals of **8** (0.64 g, 56%) ν_{max} (Nujol): 2160s(CN), 1050vs (BF_4) cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.2 (m, 30 H, aryl-H), 4.7 (s, 5 H, C_5H_5), 3.4 (t, J 1.5 Hz, 3 H, Me) (Lit. [3] δ 7.2 (m), 4.69 (s), 3.39 (t)) ppm; *m/e* (F.D.) 732 (M^+).

Reaction of $(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2CN$ *(5) with ethyl iodide*

Ethyl iodide (2 ml, excess) was added to a stirred solution of $(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2CN$ (**5**, 160 mg, 0.22 mmol) in dichloromethane (15 ml) and the resulting solution heated under reflux for 30 min. The solvent was evaporated under reduced pressure and the resulting green solid dissolved in acetone (20 ml). Addition of an aqueous solution of ammonium hexafluorophosphate gave a green precipitate which, on crystallisation from dichloromethane/diethyl ether gave pale green crystals of $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2CNEt]PF_6$ (**9**, 90 mg, 45%); ν_{max} (Nujol): 2150s (CN); 840s (PF_6) cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.2 (m, 30 H, aryl-H), 4.75 (s, 5 H, C_5H_5), 3.9 (q, J 7 Hz, 2 H, CH_2), 1.1 (t, J 7 Hz, 3 H, Me) (Lit. [3] δ 7.2 (m), 4.68 (s), 3.73 (q, J 7.5 Hz), 1.14 (t, J 7.5 Hz)) ppm.

Reaction of $(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2CN$ *(5) with allyl bromide*

Allyl bromide (1 ml, excess) was added to a solution of $(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2CN$ (**5**, 0.2 g, 0.28 mmol) in dichloromethane (15 ml) and the resulting solution stirred for 12 h at 18°C. Evaporation of the solvent under reduced pressure gave a brown solid which was then dissolved in acetone (20 ml). Addition of aqueous ammonium hexafluorophosphate gave a green precipitate which was crystallised from dichloromethane-diethyl ether to give green crystals of $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2\text{-}CNCH_2CHCH_2]PF_6$ (**10**, 0.11 g, 44%), m.p. 225°C (Found C, 59.7; H, 4.3; N, 1.6; P, 10.2, $C_{45}H_{40}F_6NP_3Ru$ calcd.: C, 59.9; H, 4.4; N, 1.6; P, 10.3%). ν_{max} (Nujol): 2150s (CN), 840vs (PF_6) cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.3 (m, 30 H, aryl-H) 5.9–5.1 (m, 3 H, $CHCH_2$), 4.8 (s, 5H, C_5H_5), 4.4 (m, 2 H, CH_2) ppm; *m/e* (F.D.) 758 (M^+).

Reaction of $(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2CN$ *(5) with benzyl bromide*

Benzyl bromide (4 ml, excess) was added to a solution of $(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2CN$ (**5**, 0.2 g, 0.28 mmol) in dichloromethane (10 ml) and the solution allowed to stand at 18°C for 48 h. Evaporation of the solvent under reduced pressure gave a green gum which was then dissolved in acetone (20 ml). Addition of an aqueous solution of ammonium hexafluorophosphate gave a green precipitate which was crystallised from dichloromethane-diethyl ether to give green needles of $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2\text{-}CNCH_2Ph]PF_6$ (**11**, 0.12 g, 45%) m.p. 185°C (dec.) (Found: C, 61.5; H, 4.6; N, 1.5. $C_{49}H_{42}F_6NP_3Ru$ calcd.: C, 61.7; H, 4.4; N, 1.5%). ν_{max} (Nujol): 2150s (CN), 840vs (PF_6) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.4–6.8 (m, 35 H, aryl-H), 4.85 (brs, 2 H, CH_2), 4.65 (s, 5 H, C_5H_5) ppm; *m/e* (F.D.) 809 (M^+).

Reaction of $(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2CN$ (5) with 2-iodoethanol

2-Iodoethanol (0.5 ml, 6 mmol) was added to a solution of $(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2CN$ (**5**, 0.20 g, 0.28 mmol) in toluene (15 ml). The solution was heated under reflux for 2 h, cooled and the solvent evaporated under reduced pressure. The resulting orange solid was extracted with dichloromethane (1 × 10 ml) and the extract chromatographed on Al_2O_3, eluting with a solution of ammonium hexafluorophosphate in acetone. The solvent was evaporated from the eluate under reduced pressure and the resulting yellow solid crystallised from dichloromethane/diethyl ether to give yellow crystals of $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2CNCH_2\text{-}CH_2OH]PF_6$ (**12**, 95 mg, 38%) m.p. 226–228°C (Found: C, 59.0; H, 4.4; N, 1.8; $C_{44}H_{40}F_6NOP_3Ru$ calcd.: C, 58.3; H, 4.4; N, 1.6%) ν_{max} (Nujol): 3320s (OH), 2145 (CN) 845s (PF_6) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.2 (m, 30 H, aryl-H), 4.68 (s, 5 H, C_5H_5), 3.8 (m, 5 H, CH_2CH_2OH) ppm; *m/e* (F.D.) 762 (M^+).

