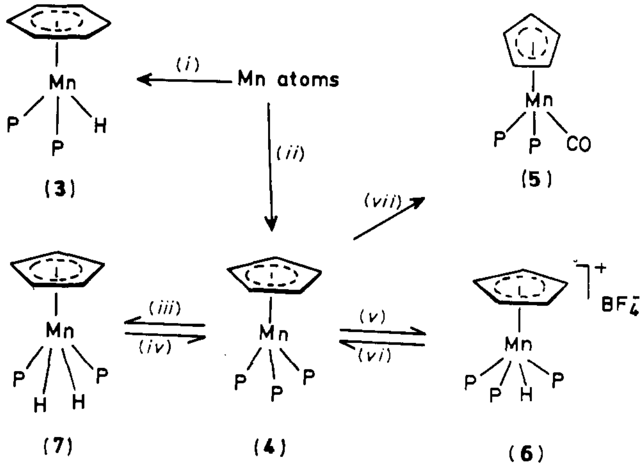
In memory of T. A. Stephenson

Synthesis using Metal Atoms of [RuH(η-C_6H_6)(PMe_3)(σ-C_6H_5)], [OsH(η-C_6H_6)(PMe_3)(σ-C_6H_5)], [MnH(η-C_6H_6)(PMe_3)$_2$], and [Mn(η-C_5H_5)(PMe_3)$_3$]: Arene Ligand-exchange Reactions of [RuH(η-C_6H_6)(PMe_3)(σ-C_6H_5)]†

Malcolm L. H. Green, David S. Joyner, and Julian M. Wallis
Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR

Co-condensation of atoms of ruthenium, osmium, or manganese with benzene–trimethylphosphine gives [RuH(η-C_6H_6)(PMe_3)(σ-C_6H_5)], [OsH(η-C_6H_6)(PMe_3)(σ-C_6H_5)], and [MnH(η-C_6H_6)(PMe_3)$_2$], respectively. Manganese atoms react with cyclopentadiene–trimethylphosphine giving [Mn(η-C_5H_5)(PMe_3)$_3$] which is protonated by HBF_4 giving [MnH(η-C_5H_5)(PMe_3)$_3$]BF_4. Heating [RuH(η-C_6H_6)(PMe_3)(σ-C_6H_5)] in [$^2H_6$]benzene, toluene, *o*-, *m*-, or *p*-xylene, or mesitylene causes ligand-exchange reactions giving [RuD(η-C_6D_6)(PMe_3)(σ-C_6D_5)], [RuH(η- C_6H_5Me)(PMe_3)(σ-C_6H_4Me-*m* or -*p*)], [RuH(η-$C_6H_4Me_2$-1,2)(PMe_3)(σ-$C_6H_3Me_2$-3,4)], [RuH(η-$C_6H_4Me_2$-1,3)(PMe_3)(σ-$C_6H_3Me_2$-3,5)], [RuH(η-$C_6H_4Me_2$-1,4)(PMe_3)(σ-C_6H_5)], and [RuH(η-$C_6H_3Me_3$-1,3,5)(PMe_3)(σ-C_6H_5)] respectively.

Co-condensation of metal atoms with a mixture of tertiary phosphines and arenes has proved to be a fruitful synthetic route to half-sandwich transition metal–η-arene–tertiary phosphine derivatives.[1–4] In a continuing study of this approach to electron-rich transition-metal compounds we have explored the synthesis of η-arene–trimethylphosphine derivatives of manganese, ruthenium, and osmium.



Scheme 1. P = PMe_3. (*i*) Co-condensation with PMe_3 and benzene, yield 2%; (*ii*) co-condensation with C_5H_6 and PMe_3; (*iii*) repeated treatment with dihydrogen at 2 atm, 20%; (*iv*) PMe_3 in toluene, >80%; (*v*) HBF_4–Et_2O in Et_2O, 82%; (*vi*) potassium hydride, >80%; (*vii*) carbon dioxide at 3 atm and 70 °C for 7 d, 77%

Results and Discussion

Co-condensation of ruthenium atoms with a mixture of benzene and trimethylphosphine affords orange crystals of [RuH(η-C_6H_6)(PMe_3)(σ-C_6H_5)], (**1**). The analytical and spectroscopic data which characterise (**1**) and all other new compounds described in this work are given in Table 1. These data will not be discussed except where interpretation is not straightforward. The structures proposed for (**1**) and other new compounds are given in Schemes 1 and 2.

The lowest-field resonance (δ 162.5) in the ^{13}C n.m.r. spectrum of (**1**) is assigned to the *ipso* carbon of the σ-phenyl ligand. The resonance is of low intensity, which is consistent with the absence of nuclear Overhauser enhancement as expected for quaternary carbon atoms. Further, the ^{13}C-{^1H} n.m.r. spectrum shows this band has the largest ^{31}P–C coupling constant. The resonance at δ 146.3 shows a smaller value for $J(^{31}P\text{–}C)$ and is assigned to the two *ortho* carbon atoms. Comparing intensities of the two resonances at δ 125.9 and 121.2 with that of *o*-C, allows them to be assigned to *m*-C and *p*-C respectively.

There are only two multiplets assignable to the hydrogen of the σ-phenyl ligand in the ^1H n.m.r. spectrum of compound (**1**). Double-resonance experiments established that the two resonances at δ 7.85 and 7.09 are coupled to each other. For example, irradiation at δ 7.09 collapses the two-hydrogen signal at δ 7.85 to a doublet (J = 0.9 Hz). This doublet coupling is assigned to J(P–H), and suggests that the signal at δ 7.85 is due to the two *ortho* hydrogen atoms. The ^{13}C n.m.r. spectrum of (**1**) was determined with selective irradiation at either δ 7.09 or 7.85 in the ^1H n.m.r. spectrum. These spectra show that the *ortho* hydrogens appear at δ 7.85 in the ^1H n.m.r. spectrum, and that the *meta* and *para* hydrogens occur coincidentally at δ 7.09. The i.r. spectrum shows a strong band at 1 947 cm^{-1} assignable to a Ru–H stretching frequency.

Osmium atoms were co-condensed with benzene and trimethylphosphine giving an orange matrix from which an orange solid was obtained. Sublimation at 80 °C (10^{-4} mmHg) afforded pale yellow crystals of [OsH(η-C_6H_6)(PMe_3)(σ-C_6H_5)], (**2**). The ^1H and ^{13}C n.m.r. spectra of (**2**) are closely similar to those of (**1**). For example, there is a high-field doublet at δ −9.74 [J(P–H) = 42.9 Hz], which may be assigned to an Os–H group.

Co-condensation of manganese atoms with benzene and trimethylphosphine gave orange-red crystals of [MnH(η-C_6H_6)(PMe_3)$_2$], (**3**). The crystals are very volatile, and sublime at room temperature at 2×10^{-2} mmHg. The photoelectron

---

† *Non-S.I. units employed:* Torr = mmHg ≈ 133 N m^{-2}, atm = 101 325 N m^{-2}, eV ≈ 1.6×10^{-19} J.

