A Convenient Synthesis of [Ru(η-C_5H_5)(PPh_3)(CO)Cl] † and the Cations [Ru(η-C_5H_5)(PPh_3)L(CO)]$^+$ [L = CO, PMe_3, or $P(OPh)_3$]

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Treatment of [Ru(η-C_5H_5)$(PPh_3)_2$Cl] with sulphur under carbon monoxide at 1—3 atm in hot toluene gives quantitative yields of [Ru(η-C_5H_5)(PPh_3)(CO)Cl], which can be further treated in warm methanol with CO, PMe_3, and $P(OPh)_3$ to give the cations [Ru(η-C_5H_5)(PPh_3)$(CO)_2$]$^+$, [Ru(η-C_5H_5)(PPh_3)(PMe_3)(CO)]$^+$, and [Ru(η-C_5H_5)(PPh_3){$P(OPh)_3$}(CO)]$^+$ respectively.

There exists an extensive chemistry of monocyclopentadienyliron complexes derived from [{Fe(η-C_5H_5)$(CO)_2$}$_2$] (1) and [Fe(η-C_5H_5)$(CO)_2$Cl] (2). These starting materials can be readily prepared in large quantities and high yield from inexpensive [$Fe(CO)_5$].[1] Controlled replacement of one or both carbonyl groups and chloride from (2) can be achieved enabling a very wide range of neutral [2,3] and cationic [3,4] monocyclopentadienyl complexes to be prepared.

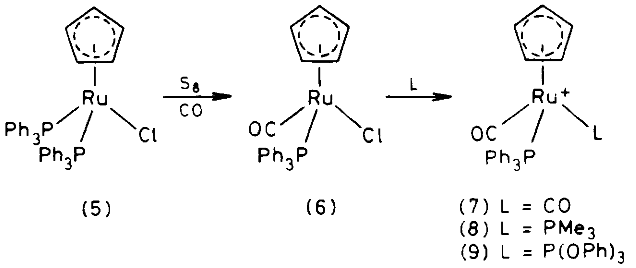
In contrast, monocyclopentadienylruthenium chemistry [5] has been little explored and is largely confined to the systems [Ru(η-C_5H_5)$(PPh_3)_2$Cl] and [Ru(η-C_5H_5)$(PPh_3)_2$L]$^+$ (L = CO, PR_3, *etc.*), which can be prepared in high yield from $RuCl_3$. The complexes [{Ru(η-C_5H_5)$(CO)_2$}$_2$] (3) and [Ru(η-C_5H_5)$(CO)_2$Cl] (4) have been prepared from [$Ru_3(CO)_{12}$] and [$Ru_4H_4(CO)_{12}$] in good yield,[6] but the cost of these reagents prohibits the large-scale syntheses necessary to explore their chemistry extensively. Stone and co-workers [7] reported a route to complex (3) from $RuCl_3$ *via* carbonylation (10 atm) to [{$Ru(CO)_3Cl_2$}$_2$]. Kruse and Angelici [8] found problems in obtaining a pure product in reproducible yields by this method and this has also been our experience. Replacement of more than one carbonyl ligand in complex (4) has not proved possible and further substitution of carbonyl and chloride is difficult to control to obtain a single product.[8,9] Stone and co-workers [7] have also reported the conversion of [Ru(η-C_5H_5)$(PPh_3)_2$Cl] (5) into the potentially useful [Ru(η-C_5H_5)(PPh_3)(CO)Cl] (6) *via* either carbonylation (150 atm) or using [$Fe_2(CO)_9$] in tetrahydrofuran. In our hands, this latter reaction gives variable yields of contaminated product. We have therefore turned our attention to devising a reliable high-yield synthesis of complex (6) under mild conditions from the readily available (5).

Results and Discussion

Heating toluene or xylene solutions of complex (5) with sulphur in the presence of CO leads to near-quantitative yields of [Ru(η-C_5H_5)(PPh_3)(CO)Cl] (6), the other product being PPh_3S identified by ^1H and ^{31}P n.m.r. spectroscopy.[10]

Treatment of methanol solutions of (6) containing NH_4PF_6 in the presence of CO, PMe_3, and $P(OPh)_3$ at 50 °C overnight gave the cations (7), (8), and (9) respectively in good yields (Scheme).

Substitution reactions of [Ru(η-C_5H_5)$(PPh_3)_2$Cl] are necessarily dissociative [equations (i) and (ii)].



