η-Cyclopentadienylcobalt Chemistry: Allylic, Alkyl, and Hydrido-derivatives

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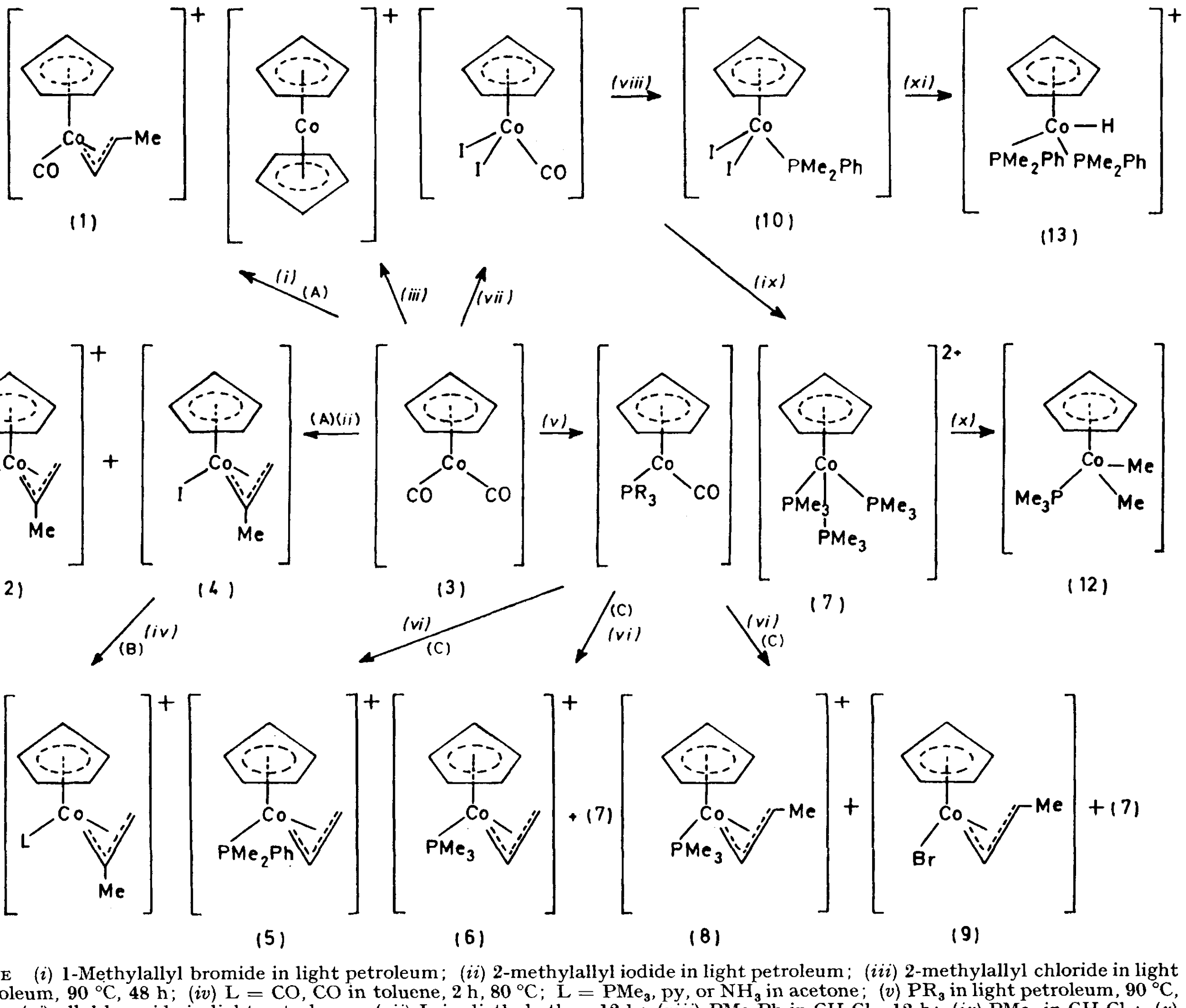
The new complexes $[Co(\eta\text{-}C_5H_5)(\eta\text{-}2\text{-}MeC_3H_4)L][PF_6]$ (L = CO, PMe_3, C_5H_5N, or NH_3), $[Co(\eta\text{-}C_5H_5)(\eta\text{-}1\text{-}MeC_3H_4)L'][PF_6]$ and $[Co(\eta\text{-}C_5H_5)(\eta\text{-}C_3H_5)L'][PF_6]$ (L' = CO or PMe_3), $[Co(\eta\text{-}C_5H_5)(\eta\text{-}2\text{-}MeC_3H_4)I]$, $[Co(\eta\text{-}C_5H_5)(PMe_3)(CO)]$, $[Co(\eta\text{-}C_5H_5)(PMe_3)_3][PF_6]_2$, $[Co(\eta\text{-}C_5H_5)(PMe_2Ph)I_2]$, $[Co(\eta\text{-}C_5H_5)(PMe_2Ph)_2H][PF_6]$, and $[Co(\eta\text{-}C_5H_5)(PMe_3)Me_2]$ have been prepared and characterised.