Table 1. Analytical and spectroscopic data

Compound and analysis[a]	N.m.r.[b]
(1) C, 53.9 (54.1); H, 6.5 (6.4)[c]	^{1}H: 7.85 (2 H, m, *o*-H), 7.09 (3 H, m, *m*- and *p*-H), 4.87 (6 H, s, η-C_6H_6), 0.96 [9 H, d, *J*(P–H) 9.0, PMe_3], −9.11 [1 H, d, *J*(P–H) 54.8, RuH] ^{31}P-{^{1}H}: 6.75 (s, PMe_3) ^{13}C: 162.5 [1 C, d, *J*(P–C) 22.5, *i*-C], 146.3 [2 C, dd, *J*(P–C) 2.4, *J*(C–H) 155.5, *o*-C], 125.9 [2 C, d, *J*(C–H) 151.4, *m*-C], 121.2 [1 C, dt, *J*(C–H) 156.8, ^{2}*J*(C–H) 7, *p*-C], 86.5 [6 C, d, *J*(C–H) 170.6, η-C_6H_6], 22.5 [3 C, dq, *J*(P–C) 31.5, *J*(C–H) 128.4, PMe_3]
(1-D)[d]	^{1}H: 0.96 [9 H, d, *J*(P–H) 9, PMe_3] ^{2}H: 7.8 (2 D, m, *o*-D], 7.1 (3 D, m, *m*- and *p*-D), 4.9 (6 D, s, η-C_6D_6), −9.1 [1 D, d, *J*(P–D) 8.2, RuD] ^{31}P-{^{1}H}: 6.39 [t, 1:1:1, *J*(P–D) 8]
(2) C, 42.4 (42.6); H, 4.7 (5.0)	^{1}H: 7.97 (2 H, m, *o*-H), 7.09 (3 H, m, *m*- and *p*-H), 4.64 (6 H, s, η-C_6H_6), 1.12 [9 H, d, *J*(P–H) 10, PMe_3], −9.74 [1 H, d, *J*(P–H) 42.9, OsH] ^{31}P-{^{1}H}: −44.5 (s, PMe_3) ^{13}C-{^{1}H}: 147.4 (2 C, s, *o*-C), 126.8 (2 C, s, *m*-C), 121.1 (1 C, s, *p*-C), 77.8 [6 C, d, *J*(P–C) 2.5, η-C_6H_6], 22.3 [3 C, d, *J*(P–C) 37, PMe_3]
(3)[e] C, 49.2 (50.4); H, 8.5 (8.8)	^{1}H: 4.36 (6 H, s, η-C_6H_6), 1.04 (18 H, vt, 2PMe_3), −10.39 [1 H, t, *J*(P–H) 82.8, MnH] ^{31}P-{^{1}H}: 24.3 (s, 2PMe_3)
(4) C, 48.1 (48.3); H, 9.0 (9.3)	^{1}H: 3.54 [5 H, q, *J*(P–H) 2.2, η-C_5H_5], 1.17 (27 H, br s, 3PMe_3) ^{31}P-{^{1}H}: 41.86 (s, 3PMe_3) ^{13}C-{^{1}H}: 73.13 (5 C, s, η-C_5H_5), 27.35 (9 C, m, 3PMe_3)
(5)[f] C, 47.8 (48.0); H, 7.6 (7.75)	^{1}H: 3.96 [5 H, t, *J*(P–H) 8, η-C_5H_5], 1.04 (18 H, t, *J′* 3.7, 2PMe_3)
(6)[g] C, 38.9 (38.6); H, 8.0 (7.6)	^{1}H[h]: 4.40 (5 H, s, η-C_5H_5), 1.52 (27 H, m, 3PMe_3), −8.73 [1, H, q, *J*(P–H) 71.8, MnH] ^{31}P-{^{1}H}[h]: 31.2 (s, 3PMe_3) ^{13}C-{^{1}H}[g–h]: 82.05 (5 C, s, η-C_5H_5), 25.37 (9 C, m, 3PMe_3)
(8)	^{1}H: 1.3 (36 H, br s, 4PMe_3), −12.32 (1 H, sxt, *J* 13.9, RhH) ^{1}H-{^{31}P}: 1.3 (36 H, br s, 4PMe_3), −12.32 [1 H, d, *J*(Rh–H) 12.5, RhH] ^{31}P-{^{1}H}: −22.38 [d, *J*(Rh–P) 145.9, 4PMe_3] ^{31}P-{Me}: −22.38 [dd, *J*(Rh–P) 146, *J*(P–H) 13.6, 4PMe_3]
(9-*m*) and **(9-*p*)**	^{1}H: common to both *meta* and *para* isomers: 5.07, 4.88, 4.83, 4.79, 4.62 (5 multiplets, each of integral 1, aromatic C–H of η-C_6H_5Me), 1.73 (3 H, s, Me of η-C_6H_5Me), 1.01 [9 H, d, *J*(P–H) 8.7, PMe_3] Due to *meta* isomer: 7.72 (1 H, s, H_a), 7.59 [1 H, d, *J*(H–H) 7.5, H_c or H_f], 7.02 [1 H, t, *J*(H–H) 7.3, H_d], 6.89 [1 H, d, *J*(H–H) 7, H_f or H_c], 2.35 (3 H, s, Me of σ-C_6H_4Me), −9.34 [1 H, d, *J*(P–H) 55.2, RuH] Due to *para* isomer: 7.70 [2 H, dd, *J*(H–H) 8, *J*(P–H) 1.1, *o*-$H_{b,b'}$], 6.94 [2 H, d, *J*(H–H) 8, *m*-$H_{e,e'}$], 2.33 (3 H, s, Me of σ-C_6H_4Me), −9.33 [1 H, d, *J*(P–H) 55.2, RuH]
(10) *m/z* 389 (P^+)	^{1}H: 7.61 (1 H, s, H_a), 7.48 [1 H, d, *J*(H–H) 7.4, H_b or H_c], 6.92 [1 H, d, *J*(H–H) 7.4, H_c or H_b], 4.99 [1 H, d, *J*(H–H) 5.4, H_d or H_g], 4.86 [1 H, d, *J*(H–H) 5.4, H_g or H_d], 4.80 [1 H, t, *J*(H–H) 5.5, H_e or H_f], 4.70 [1 H, t, *J*(H–H) 5.5, H_f or H_e], 2.28 (3 H, s, Me_v or Me_w), 2.23 (3 H, s, Me_w or Me_v), 1.77 (3 H, s, Me_x or Me_y), 1.75 (3 H, s, Me_y or Me_x), 1.01 [9 H, d, *J*(P–H) 9.5, PMe_3], −9.62 [1 H, d, *J*(P–H) 55.2, RuH]
(11) *m/z* 389 (P^+)	^{1}H: 7.48 (2 H, s, *o*-H), 6.69 (1 H, s, *p*-H), 4.95 [1 H, dt, *J*(H–H) 5.5, 2.0, H_c], 4.79 (1 H, br s, H_f), 4.66 [1 H, d, *J*(H–H) 5.5, H_d or H_e], 4.55 [1 H, d, *J*(H–H) 5.4, H_e or H_d], 2.34 (6 H, s, 2Me of σ-$C_6H_3Me_2$), 1.91 (3 H, s, Me_y or Me_z), 1.72 (3 H, s, Me_z or Me_y), 1.03 [9 H, d, *J*(P–H) 8.7, PMe_3], −9.55 [1 H, d, *J*(P–H) 55.8, RuH]
(12) *m/z* 389 (P^+)	^{1}H: 7.78 (2 H, m, *o*-H), 7.07 (3 H, m, *m*- and *p*-H), 4.85 (4 H, AA′BB′ system, η-C_6H_4), 1.76 (6 H, s, 2Me of η-$C_6H_4Me_2$), 0.98 [9 H, d, *J*(P–H) 9.3, PMe_3], −9.61 [1 H, d, *J*(P–H) 55.8, RuH]
(13)	^{1}H: 7.67 (2 H, br s, *o*-H), 7.08 (3 H, m, *m*- and *p*-H), 4.57 (3 H, s, η-C_6H_3), 1.81 (9 H, s, η-C_6Me_3), 1.00 [9 H, d, *J*(P–H) 8.8, PMe_3], −9.92 [1 H, d, *J*(P–H) 56.6, RuH]