Reaction of $(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2CN$ (5) with cyclohexene oxide

Cyclohexene oxide (0.5 ml, 4.9 mmol) was added to a stirred solution of $(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2CN$ (**5**, 0.20 g, 0.28 mmol) in dichloromethane (5 ml). HBF_4Me_2O (0.3 ml) was added and the resulting solution stirred at 18°C for 15 min. The solvent was evaporated under reduced pressure and the resulting solid crystallised from dichloromethane/diethyl ether to give green crystals of $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2CN\overline{CHCHOH(CH_2)_3CH_2}]BF_4$ (**13**, 66 mg, 26%) m.p. 230°C (Found: C, 63.2; H, 4.9; N, 1.7; P, 7.0. $C_{48}H_{46}BF_4NOP_2Ru$ calcd.: C, 63.8; H, 5.1; N, 1.6; P, 6.9%). ν_{max} (Nujol): 3490m (OH), 2150s (CN), 1090s (BF_4) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.25 (m, 30 H, aryl-H), 4.7 (s, 5 H, C_5H_5), 1.8–0.8 (m, 12 H) ppm; *m/e* (F.D.) 816 (M^+).

Reaction of phenylisonitrile with $(\eta^5\text{-}C_5H_5)Fe(Ph_2PCH_2CH_2PPh_2)Br$ (1)

Phenylisonitrile (0.5 ml of a 55% solution in toluene) was added to a solution of $(\eta^5\text{-}C_5H_5)Fe(Ph_2PCH_2CH_2PPh_2)Br$ (**1**, 0.22 g, 0.37 mmol) in distilled methanol (15 ml). Ammonium hexafluorophosphate (0.11 g, 0.67 mmol) was added and the brown solution heated under reflux for 30 min. The solvent was evaporated under reduced pressure and the resulting solid extracted with dichloromethane (15 ml). The solvent was evaporated under reduced pressure and the resulting brown solid was washed with light petroleum ether (40–60°C, 2 × 10 ml). Crystallisation from dichloromethane/diethyl ether gave brown crystals of $[(\eta^5\text{-}C_5H_5)Fe(Ph_2PCH_2CH_2\text{-}PPh_2)CNPh]PF_6$ (**14**, 95 mg, 33%) m.p. > 240°C (Found: C, 58.8; H, 4.7; N, 1.9. $C_{38}H_{34}F_6FeNP_3$ calcd.: C, 59.4; H, 4.4; N, 1.8%) ν_{max} (Nujol): 2090vs (CN); 1590m; 840vs (PF_6) cm^{-1}; ^1H NMR ($(CD_3)_2CO$) δ 7.9, 7.5, 7.2, 6.4 (m, 35 H, aryl-H), 4.9 (t, *J* 1 Hz, 5 H, C_5H_5), 2.45, 2.2 (m, 4 H, CH_2CH_2) ppm.

Reaction of phenylisonitrile with $(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl$ (2)

Phenylisonitrile (0.5 ml of a 55% solution in toluene) was added to a solution of

(η^5-C_5H_5)Ru(PPh_3)$_2$Cl (**2**, 0.20 g, 0.28 mmol) and ammonium hexafluorophosphate (0.15 g, 0.90 mmol) in methanol (10 ml). The solution was heated under reflux for 30 min and a pale green solid was precipitated. On cooling to room temperature the supernatant was removed by filtration and the residue crystallised from dichloromethane/diethyl ether as pale yellow monoclinic crystals of [(η^5-C_5H_5)-Ru(PPh_3)$_2$CNPh]PF_6 (**15**, 135 mg, 51%) m.p. 225-227°C (Found: C, 64.0; H, 4.9; N, 1.7, $C_{48}H_{40}F_6NP_3Ru$ calcd.: C, 61.3; H, 4.3; N, 1.5%) ν_{max} (Nujol): 2120vs (CN), 840vs (PF_6) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.5-6.9 (m, 35 H, aryl-H), 4.75 (s, 5 H, C_5H_5) ppm; *m/e* (F.D.) 794 (M^+).

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