RECENTLY we have proposed rules concerning the regiospecificity of the addition of nucleophiles to organometallic cations.[1] Part of the rules specify that addition to an allylic group will be at a terminal carbon if the metal centre is electron poor, whilst if the metal centre is very electron rich the addition may take place at the central carbon, as is found for the addition of Me to $[M(\eta\text{-}C_5H_5)_2(\eta\text{-}C_3H_5)]^+$ giving the metallacyclobutane derivative $[W(\eta\text{-}C_5H_5)_2(CH_2CHMeCH_2)]$.[2] In an attempt to provide further evidence for this proposal we sought a series of transition-metal η-allylic cations where, by variation of other ligands attached to the metal, we might alter the electron richness of the metal centre and thereby alter the position of addition of a nucleophile to the allyl group.

The choice of suitable allylic cations is limited by the



SCHEME (*i*) 1-Methylallyl bromide in light petroleum; (*ii*) 2-methylallyl iodide in light petroleum; (*iii*) 2-methylallyl chloride in light petroleum, 90 °C, 48 h; (*iv*) L = CO, CO in toluene, 2 h, 80 °C; L = PMe_3, py, or NH_3 in acetone; (*v*) PR_3 in light petroleum, 90 °C, 12 h; (*vi*) allyl bromide in light petroleum; (*vii*) I_2 in diethyl ether, 12 h; (*viii*) PMe_2Ph in CH_2Cl_2, 12 h; (*ix*) PMe_3 in CH_2Cl_2; (*x*) LiMe in diethyl ether, −20 °C; (*xi*) isopropylmagnesium bromide in thf, −30 °C, 1 min other rules governing the regiospecificity of nucleophilic addition. For example, an allylic cation which also contained an *even*-electron organic ligand would not be suitable since the nucleophilic addition would occur preferentially at the even-electron ligand;[1] *i.e.* complexes such as $[Mo(\eta\text{-}C_6H_6)L_2(\eta\text{-}C_3H_5)]^+$ would be unsuitable. Examination of the literature, in the light of the rules, revealed the complexes $[M(\eta\text{-}C_5H_5)(\eta\text{-}C_3H_5)L]^+$ (L = CO, M = Co or Rh)[3,4] to be readily accessible.

We therefore set out to prepare a series of related complexes $[Co(\eta\text{-}C_5H_5)(\eta\text{-allyl})L]^+$ where L represents donor ligands of differing donor ability, such as NH_3, PR_3, and CO. These studies are described below.