[a] Calculated values in parentheses. Infrared spectra were determined as mulls in liquid paraffin. [b] Given as: chemical shift (δ) [relative intensity, multiplicity, *J* in Hz, assignment]. Measured in [$^2H_6$]benzene, unless otherwise stated. The labelling of nuclei is given in the Schemes. [c] ν(Ru–H) 1 947s cm^{-1}. Mass spectrum: *m/z* 333 (P^+). [d] ν(C–D) 2 245m, ν(Ru–D) 1 380 cm^{-1}. Mass spectrum: *m/z* 345 (P^+). [e] Mass spectrum: *m/z* 286 (P^+), 285 (P^+ − H), 209 (P^+ − H − PMe_3), and 133 (P^+ − H − 2PMe_3). [f] ν(C–O) 1 845 cm^{-1}. [g] ν(Mn–H) 1 955br w cm^{-1}. [h] In CD_3OD.

spectrum of (**3**) showed a first ionisation potential at 6.06 eV. The i.r. spectrum showed a medium intensity broad band at 1 722 cm^{-1} assignable to a Mn–H stretching frequency. Co-condensation of manganese atoms with cyclopentadiene and trimethylphosphine afforded high yields of yellow crystals of [Mn(η-C_5H_5)(PMe_3)$_3$], (**4**). In a typical 4-h experiment, 8 g of (**4**) were obtained. The compound (**4**) has been described previously.[5] The photoelectron spectrum of (**4**) shows a first ionisation potential at 5.28 eV.[6]

Treatment of (**4**) with carbon dioxide (3 atm) at 70 °C for 7 d gives the monocarbonyl [Mn(η-C_5H_5)(PMe_3)$_2$(CO)] (**5**) in high yield. The i.r. spectrum shows a sharp band at 1 845 cm^{-1} assignable to a single, terminal C=O group. Treatment of (**4**) in diethyl ether with tetrafluoroboric acid in diethyl ether gave an immediate bright yellow precipitate. Crystallisation from methanol gave large cubic orange crystals of [MnH(η-C_5H_5)(PMe_3)$_3$]BF_4, (**6**). On treatment of (**6**) with a suspension of potassium hydride in light petroleum, (**4**) is reformed in essentially quantitative yield.

Treatment of compound (**4**) with dihydrogen (10 atm) for 2 d gave a mixture (*ca.* 1:1) of the dihydrido derivative [MnH_2(η-C_5H_5)(PMe_3)$_2$], (**7**), together with unreacted (**4**). Seven successive treatments of the reaction mixture with dihydrogen increased the ratio of (**7**):(**4**) to 9:1. Recrystallisation gave orange crystals of (**7**) which the ^{1}H n.m.r. spectrum showed to contain no (**4**). A broad, medium-intensity band at 1 790 cm^{-1}

Table 2. Rates of hydrogen–deuterium exchange into the σ-phenyl and η-arene positions

T/K	k(arene)/s^{-1}	k(phenyl)/s^{-1}
313	$(1.17 \pm 0.2) \times 10^{-6}$	$(6.62 \pm 0.4) \times 10^{-7}$
323	$(3.45 \pm 0.2) \times 10^{-6}$	$(1.72 \pm 0.4) \times 10^{-6}$
333	$(4.97 \pm 0.2) \times 10^{-6}$	$(5.89 \pm 0.4) \times 10^{-6}$
352	$(1.06 \pm 0.2) \times 10^{-5}$	$(1.49 \pm 0.4) \times 10^{-5}$
373	$(4.76 \pm 0.2) \times 10^{-5}$	$(1.23 \pm 0.4) \times 10^{-4}$

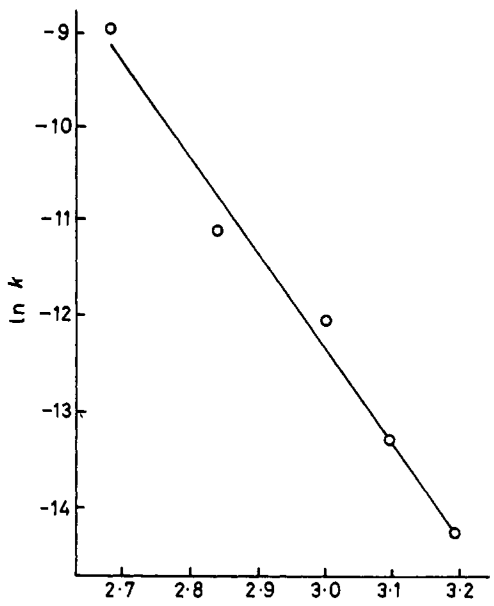


Figure 1. Arrhenius plot for η-benzene exchange by [$^2H_6$]benzene in compound (**1**)

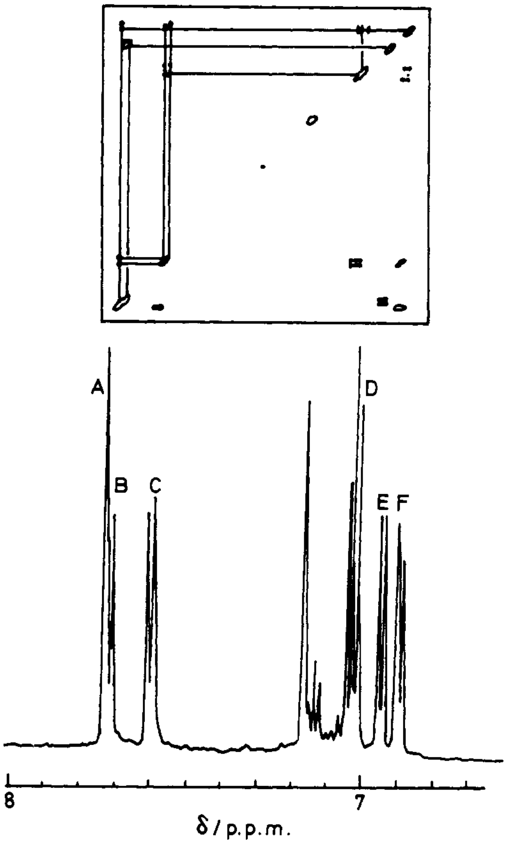


Figure 2. COSY-45 n.m.r. spectrum of the *m* and *p* isomers of compound (**9**)

in the i.r. spectrum may be assigned to ν(Mn–H). Treatment of (**7**) with PMe_3 reformed (**4**) in high yield.