Scheme.

$$[\mathrm{Ru}(\eta\text{-}C_5H_5)(PPh_3)_2Cl] \rightleftharpoons [\mathrm{Ru}(\eta\text{-}C_5H_5)(PPh_3)Cl] + PPh_3 \quad \text{(i)}$$
$$\text{18 electrons} \qquad\qquad \text{16 electrons}$$

$$[\mathrm{Ru}(\eta\text{-}C_5H_5)(PPh_3)Cl] + L \rightleftharpoons [\mathrm{Ru}(\eta\text{-}C_5H_5)(PPh_3)(L)Cl] \quad \text{(ii)}$$
$$\text{16 electrons} \qquad\qquad \text{18 electrons}$$

The role of sulphur in the transformation of complex (5) to (6) is the oxidation of free triphenylphosphine to triphenylphosphine sulphide. Little prior use has been made of this reaction.[10] Cation (7) has been previously reported from reaction of (6) with 100 atm of CO in the presence of $AlCl_3$ or $BF_3{\cdot}Et_2O$ in benzene [11] or from [Ru(η-C_5H_5)H(PPh_3)(CO)] in a similar reaction.[6] The mild conditions described here, warm methanol, 1—3 atm of CO, reflect the increasing ease of ionisation in the series (4), (6), and (5). Whereas the conversion of complex (4) into [Ru(η-C_5H_5)$(CO)_3$]$^+$ requires 18 atm of CO at 45 °C for 60 h,[12] transformation of (5) to [Ru(η-C_5H_5)$(PPh_3)_2$(CO)]$^+$ goes at room temperature and atmospheric pressure.[13] The new cations (8) and (9) represent the first examples of the species [Ru(η-C_5H_5)$L^1L^2L^3$]$^+$ and were prepared from (6) in the presence of excess of ligand, clean monosubstitution being observed. In the case of (8), this clean selectivity is a considerable advantage over the other possible route; preparation of [Ru(η-C_5H_5)(PPh_3)(PMe_3)Cl] [14] from (5) and subsequent carbonylation. The spectroscopic data for complexes (7)—(9) are unexceptional and require no comment.

We are further investigating the chemistry of the chiral cations (8) and (9) and other similar species in order to probe the effects of electronic fine tuning on the cyclopentadienyl ligand and the metal centre.[15]

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† Carbonylchloro(1—5-η-cyclopentadienyl)(triphenylphosphine)ruthenium(II).

Non-S.I. unit employed: atm = 101 325 Pa.

Experimental

All reactions and purifications were performed under a nitrogen atmosphere using standard vacuum-line and Schlenk-tube techniques.[16] Reactions carried out at >1 atm pressure were performed in Fischer-Porter bottles. Xylene refers to the mixture of xylenes (b.p. 138—142 °C) supplied by Fisons Ltd. Toluene and xylene were dried over sodium diphenylketyl 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.

Infrared spectra were recorded on a Perkin-Elmer 257 instrument, n.m.r. spectra on Perkin-Elmer R24B (60 MHz, ^1H), Bruker WH90 (36.43 MHz, ^{31}P), and Bruker WH300 (300 MHz, ^1H; 121.49 MHz, ^{31}P) spectrometers. Mass spectra were obtained on a VG Micromass ZAB1F instrument using the field desorption technique. Elemental analyses were performed by Dr. F. B. Strauss of this department. Chromatography was carried out using alumina (Grade IV/V). The complex $[Ru(\eta\text{-}C_5H_5)(PPh_3)_2Cl]$ was prepared by literature methods.[17] Trimethylphosphine was prepared by the method of Schmidbaur and Wolfsberger.[18]

$[Ru(\eta\text{-}C_5H_5)(PPh_3)(CO)Cl]$ (6).—A suspension of $[Ru(\eta\text{-}C_5H_5)(PPh_3)_2Cl]$ (2.2 g, 3.0 mmol) and sulphur (0.2 g, 6.2 mmol) in toluene (50 cm^3) was pressurised with carbon monoxide (2 atm) in a Fischer-Porter bottle (100 cm^3). The mixture was stirred for 8 h at 120 °C and slowly lightened in colour over this period. The resulting solution was cooled and the solvent removed under reduced pressure. Extraction of the residue with dichloromethane (2 × 30 cm^3) and concentration to 15 cm^3 gave a bright orange solution. This was put on an alumina column (2 × 20 cm) in diethyl ether and washed through with diethyl ether followed by dichloromethane to elute PPh_3S. The product band was rapidly eluted with acetone, solvent was removed, and the residue crystallised from dichloromethane–light petroleum (1 : 3) as orange-yellow blocks, yield 1.4 g (95%). $\nu_{max.}$ (Nujol) at 1 958s cm^{-1} (CO); ^1H n.m.r. (C_6D_6) δ 7.6—7.0 (m, 15 H, aryl H) and 4.65 (s, 5 H, C_5H_5); $^{31}P\text{-}\{^1H\}$ n.m.r. (C_6H_6) δ 48.5.