Analytical and spectroscopic data

Complex	Colour	Analytical data (%) [a] C	H	^1H N.m.r.[b]
(1) $[Co(\eta\text{-}C_5H_5)(\eta\text{-}1\text{-}MeC_3H_4)(CO)][PF_6]$	Yellow	34.0 (34.1)	3.5 (3.4)	8.06, **3**, *d* [$J(H_c\text{–}Me)$ 6.1], Me; 7.51, **1**, *d* [$J(H_c\text{–}H_a)$ 11.8], H_a; 6.19, **1**, *c*, H_b; H_b; 5.58, **1**, *d* [$J(H_c\text{–}H_s)$ 6.9], H_s; 4.47—4.10, **1**, *c*, H_c; 4.04, **5**, *s*, C_5H_5 [c–e]
(2) $[Co(\eta\text{-}C_5H_5)(\eta\text{-}2\text{-}MeC_3H_4)(CO)][PF_6]$	Yellow	34.1 (34.1)	3.5 (3.4)	7.58, **3**, *s*, Me; 7.24, **2**, *s*, H_a; 5.38, **2**, *s*, H_s; 3.94, **5**, *s*, C_5H_5 [c,f]
(4) $[Co(\eta\text{-}C_5H_5)(\eta\text{-}2\text{-}MeC_3H_4)I]$	Red-black	35.8 (35.3)	4.4 (3.9) [g]	7.99, **3**, *s*, Me; 6.92, **2**, *s*, H_a; 5.17, **2**, *s*, H_s; 4.79, **5**, *s*, C_5H_5 [c,h]
$[Co(\eta\text{-}C_5H_5)(PMe_3)(CO)]$	Red	[i]		8.82, **9**, *d* [$J(^{31}P\text{–}Me)$ 9.3], PMe_3; 5.2, **5**, *d* [$J(^{31}P\text{–}C_5H_5)$ 1.2], C_5H_5 [j,k]
(5) $[Co(\eta\text{-}C_5H_5)(\eta\text{-}C_3H_5)(PMe_2Ph)][PF_6]$	Orange	42.6 (42.9)	5.0 (4.7)	8.52, **2**, *t* [$J(^{31}P\text{–}H_a) = J(H_c\text{–}H_a)$ 11.2], H_a; 8.09, **6**, *d* [$J(^{31}P\text{–}Me)$ 9.7], Me; 5.77, **2**, *d* [$J(H_c\text{–}H_s)$ 6.8], H_s; 4.63, **5**, *d* [$J(^{31}P\text{–}C_5H_5)$ 1.2], C_5H_5; 4.66—4.41, **1**, *c*, H_c; 3.56—2.16, **5**, *c*, Ph [c]
(6) $[Co(\eta\text{-}C_5H_5)(\eta\text{-}C_3H_5)(PMe_3)][PF_6]$	Orange	34.6 (34.2)	5.2 (4.9)	8.54, **2**, *t* [$J(^{31}P\text{–}H_a) = J(H_c\text{–}H_a)$ 10.5], H_a; 8.4, **9**, *d* [$J(^{31}P\text{–}Me)$ 9.8], PMe_3; 5.91, **2**, *d* [$J(H_c\text{–}H_s)$ 7.1], H_s; 4.52, **5**, *d* [$J(^{31}P\text{–}C_5H_5)$ 1.2], C_5H_5; 4.68—4.33, **1**, *c*, H_c
(8) $[Co(\eta\text{-}C_5H_5)(\eta\text{-}1\text{-}MeC_3H_4)(PMe_3)][PF_6]$	Orange	36.0 (36.0)	5.4 (5.3)	8.75, **1**, *t* [$J(^{31}P\text{–}H_a) = J(H_c\text{–}H_a)$ 11.8], H_a; 8.38, **9**, *d* [$J(^{31}P\text{–}Me)$ 9.9], PMe_3; 8.26, **3**, *d* [$J(H_c\text{–}Me)$ 6.2], Me; 7.66—7.27, **1**, *c*, H_b; 6.04, **1**, *d* [$J(H_c\text{–}H_s)$ 6.4], H_s; 4.41—4.71, **1**, *c*, H_c; 4.55, **5**, *d* [$J(^{31}P\text{–}C_5H_5)$ 1.3], C_5H_5 [c]