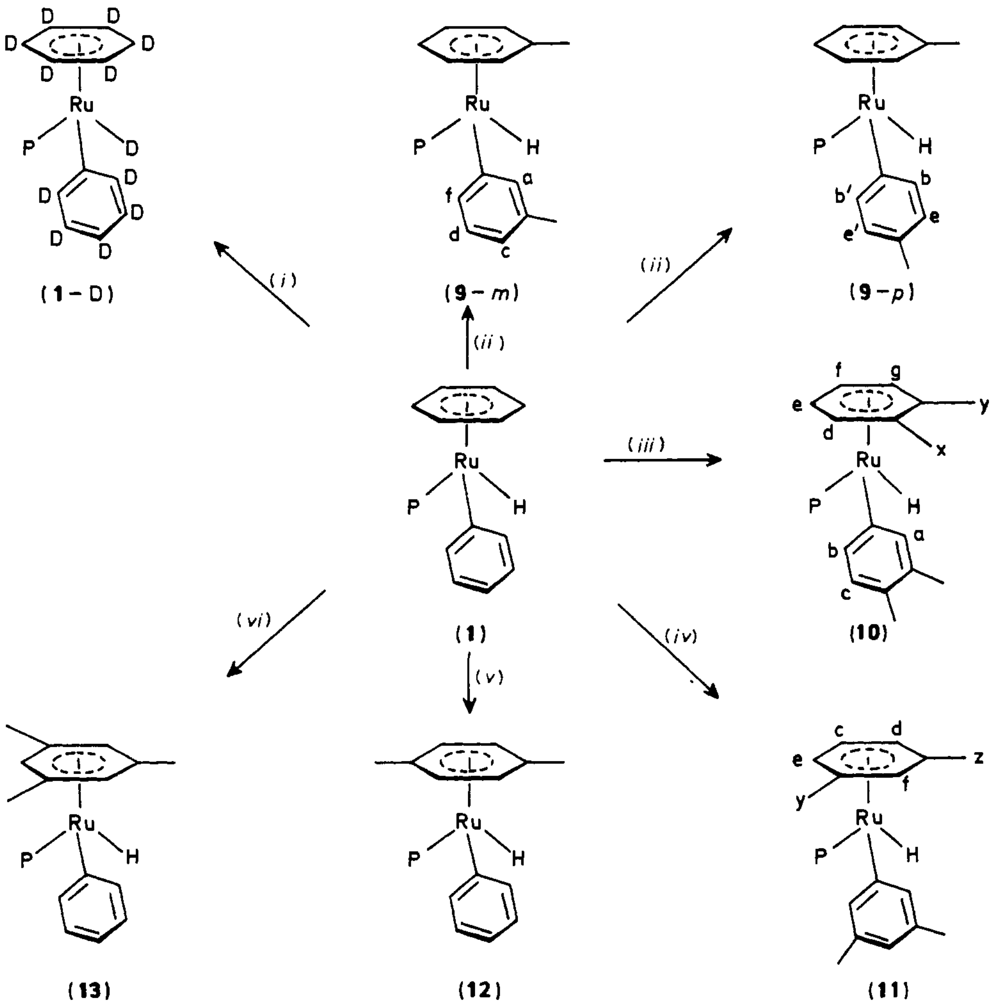
Reaction of rhodium atoms with benzene–trimethylphosphine (4:1) afforded pale yellow sublimable (80 °C, 10^{-2} mmHg) crystals. The ^{1}H n.m.r. spectrum showed a broad singlet at δ 1.3 of relative intensity 36, and a high-field sextet at δ −12.32 with J(P–H) = 13.9 Hz. The ^{31}P-{^{1}H} n.m.r. spectrum showed a doublet at δ −22.38, with J(Rh–P) = 145.9 Hz. The data show the compound to be $[RhH(PMe_3)_4]$, (**8**). The ^{1}H-{^{31}P} n.m.r. spectrum showed the hydride resonance to be a doublet with J(^{103}Rh–H) 12.5 Hz. The appearance of the hydride resonance as a 'sextet' in the ^{1}H n.m.r. spectrum can be explained by the near equality of ^2J(P–H) = 13.9 and ^1J(Rh–H) = 12.5.

Intermolecular Ligand-exchange Reactions of Compound (**1**).—Compound (**1**) was heated to *ca.* 80 °C in deuteriobenzene for 20 h and the ^{1}H n.m.r. spectrum was monitored at regular intervals. The spectra clearly showed that the molecule had undergone clean exchange reactions in which the hydrido, σ-phenyl, and η-benzene ligands were replaced by deuteriated analogues and a strong band assignable to benzene (δ 7.23) appeared. The ^{31}P-{^{1}H} n.m.r. spectrum of the thermally treated product showed a 1:1:1 triplet at δ 6.39, with J(P–D) = 8 Hz, confirming that the hydride ligand had been replaced with a deuteride ligand (^{2}H, I = 1). The ^{2}H n.m.r. spectrum of the thermally exchanged product, (**1**-D), supports the formulation $[RuD(\eta\text{-}C_6D_6)(PMe_3)(\sigma\text{-}C_6D_5)]$, as does the mass spectrum, which shows a highest peak at m/z = 345 corresponding to the parent ion.

The kinetics of the reaction of (**1**) with perdeuteriobenzene were studied. The data show that this complex exchange reaction occurs in a smooth and reproducible manner over a range of temperatures. Since the concentration of perdeuteriobenzene remained in large excess over that of (**1**), pseudo-first-order kinetics were obeyed. Table 2 summarises exchange rates obtained for different temperatures. A plot of ln k *vs.* $1/T$ was linear (Figure 1). The data show the activation energy E_a to be 51 ± 10 kJ mol^{-1}. Compound (**1**) is photochemically inert and photolysis for 1 week in perdeuteriobenzene caused no exchange reactions (n.m.r.).

The thermal reactions of compound (**1**) with toluene, *o*-, *m*-, and *p*-xylene, and mesitylene have been monitored by n.m.r. spectroscopy. In each case steady and clean reactions occurred and the appearance of the n.m.r. sample showed no evidence for decomposition to solid material. The reaction products were identified by ^{1}H n.m.r. spectroscopy; also, in some cases, the product was isolated from the n.m.r. sample tube and the mass spectrum was determined. Heating (**1**) in toluene for 3 d resulted in the appearance of two new hydride resonances, and the absence of any peaks due to (**1**). The mass spectrum of the products showed no parent ion corresponding to (**1**), and the highest band at m/z = 269 corresponds to the fragment $[Ru(\eta\text{-}C_6H_5Me)(PMe_3)]^+$. The ^{1}H n.m.r. spectrum of the product may be assigned unambiguously to a mixture of the *meta* and *para* isomers $[RuH(\eta\text{-}C_6H_5Me)(PMe_3)\{\sigma\text{-}C_6H_4Me\text{-}m \text{ or } \text{-}p\}]$, (**9**-*m*) or (**9**-*p*), in the ratio *ca.* 2:1, respectively.