The reaction was also carried out in xylene at 120 °C, maintaining the pressure of CO at 1 atm by means of a manostat to give, after identical work-up, complex (6) in 93% yield.

$[Ru(\eta\text{-}C_5H_5)(PPh_3)(CO)_2]PF_6$ (7).—A suspension of $[Ru(\eta\text{-}C_5H_5)(PPh_3)(CO)Cl]$ (0.4 g, 0.8 mmol) and NH_4PF_6 (0.3 g, 1.8 mmol) in methanol (40 cm^3) was stirred (50 °C) under CO (3 atm) for 10 h. The pale yellow solution was transferred to a Schlenk apparatus and solvent was removed under reduced pressure. Extraction with dichloromethane (2 × 25 cm^3) and concentration to 10 cm^3 followed by slow addition of diethyl ether gave, on cooling (−30 °C), white microcrystalline (7), yield 0.4 g (82%). $\nu_{max.}$ (Nujol) at 2 075s (CO) and 2 030s cm^{-1} (CO); ^1H n.m.r. $[(CD_3)_2CO]$ δ 7.65 (m, 15 H, aryl H) and 5.92 (s, 5 H, C_5H_5); $^{31}P\text{-}\{^1H\}$ n.m.r. $[(CD_3)_2CO]$ δ 62.4.

$[Ru(\eta\text{-}C_5H_5)(PPh_3)(PMe_3)(CO)]PF_6$ (8).—A mixture of $[Ru(\eta\text{-}C_5H_5)(PPh_3)(CO)Cl]$ (0.6 g, 1.2 mmol), NH_4PF_6 (0.5 g, 3.1 mmol), and PMe_3 (1 cm^3, 10 mmol) in methanol (50 cm^3) was stirred at 50 °C for 12 h. The pale yellow solution was evaporated to dryness and the residue crystallised from dichloromethane–diethyl ether (1 : 3) to yield beige microcrystals, yield 0.74 g (90%) (Found: C, 48.15; H, 4.30. $C_{27}H_{29}F_6OP_3Ru$ requires C, 47.85; H, 4.30%). $\nu_{max.}$ (Nujol) at 1 995s cm^{-1} (CO); ^1H n.m.r. $[(CD_3)_2CO]$ δ 7.6 (m, 15 H, aryl H), 5.45 (s, 5 H, C_5H_5), and 1.49 (d, 9 H, J 10.6 Hz, PMe_3); $^{31}P\text{-}\{^1H\}$ n.m.r. $[(CD_3)_2CO]$ δ 1.4 (d, J 30.4, PMe_3) and 49.2 (d, J 30.4 Hz, PPh_3). m/z 533 $[M^+]$.

$[Ru(\eta\text{-}C_5H_5)(PPh_3)\{P(OPh)_3\}(CO)]PF_6$ (9). A mixture of $[Ru(\eta\text{-}C_5H_5)(PPh_3)(CO)Cl]$ (0.5 g, 1.0 mmol), NH_4PF_6 (0.5 g, 3.1 mmol), and $P(OPh)_3$ (2 cm^3, 7.6 mmol) in methanol (50 cm^3) was stirred at 60 °C for 14 h. Work-up as for complex (8) gave white crystals of (9) containing 1 mol of dichloromethane of crystallisation, yield 0.65 g, 70% (Found: C, 51.75; H, 3.90. $C_{43}H_{37}Cl_2F_6O_4P_3Ru$ requires C, 51.8; H, 3.70). $\nu_{max.}$ (Nujol) at 2 015s cm^{-1} (CO); ^1H n.m.r. $[(CD_3)_2CO]$ δ 7.6—7.0 (m, 30 H, aryl H), 5.60 (s, 2 H, CH_2Cl_2), and 5.34 (s, 5 H, C_5H_5); $^{31}P\text{-}\{^1H\}$ n.m.r. $[(CD_3)_2CO]$ δ 45.3 (d, J 48.5, PPh_3) and 132.2 [d, J 48.5 Hz, $P(OPh)_3$]. m/z 767 $[M^+]$.

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