(9) $[Co(\eta\text{-}C_5H_5)(\eta\text{-}1\text{-}MeC_3H_4)Br]$	Red-black	42.0 (41.7)	4.6 (4.6) [l]	8.47, **3**, *d* [$J(H_b\text{–}Me)$ 4.7], Me; 7.04, **1**, *d* [$J(H_c\text{–}H_a)$ 10.4], H_a; 6.36—5.89, **2**, *c*, H_b, H_c; 5.48, **5**, *s*, C_5H_5; 5.31, **1**, *d* [$J(H_c\text{–}H_s)$ 5.1], H_s [j,m]
$[Co(\eta\text{-}C_5H_5)(\eta\text{-}2\text{-}MeC_3H_4)(PMe_3)][PF_6]$	Orange	35.7 (36.0)	5.4 (5.3)	8.64, **2**, *c*, *d* [$J(^{31}P\text{–}H_a)$ 12.3], H_a; 8.42, **9**, *d* [$J(^{31}P\text{–}Me)$ 9.9], PMe_3; 7.73, **3**, *s*, Me; 6.05, **2**, *c*, H_s; 4.63, **5**, *d* [$J(^{31}P\text{–}C_5H_5)$ 1.1], C_5H_5 [c]
$[Co(\eta\text{-}C_5H_5)(\eta\text{-}2\text{-}MeC_3H_4)(py)][PF_6]$	Dark red	42.0 (4.7)	4.7 (4.2) [n]	8.16, **2**, *s*, H_a; 7.92, **3**, *s*, Me; 4.62, **5**, *s*, C_5H_5; 4.51, **2**, *s*, H_s; 2.61, **2**, *c*, *t* (*J* 6.0), H^2, $H^{2'}$ (py); 2.1, **1**, *c*, *t* (*J* 7.7), H^3 (py); 1.02, **2**, *c*, *d* (*J* 4.7), H^1, $H^{1'}$ (py) [c]
$[Co(\eta\text{-}C_5H_5)(\eta\text{-}2\text{-}MeC_3H_4)(NH_3)][PF_6]$	Dark red	31.9 (31.7)	4.4 (4.4) [o]	8.80—9.10, **3**, *br*, NH_3; 8.23, **2**, *s*, H_a; 7.93, **4**, *s*, Me; 4.88, **2**, *s*, H_s; 4.61, **5**, *s*, C_5H_5 [c]
(7) $[Co(\eta\text{-}C_5H_5)(PMe_3)_3][PF_6]_2$	Yellow	26.2 (26.2)	4.7 (5.0)	8.43—8.13, **27**, *c*, Me; 4.21, **5**, *c*, C_5H_5 [c]
(10) $[Co(\eta\text{-}C_5H_5)(PMe_2Ph)I_2]$	Dark purple	30.6 (30.2)	3.2 (3.1)	7.25, **6**, *d* [$J(^{31}P\text{–}Me)$ 11.2], Me; 4.62, **5**, *s*, C_5H_5; 2.25—1.30, **5**, *c*, Ph [p]
(13) $[Co(\eta\text{-}C_5H_5)(PMe_2Ph)_2H][PF_6]$	Yellow	46.7 (46.2)	5.3 (5.1)	8.36—8.21, **12**, *c*, Me; 4.69, **5**, *s*, C_5H_5; 2.48, **10**, *c*, Ph; 25.2, **1**, *t* [$J(^{31}P\text{–}H)$ 76.5], Co–H [c]
(12) $[Co(\eta\text{-}C_5H_5)(PMe_3)Me_2]$	Orange	51.7 (52.2)	8.8 (8.7)	9.64, **6**, *d* [$J(^{31}P\text{–}Me)$ 5.8], Me; 8.97, **9**, *d* [$J(^{31}P\text{–}Me)$ 9.10], PMe_3; 5.4, **5**, *s*, C_5H_5 [j,q]