The ^{1}H n.m.r. spectrum of (**9**) showed two sets of five resonances assignable to two σ-tolyl ligands (in the ratio of 2:1),



Scheme 2. P = PMe_3. (*i*) [$^2H_6$]Benzene at 80 °C for 20 h, yield >80%; (*ii*) toluene at 100 °C for 2 weeks, 60%; (*iii*) *o*-xylene at 100 °C for 4 d, 30%; (*iv*) *m*-xylene at 100 °C for 4 d, 30%; (*v*) *p*-xylene at 100 °C for 4 d, 30%; (*vi*) mesitylene at 100 °C for 4 d, 89%

as would be expected. However, it appears that a change in the methyl position on the σ-tolyl groups does not significantly affect the chemical shifts of the η-toluene hydrogens, nor, indeed, that of the PMe hydrogens. The methyl resonances for the two σ-tolyl groups occur as singlets at δ 2.35 for (**9**-*m*) and at 2.33 for (**9**-*p*). The doublet hydride at δ −9.34 [*J*(P–H) = 55.2 Hz] is assigned to (**9**-*m*), and the less intense hydride resonance at δ −9.33 [*J*(P–H) = 55.2 Hz] to (**9**-*p*). In the region δ 7.8—6.8 there is a singlet (δ 7.72), four doublets (δ 7.70, 7.59, 6.94, and 6.89) and one triplet (δ 7.02). A ^1H–^1H COSY-45 n.m.r. experiment (Figure 2), in the range δ 7.8—6.9, allows assignment of the bands. The resonances B and E are assigned to the *para* isomer, (**9**-*p*). Resonance B (δ 7.70) shows a small doublet coupling (*J* = 1.1 Hz) which is assigned to phosphorus coupling to the *ortho* hydrogens of the σ-tolyl group in (**9**-*p*). Correspondingly, resonance E is assigned to the *meta* hydrogens of (**9**-*p*). The remaining resonances were assigned to (**9**-*m*) (Table 1).

Heating a solution of compound (**1**) in *o*-xylene gave brown crystalline [$RuH(\eta$-$C_6H_4Me_2$-1,2)(PMe_3)(σ-$C_6H_3Me_2$-3,4)], (**10**). The ^1H n.m.r. spectrum showed a doublet hydride [*J*(P–H) = 55.2 Hz] at δ −9.62, and a doublet trimethylphosphine resonance at δ 1.01 [*J*(P–H) = 9.5 Hz]; these are assigned to a Ru(H)(PMe_3) unit. Four multiplets in the η-arene region, together with two methyl resonances at δ 1.75 and 1.77 are assigned to the η-1,2-dimethylbenzene ligand. The chirality of the metal centre makes the four aromatic hydrogens chemically inequivalent. Three multiplets at low field (δ 7.7—6.9) and two singlet methyl resonances at δ 2.28 and 2.23 are assigned to a σ-bound 3,4-dimethylphenyl ligand. The mass spectrum showed a highest band at *m*/*z* 389 assignable to the ion [$RuH(C_6H_4Me_2)(PMe_3)(C_6H_3Me_2)]^+$.

Heating compound (**1**) in *m*-xylene gave a brown solution and the ^1H n.m.r. spectrum of the product showed the absence of starting material. The presence of only one doublet at δ 1.03 [*J*(P–H) = 8.7 Hz] due to a co-ordinated trimethylphosphine ligand, and only one doublet hydride at δ −9.55 [*J*(P–H) = 55.8 Hz], indicated a single organometallic product. The ^1H n.m.r. spectrum of the product shows it to be the compound [$RuH(\eta$-$C_6H_4Me_2$-1,3)(PMe_3)(σ-$C_6H_3Me_2$-3,5)], (**11**). Since (**11**) is chiral there are four bands due to the η-C_6H_4 hydrogens and two bands, at δ 1.91 and 1.72, assignable to the Me_y and Me_z groups. The singlets at δ 2.34, 7.48, and 6.69 can be assigned to a σ-3,5-dimethylphenyl ligand and confirm the position of the ruthenium centre with respect to the two methyl groups. The mass spectrum shows a highest band at *m*/*z* 389, corresponding to the parent ion.

The ^1H n.m.r. spectrum of the product of heating compound

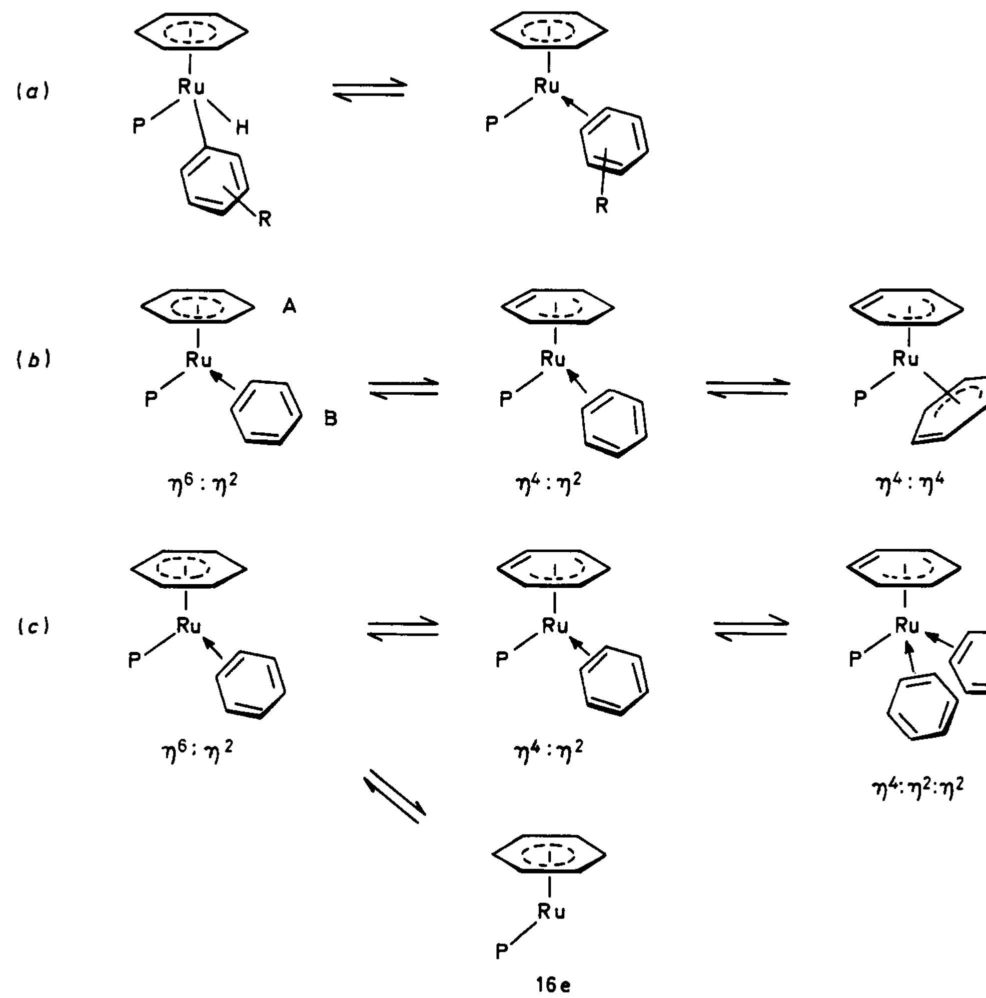


Figure 3. (*a*) Reversible oxidative addition–reductive elimination of Ru(σ-aryl)H $\rightleftharpoons$ Ru(η^2-arene): equilibrium between *meta* and *para* isomers of compound (**9**). (*b*) Reversible ring-slip steps: η^6 to η^4; η^4 to η^2. Intramolecular exchange of A and B. (*c*) Two possible pathways for intermolecular exchange of η^2-arene with free arene

(**1**) in *p*-xylene showed only one high-field resonance, indicative of a single arene ruthenium hydride species, [RuH(η-$C_6H_4Me_2$-1,4)(PMe_3)(σ-C_6H_5)], (**12**). The AA′BB′ system at δ 4.85 is typical for the four hydrogens of a η-*p*-xylene ligand and the singlet at δ 1.76 is attributable to the equivalent methyl groups of this ligand. The two multiplets at δ 7.78 and 7.07 of relative intensity 2:3 respectively are assigned, by analogy with the assignment for (**1**), to the σ-bound phenyl group.

Heating compound (**1**) in mesitylene afforded a brown compound which the ^1H n.m.r. spectrum showed to be [RuH(η-$C_6H_3Me_3$-1,3,5)(PMe_3)(σ-C_6H_5)], (**13**). The ^1H n.m.r. spectrum of (**13**) shows variable-temperature behaviour. A broad singlet at δ 7.67 became sharp at 60 °C. On cooling below room temperature the signal broadened and at 0 °C it disappeared into the baseline. Further cooling produced two new broad resonances, in the ratio of 1:1, symmetrically displaced about the position of the original broad singlet. These two signals sharpened further as the temperature was lowered to −60 °C. This behaviour can be interpreted in terms of hindered rotation of the σ-phenyl group about the Ru–C bond. At high temperature there is rapid rotation and a singlet is observed. On cooling, however, rotation becomes slow on the n.m.r. time-scale and two resonances, corresponding to the two chemically distinct *ortho* hydrogens, are observed. The two *ortho* hydrogens show a large difference in chemical shift at low temperature. However, the multiplet due to the *meta* hydrogens does not change its shape significantly, but undergoes a gradual shift to low field on cooling.

In conclusion, the reactions and structures proposed for the compounds described above are shown in Scheme 2. It is noteworthy that the reaction of ruthenium atoms with benzene–trimethylphosphine forms the compound (**1**) rather than the known [Ru(η-C_6H_6)(PMe_3)$_2$].[5] The compounds [Ru(η-arene)(PR_3)$_2$], where arene = C_6Me_6 or $C_6H_4Pr^iMe$, and R_3 = Ph_3, Me_3, or Me_2Ph, have also been described.[7] The compounds [RuH(η-C_6H_6)(PPr^i_3)R], where R = H, Ph, or C_6H_5Me, are close analogues of (**1**) and (**9**).[8] Analogues of (**2**), namely, [OsH(η-C_6H_6)(PPr^i_3)(Me)][9] and [Os(η-C_6H_6)-(CO)$_2$R],[10] have been reported.

The products of the ligand-exchange reactions of compound (**1**) are shown in Scheme 2. In all cases the η-benzene is replaced by the solvent arene. However, the σ-phenyl group is not replaced when the solvent arene is *p*-xylene or mesitylene. We note also the absence of products in which the σ-aryl groups have *ortho* methyl groups as substituents. We propose that σ-*o*-methylaryl ligands are not formed as a consequence of steric inhibition. This postulate, therefore, accounts for the absence of σ-aryl ligands derived from *p*-xylene and mesitylene.

Key equilibria which can account for the ligand-exchange reactions are given in Figure 3: they draw, in part, on analogous processes, for example, those described for $[RhH(\eta\text{-}C_5Me_5)(PMe_3)Ph]$.[11]

Experimental

All preparations and reactions described were carried out under an atmosphere of nitrogen (< 10 p.p.m. oxygen) using standard Schlenk-vessel and vacuum-line techniques. Solvents were pre-dried over molecular sieves and then distilled from potassium (toluene, benzene, cyclohexane), sodium–potassium alloy [pentane, light petroleum (b.p. 40—60 °C), diethyl ether, tetrahydrofuran (thf)], or phosphorus pentoxide (dichloromethane), under an inert atmosphere.

Metal vapour synthesis (m.v.s.) experiments were carried out using both the 10-kW bell-jar reactor and the twin-hearth bell-jar reactor.[12] Both vapour synthesis machines were operated in the positive hearth mode. Metal vapour synthesis reactions were carried out using a pre-melted ingot of the appropriate metal. This was required to minimise outgassing during the reaction which would lead to deterioration of the vacuum. In a typical reaction, the electron-gun furnace was turned on when a vacuum better than 10^{-5} Torr was achieved. Ligand vapour was condensed onto the walls of the vessel (maintained at liquid-nitrogen temperature) prior to evaporation of the metal sample. The metal was evaporated using the appropriate power and the rate of ligand entry adjusted so that a vacuum of $< 10^{-4}$ Torr was maintained. Over the period of the co-condensation (typically 3—4 h) a matrix formed on the wall of the vessel which varied in appearance from pale yellow to dark red, depending upon the metal and ligand. At the end of the reaction the apparatus was isolated from the cryopump and the cooling shroud of liquid nitrogen emptied. The apparatus was filled with dinitrogen and allowed to warm to room temperature (r.t.). As the matrix melted the product collected in the gutter and was washed out by the appropriate solvent under a positive pressure of nitrogen to a collection vessel.

Elemental analyses were performed by the Analysis Department in this laboratory, or, in the case of very air-sensitive materials, by the Analytische Laboratorien, 5270 Gummersbach 1 Elbach, West Germany.

Infrared spectra were recorded on a Pye-Unicam SP2000 double-beam, grating spectrophotometer, or on a Perkin-Elmer 457 double-beam grating spectrophotometer. Nuclear magnetic resonance spectra were recorded on a JEOL PMX60 (^{1}H n.m.r., 60 MHz, continuous wave), a Bruker WH300 (^{1}H n.m.r., 300 MHz), a Bruker WH250 (heteronuclear n.m.r., 250 MHz), or a Bruker WH500 spectrometer (^{1}H n.m.r., 500 MHz). Abbreviations used in multiplicities are s = singlet, d = doublet, t = triplet, q = quartet, sxt = sextet, m = multiplet, and vt = virtual triplet. Spectra were referenced using the residual protio-solvent peaks, with chemical shifts in p.p.m. and coupling constants in Hz. Low-resolution mass spectra were recorded on an AEI MS902 mass spectrometer.

Photoelectron spectra were recorded on a PES Laboratories 0078 spectrometer using a heated inlet system. The spectrometer was calibrated using ionisation potentials of He, Xe, and N_2.