[a] Calculated values are given in parentheses. [b] Given as chemical shift (τ), **relative intensity,** *multiplicity* (*J* in Hz), assignment, *etc.* [c] In $(CD_3)_2CO$. [d] ν(CO) at 2 085 cm^{-1}. [e] H_a = *anti*-H, H_b = C*H*Me, H_s = *syn*-H, H_c = central H. [f] ν(CO) at 2 083 cm^{-1}. [g] I, 41.6 (41.2%). [h] Mass spectrum, *m/e* 306. [i] Thermally unstable at room temperature. [j] In C_6D_6. [k] Mass spectrum, *m/e* 228. [l] Br, 31.0 (30.9%). [m] Mass spectrum, *m/e* 260 for ^{81}Br. [n] N, 3.4 (3.5%). [o] N, 3.9 (4.1%). [p] In $CDCl_3$. [q] Mass spectrum, *m/e* 230.

RESULTS AND DISCUSSION

Chemical Studies.—The various synthetic strategies adopted in the synthesis of complexes of the class $[Co(\eta\text{-}C_5H_5)(\eta\text{-allyl})L]^+$ are shown in the Scheme. The complexes $[Co(\eta\text{-}C_5H_5)(\eta\text{-}CHMeCHCH_2)(CO)][PF_6]$ (1) and $[Co(\eta\text{-}C_5H_5)(\eta\text{-}CH_2CMeCH_2)(CO)][PF_6]$ (2) were prepared by the known route (A), namely by treatment of $[Co(\eta\text{-}C_5H_5)(CO)_2]$ (3) with the appropriate allyl halide. This route was not always successful; for example, treatment of (3) with 2-methylallyl chloride gave $[Co(\eta\text{-}C_5H_5)_2][PF_6]$ as the major isolated product. Also, the second carbonyl ligand could be displaced by halide, thus leading to the formation of the neutral complex $[Co(\eta\text{-}C_5H_5)(\eta\text{-}CH_2CMeCH_2)I]$, (4), during the synthesis of (2) from (3) and allyl iodide. Complex (4) was found to be a useful precursor for the desired cations since it readily reacted with donor ligands such as L = CO, PMe_3, C_5H_5N, and NH_3 giving the cations $[Co(\eta\text{-}C_5H_5)(\eta\text{-}CH_2CMeCH_2)L]^+$ which were isolated as hexafluorophosphate salts. In contrast, attempts to prepare complexes such as $[Co(\eta\text{-}C_5H_5)(\eta\text{-}C_3H_5)(PPh_3)][PF_6]$ by direct replacement of CO by PPh_3 in $[Co(\eta\text{-}C_5H_5)(\eta\text{-}C_3H_5)(CO)][PF_6]$ led instead to loss of the allyl group, as $[PPh_3(C_3H_5)][PF_6]$, and formation of $[Co(\eta\text{-}C_5H_5)(PPh_3)(CO)]$. The complexes $[Co(\eta\text{-}C_5H_5)(\eta\text{-}C_3H_5)(PMe_2Ph)][PF_6]$ (5) and $[Co(\eta\text{-}C_5H_5)(\eta\text{-}C_3H_5)(PMe_3)][PF_6]$ (6) could, however, be prepared by treatment of the corresponding phosphine carbonyl $[Co(\eta\text{-}C_5H_5)\text{-}$

$(PR_3)(CO)]$ with allyl bromide. A by-product in the synthesis of (6) was the complex $[Co(\eta\text{-}C_5H_5)(PMe_3)_3][PF_6]_2$ (7). Clearly the reaction may be quite complex. Indeed, treatment of $[Co(\eta\text{-}C_5H_5)(PMe_3)(CO)]$ with but-2-enyl bromide gave the complexes (7), $[Co(\eta\text{-}C_5H_5)(\eta\text{-}1\text{-}MeC_3H_4)(PMe_3)][PF_6]$ (8), and also $[Co(\eta\text{-}C_5H_5)(\eta\text{-}1\text{-}MeC_3H_4)Br]$ (9). Finally, we found that treatment of $[Co(\eta\text{-}C_5H_5)(CO)I_2]$ with PMe_2Ph gave $[Co(\eta\text{-}C_5H_5)(PMe_2Ph)I_2]$ (10), whereas with PMe_3 the salt $[Co(\eta\text{-}C_5H_5)(PMe_3)_3]I_2$ (11) was formed.

Data characterising the new complexes are given in the Table.

As intended, we explored the reactions between a number of the above cations $[Co(\eta\text{-}C_5H_5)(\eta\text{-allyl})L]^+$ and nucleophiles such as H^- and Me^-. In all cases rapid reaction occurred giving unstable yellow species which were soluble in hydrocarbon solvents. It was not possible to isolate cobalt products in most cases due to rapid thermal decomposition to dark materials. However, treatment of (6) with methyl-lithium gave unexpectedly the dimethyl derivative $[Co(\eta\text{-}C_5H_5)(PMe_3)Me_2]$ (12). We examined the volatile products of the reaction of some of the allylic cations with nucleophiles. However, the data do not provide unambiguous evidence for the nature of the initial organometallic products, *i.e.* we cannot tell where or indeed whether nucleophilic addition has occurred on the η^3-allyl cation.