(η-*Benzene*)*hydrido*(σ-*phenyl*)(*trimethylphosphine*)*ruthenium*, (**1**).—Ruthenium atoms (1.2 g, 12 mmol) were evaporated from the twin-hearth m.v.s. machine over a period of 3.5 h, using a beam current of 300 mA at 6 kV. Simultaneously a mixture of trimethylphosphine (16.3 g, 0.21 mol) and benzene (106.2 g, 1.4 mol) was condensed onto the walls of the reaction vessel. After warming to room temperature (r.t.) the brown matrix was washed out of the machine using thf (1 000 cm^3). The brown solution was filtered through a bed of Celite and concentrated to a red-brown oil under reduced pressure. Extraction with light petroleum (3 × 150 cm^3), followed by filtering through a bed of Celite and concentrating to *ca.* 100 cm^3, resulted in the formation of orange-brown feathery crystals on cooling to −20 °C. Isolation of the crystals resulted in their degradation to a powder on drying *in vacuo*. Recrystallisation from pentane yielded metallic lustred brown crystals. Yield 520 mg (13% based on metal evaporated from the furnace).

Table 3. Effect of heating $[RuH(\eta\text{-}C_6H_6)(PMe_3)(\sigma\text{-}C_6H_5)]$ in $[^2H_6]$benzene

Resonance/p.p.m.	7.85	7.23	4.87	0.96	−9.11
Assignment	*o*-H	C_6H_6	$\eta\text{-}C_6H_6$	PMe_3	RuH
Integral t = 0	20	35	64	104	10
Integral t = 20 h	9	121	23	106	6

(η-[$^2H_6$]*Benzene*)*deuterio*(σ-[$^2H_5$]*phenyl*)(*trimethylphosphine*)*ruthenium*, (**1-D**).—The compound $[RuH(\eta\text{-}C_6H_6)(PMe_3)(\sigma\text{-}C_6H_5)]$ (50 mg, 0.15 mmol) was dissolved in [$^2H_6$]benzene (1.0 cm^3) and sealed into a 5-mm n.m.r. tube. This was heated from 40 to 80 °C over 20 h and the ^{1}H n.m.r. spectrum was monitored. The reaction was shown to occur essentially quantitatively. Hydrogen-1 n.m.r. data are given in Table 3.

(η-*Benzene*)*hydrido*(σ-*phenyl*)(*trimethylphosphine*)*osmium*, (**2**).—Osmium atoms (0.9 g, 4.7 mmol) were evaporated on the twin-hearth m.v.s. machine over a period of 3 h. The vapour was co-condensed with a mixture of trimethylphosphine and benzene (100 cm^3, 20% PMe_3 w/w). The power used to evaporate the osmium was 300 mA at 5 kV throughout. After warming to r.t., the orange-brown matrix was extracted with thf (300 cm^3). The brown extract was filtered on a bed of Celite, and solvent was removed from the filtrate under reduced pressure giving a brown solid. This was extracted with light petroleum (4 × 100 cm^3). The extract was filtered on a bed of Celite and the orange-yellow filtrate was concentrated to *ca.* 20 cm^3 and cooled to −80 °C. The resulting orange powder was collected and dried *in vacuo*. Sublimation (80 °C, 10^{-4} mmHg) afforded very pale yellow microcrystals. Yield 100 mg.

(η-*Benzene*)*hydridobis*(*trimethylphosphine*)*manganese*, (**3**).—Manganese atoms (8.8 g, 0.16 mol) were condensed with a mixture of benzene and trimethylphosphine (120 cm^3, 20% PMe_3 w/w) on the large m.v.s. machine, over a period of 4 h. After warming to r.t. the deep brown matrix was extracted with thf (1 500 cm^3). The extract was filtered on a bed of Celite and the solvent was removed from the filtrate under reduced pressure giving a brown-black solid. This was extracted with light petroleum (3 × 150 cm^3), and the resulting red solution was filtered on a bed of Celite. The filtrate was concentrated to *ca.* 30 cm^3 under reduced pressure. Cooling to −80 °C gave red crystals of $[MnH(\eta\text{-}C_6H_6)(PMe_3)_2]$. Yield 750 mg (2% based on metal evaporated).

(η-*Cyclopentadienyl*)*tris*(*trimethylphosphine*)*manganese*, (**4**).—Manganese atoms (8.8 g, 0.16 mol) were co-condensed with a mixture of freshly distilled cyclopentadiene (98.9 g, 1.5 mol) and trimethylphosphine (18.1 g, 0.24 mol) over a period of 4 h. The power used to evaporate the manganese on the large m.v.s. machine was 40 mA at 4.8 kV. The matrix was warmed to r.t. and extracted from the machine with diethyl ether (1 500 cm^3). The extract was filtered on a bed of Celite. The solvent was removed from the filtrate under reduced pressure giving a brown oil which was extracted with light petroleum (300 cm^3). The extract was filtered on a bed of Celite and the solvent was removed from the filtrate giving a brown oil. Repeating the light petroleum extraction, followed by concentration to *ca.* 100 cm^3 and cooling to -80 °C, yielded very dark yellow crystals. Concentration of the mother-liquor and further cooling afforded a second crop of crystals. The combined yield was 8.2 g (15% based on manganese evaporated from the furnace).

[Mn(η-C_5H_5)(PMe_3)$_2$(CO)], (**5**).—The compound [Mn(η-C_5H_5)(PMe_3)$_3$] (0.6 g, 1.72 mmol) in light petroleum (b.p. 100—120 °C, 100 cm^3) was treated with carbon dioxide (3 atm) at 70 °C for 7 d. The volatiles were removed under reduced pressure and the resultant yellow solid was extracted into light petroleum (b.p. 40—60 °C, 100 cm^3) giving a yellow solution. This was filtered from a fine white precipitate, and the filtrate was concentrated to 10 cm^3 and cooled to -80 °C, giving yellow crystals. These were collected and the mother-liquor was concentrated to 5 cm^3 and cooled to -80 °C giving a second batch of yellow crystals. The combined products were washed with light petroleum (b.p. 30—40 °C) at -80 °C and dried *in vacuo*. Total yield 0.4 g (77%).

(η-*Cyclopentadienyl*)*hydridotris*(*trimethylphosphine*)*manganese Tetrafluoroborate*, (**6**).—The compound [Mn(η-C_5H_5)(PMe_3)$_3$] (100 mg, 0.28 mmol) in diethyl ether was cooled to -78 °C and tetrafluoroboric acid (10%) was added (4 drops). On warming to r.t. a bright yellow precipitate separated out, which was washed with diethyl ether (3 × 20 cm^3) and dried *in vacuo*. Recrystallisation from methanol (30 cm^3) afforded cubic orange crystals of [MnH(η-C_5H_5)(PMe_3)$_3$]BF_4. Yield 100 mg (82%).

Reaction of [MnH(η-C_5H_5)(PMe_3)$_3$]BF_4 *with Potassium Hydride*.—The compound [MnH(η-C_5H_5)(PMe_3)$_3$]BF_4 (20 mg, 0.05 mmol) was suspended in thf (20 cm^3) and excess of potassium hydride suspended in light petroleum (b.p. 60—80 °C) was added. Stirring at r.t. for 6 h afforded a yellow solution containing excess of potassium hydride. Removal of solvent and extraction with light petroleum (b.p. 40—60 °C, 2 × 10 cm^3) yielded yellow crystals on concentration and cooling to -20 °C. The crystals, formed in high yield, were shown to be [Mn(η-C_5H_5)(PMe_3)$_3$].