Finally, we note that treatment of $[Co(\eta\text{-}C_5H_5)(PMe_2Ph)I_2]$ with isopropylmagnesium bromide, followed by addition of aqueous ammonium hexafluorophosphate, gives the hydride salt $[Co(\eta\text{-}C_5H_5)(PMe_2Ph)_2H][PF_6]$, (13). Related hydride salts have been described recently.[5]

EXPERIMENTAL

All reactions and manipulations were carried out under dinitrogen or *in vacuo*. All solvents were dried and distilled. Hydrogen-1 n.m.r. spectra were determined using a Bruker (90 MHz) or JEOL (60 MHz) instrument. Microanalyses were by A. Bernhardt or by the microanalytical department of this laboratory. Infrared spectra were recorded as mulls on a Perkin-Elmer 457 instrument and were calibrated with polystyrene film. Mass spectra were determined using an A.E.I. M.S.9 spectrometer.

Carbonyl(η-cyclopentadienyl)(η-1-methylallyl)cobalt Hexafluorophosphate (1).—The complex $[Co(\eta\text{-}C_5H_5)(CO)_2]$ (3) (1 cm³, 1.4 g, 7.78 mmol) in dry tetrahydrofuran (10 cm³) was treated with but-2-enyl bromide (3 g, 22.22 mmol) and the mixture was heated at 60 °C for 5 h. A yellow precipitate formed, which was filtered off, washed with light petroleum, and extracted with water. Addition of aqueous $[NH_4][PF_6]$ (1 g in 10 cm³) gave a yellow precipitate which was recrystallised from acetone–water as yellow flakes of $[Co(\eta\text{-}C_5H_5)(\eta\text{-}1\text{-}MeC_3H_4)(CO)][PF_6]$, 35%.

Carbonyl(η-cyclopentadienyl)(η-2-methylallyl)cobalt Hexafluorophosphate (2) *and (η-Cyclopentadienyl)iodo(η-2-methylallyl)cobalt* (4).—Complex (3) (1.0 cm³, 1.4 g, 7.78 mmol) in light petroleum (b.p. 100—120 °C, 30 cm³) was treated with 2-methylallyl iodide (6 g, 33.0 mmol, excess). The mixture was left to stand at room temperature (r.t.) for 12 h and yellow and black crystals separated. These were washed with light petroleum, and the yellow crystals were extracted with water; addition of $[NH_4][PF_6]$ (1 g in 10 cm³) gave a yellow precipitate. This was recrystallised from acetone–water, giving yellow *crystals* of $[Co(\eta\text{-}C_5H_5)(\eta\text{-}2\text{-}MeC_3H_4)(CO)][PF_6]$, *ca.* 15%.

The black crystals were insoluble in water. They dissolved in toluene giving a dark red solution. Addition of light petroleum followed by cooling at −40 °C for 12 h gave black-red crystals of the neutral complex $[Co(\eta\text{-}C_5H_5)(\eta\text{-}2\text{-}MeC_3H_4)I]$, *ca.* 35%.

Reaction of $[Co(\eta\text{-}C_5H_5)(\eta\text{-}2\text{-}MeC_3H_4)I]$ *with* CO.—Complex (4) (0.3 g, 0.98 mmol) in toluene (20 cm³) was heated at 80 °C and carbon monoxide was passed through the solution for 2 h. A yellow precipitate was formed which was washed with light petroleum and extracted with water. Addition of aqueous $[NH_4][PF_6]$ (1 g in 10 cm³) gave a yellow precipitate which was crystallised from acetone–water as yellow *crystals*. Comparison of the i.r. spectrum with that of a separately prepared and fully characterised sample showed it to be $[Co(\eta\text{-}C_5H_5)(\eta\text{-}2\text{-}MeC_3H_4)(CO)][PF_6]$, *ca.* 70%.

Reaction of $[Co(\eta\text{-}C_5H_5)(CO)_2]$ *with Methylallyl Chloride.*—The compound $[Co(\eta\text{-}C_5H_5)(CO)_2]$ (1.0 cm³, 1.4 g, 7.78 mmol) in light petroleum (30 cm³) was treated with methylallyl chloride (3 g, 33.15 mmol). The mixture was heated for 48 h at 70 °C and a small amount of a yellow precipitate formed. The temperature was increased to 90 °C and the reaction mixture was left for another 48 h. The yellow precipitate was washed with light petroleum and extracted with water. Addition of $[NH_4][PF_6]$ (1 g in 10 cm³) gave a yellow precipitate which was crystallised from acetone–water. Comparison of the ¹H n.m.r. and i.r. spectra with those of an authentic sample showed that the complex was $[Co(\eta\text{-}C_5H_5)_2][PF_6]$, *ca.* 23%.