(η-*Cyclopentadienyl*)*dihydridobis*(*trimethylphosphine*)*manganese*, (**7**).—The compound [Mn(η-C_5H_5)(PMe_3)$_3$] (400 mg, 1.12 mmol) in light petroleum (20 cm^3) was treated with dihydrogen at 10 atm for 24 h. The solvent was removed under reduced pressure and the yellow residue was redissolved in light petroleum (20 cm^3). The solution was again treated with dihydrogen at 10 atm for 24 h. This cycle was repeated seven times. The ^{1}H n.m.r. spectrum of the product showed the ratio (**7**):(**4**) to be 9:1. This was then recrystallised from light petroleum (*ca.* 10 cm^3) at -78 °C giving orange crystals which were collected, washed with light petroleum (2 × 10 cm^3, at -78 °C), and dried *in vacuo*. The ^{1}H n.m.r. spectrum showed only bands assignable to compound (**7**). Yield *ca.* 15%. ^{1}H N.m.r. in [$^2H_6$]benzene: δ 3.99 (5 H, s, η-C_5H_5), 1.16 (18 H, m, 2PMe_3), and -9.97 [2 H, t, *J*(P–H) 99.0 Hz, MnH_2].

Hydridotetrakis(*trimethylphosphine*)*rhodium*, (**8**).—Rhodium atoms (0.5 g, 4.9 mmol) were evaporated from the twin-hearth m.v.s. machine over 3.5 h, using a power of 180 mA at 4.2 kV. Simultaneously benzene and trimethylphosphine (70 cm^3, 20% PMe_3 w/w) were condensed on to the reaction vessel. Warming to r.t. gave an orange matrix which was extracted with warm thf (1 500 cm^3) and filtered on a bed of Celite, giving a yellow-orange solution. Removal of volatiles under reduced pressure afforded a deep red oil, which was extracted with light petroleum (3 × 100 cm^3). Concentration and cooling to -30 °C gave orange crystals, which could be sublimed at 80 °C (10^{-2} mmHg) to yield pale yellow microcrystals of [RhH(PMe_3)$_4$] (100 mg).

Hydrido(η-*toluene*)(m- *and* p-*tolyl*)(*trimethylphosphine*)*ruthenium*, (**9**-*m*) *and* (**9**-*p*).—The compound [RuH(η-C_6H_6)(PMe_3)(σ-C_6H_5)] (50 mg, 0.15 mmol) in toluene (30 cm^3) was heated to 100 °C for 2 weeks. After cooling to r.t. the solvent was removed under reduced pressure. The brown residue was extracted with light petroleum (2 × 10 cm^3), filtered, and the filtrate was concentrated to 55 cm^3 giving a brown powder. This was shown to be a 2:1 mixture of the *m*- and *p*-tolyl isomers of [RuH(η-C_6H_5Me)(PMe_3)(C_6H_4Me-*m* or -*p*)]. The combined yield was 33 mg (60%).

Hydrido(η-1,2-*dimethylbenzene*)(σ-3,4-*dimethylphenyl*)(*trimethylphosphine*)*ruthenium*, (**10**).—The compound [RuH(η-C_6H_6)(PMe_3)(σ-C_6H_5)] (20 mg, 0.06 mmol) in dry, distilled *o*-xylene (10 cm^3) was heated at 100 °C for 4 d. The volatile components were removed under reduced pressure. The residue was extracted with light petroleum (2 × 15 cm^3). The extract was filtered and the filtrate was concentrated giving a brown powder. Yield 30%.

Hydrido(η-1,3-*dimethylbenzene*)(σ-3,5-*dimethylphenyl*)(*trimethylphosphine*)*ruthenium*, (**11**).—The compound [RuH(η-C_6H_6)(PMe_3)(σ-C_6H_5)] (20 mg, 0.06 mmol) in dry, distilled *m*-xylene (10 cm^3) was heated at 100 °C for 4 d. The volatile components were removed under reduced pressure. The residue was extracted with light petroleum (2 × 15 cm^3). The extract was filtered and the filtrate was concentrated giving a brown powder. Yield 30%.

Hydrido(η-1,4-*dimethylbenzene*)(σ-*phenyl*)(*trimethylphosphine*)*ruthenium*, (**12**).—The compound [RuH(η-C_6H_6)(PMe_3)(σ-C_6H_5)] (20 mg, 0.06 mmol) in dry, distilled *p*-xylene (10 cm^3) was heated at 100 °C for 4 d. The volatile components were removed under reduced pressure. The residue was extracted with light petroleum (2 × 15 cm^3). The extract was filtered and the filtrate was concentrated giving a brown powder. Yield 30%.

Hydrido(η-*mesitylene*)(σ-*phenyl*)(*trimethylphosphine*)*ruthenium*, (**13**).—The compound [RuH(η-C_6H_6)(PMe_3)(σ-C_6H_5)] (20 mg, 0.06 mmol) in dry, distilled mesitylene (10 cm^3) was heated to 100 °C for 4 d. The resulting brown solution was concentrated under reduced pressure to a brown oil. Extraction with light petroleum (2 × 20 cm^3) followed by filtration and concentration of the filtrate gave a brown powder. Yield 20 mg (89%).

Acknowledgements

We thank the S.E.R.C. for a grant (to J. M. W.) and the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support.

References

1 S. D. Ittel and C. A. Tolman, *Organometallics*, 1982, **1**, 1432.
2 M. L. H. Green and L. L. Wong, *J. Chem. Soc., Chem. Commun.*, 1984, 771; *J. Chem. Soc., Dalton Trans.*, 1987, 411.
3 M. L. H. Green, D. O'Hare, and J. M. Wallis, *J. Chem. Soc., Chem. Commun.*, 1984, 233; M. L. H. Green and G. Parkin, *ibid.*, 1985, 771; 1984, 1467.
4 M. L. H. Green and J. M. Wallis, *Polyhedron*, 1986, **5**, 1442.

5 H. Werner and B. Juthani, *J. Organomet. Chem.*, 1977, **129**, C39.

6 J. C. Green, unpublished work.

7 H. Werner, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 927.

8 R. Kletzin and H. Werner, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 873.

9 H. Werner and K. Poder, *J. Organomet. Chem.*, 1986, **310**, C51.

10 P. K. Rush, S. K. Noh, and M. Brookhart, *Organometallics*, 1986, **5**, 1745.

11 W. D. Jones and F. J. Feher, *J. Am. Chem. Soc.*, 1984, **106**, 1650; *Organometallics*, 1983, **2**, 562.

12 M. L. H. Green, 'Frontiers of Chemistry,' I.U.P.A.C., ed. K. J. Laidler, Pergamon, Oxford, 1982, p. 229; M. L. H. Green, *J. Organomet. Chem.*, 1980, **200**, 119; F. G. N. Cloke and M. L. H. Green, *J. Chem. Soc., Dalton Trans.*, 1981, 1938; J. M. Wallis, D.Phil. Thesis, Oxford, 1984; F. G. N. Cloke, D.Phil. Thesis, Oxford, 1978.

Received 3rd February 1987; *Paper* 7/186