Reaction of $[Co(\eta\text{-}C_5H_5)(\eta\text{-}C_3H_5)(CO)][PF_6]$ *with* PPh_3.—The complex $[Co(\eta\text{-}C_5H_5)(\eta\text{-}C_3H_5)(CO)][PF_6]$ (0.35 g, 1.03 mmol) in acetone (30 cm³) was treated with an excess of PPh_3. After 2 h at 70 °C the initially yellow solution became red. The solvent was removed under reduced pressure and the residue was extracted with toluene. The red extract was concentrated and light petroleum was added. Cooling to *ca.* −20 °C gave red *crystals*. Comparison of the i.r. and ¹H n.m.r. spectra with those of an authentic sample showed them to be $[Co(\eta\text{-}C_5H_5)(PPh_3)(CO)]$, *ca.* 60%.

The white solid which was not extracted with toluene was crystallised from acetone–water as white crystals. They were identified as $[PPh_3(CH_2CH{=}CH_2)][PF_6]$ by comparison of the i.r. spectrum with that of an authentic sample.

Preparation of the Complexes $[Co(\eta\text{-}C_5H_5)(PR_3)(CO)]$ ($PR_3 = PPh_3$, PMe_2Ph, *or* PMe_3).—The complex $[Co(\eta\text{-}C_5H_5)(PPh_3)(CO)]$ was prepared by the method of King.[6] Thus (3) (1 cm³, 1.4 g, 7.78 mmol) in light petroleum (50 cm³) was treated with PPh_3 (2.1 g, 8 mmol) and the mixture was heated at 90 °C for 12 h. Gas evolution was observed. The solution was cooled at −40 °C giving prismatic red *crystals* of $[Co(\eta\text{-}C_5H_5)(PPh_3)(CO)]$.

The complexes $[Co(\eta\text{-}C_5H_5)(PMe_2Ph)(CO)]$ and $[Co(\eta\text{-}C_5H_5)(PMe_3)(CO)]$, were prepared similarly. For $[Co(\eta\text{-}C_5H_5)(PMe_3)(CO)]$ only 2 h at 90 °C was required.

The PPh_3 and PMe_2Ph complexes were characterised by comparison of their i.r. and ¹H n.m.r. spectra with those of authentic samples; $[Co(\eta\text{-}C_5H_5)(PMe_3)(CO)]$ was found to be pyrophoric and it was characterised by ¹H n.m.r., i.r., and mass spectroscopy. The yields were *ca.* 80%.

(η-Allyl)(η-cyclopentadienyl)(dimethylphenylphosphine)cobalt Hexafluorophosphate (5).—The complex [Co(η-C_5H_5)(PMe_2Ph)(CO)] (1 g, 3.45 mmol) in light petroleum (50 cm^3) was cooled to *ca.* −10 °C and treated dropwise with allyl bromide (1.0 g, 8.26 mmol). An orange-brown precipitate was formed immediately, and a gas was evolved. The precipitate was washed with light petroleum (b.p. 60—80 °C) and dissolved in water. Addition of aqueous [NH_4][PF_6] (1 g in 10 cm^3) gave an orange precipitate which was recrystallised from acetone–water, yield *ca.* 20%.

(η-Allyl)(η-cyclopentadienyl)(trimethylphosphine)cobalt Hexafluorophosphate, (6).—The complex [Co(η-C_5H_5)(PMe_3)(CO)] (1.4 g, 6.14 mmol) in light petroleum (b.p. 100—120 °C) (30 cm^3) was cooled to *ca.* −10 °C and treated dropwise with allyl bromide (1 g, 8.26 mmol). A yellow precipitate formed within seconds. The mixture was left to stand at room temperature for 30 min. The yellow precipitate was dissolved in water and addition of aqueous [NH_4][PF_6] (1 g in 10 cm^3) gave a yellow precipitate. This was dissolved in the minimum quantity of acetone and chromatographed on an alumina column in light petroleum (b.p. 60—80 °C). Elution with diethyl ether–acetone (1 : 1) caused an orange band to develop. This was collected, concentrated under reduced pressure, and water was added. After 12 h orange *needles* of [Co(η-C_5H_5)(η-C_3H_5)(PMe_3)][PF_6] were obtained, *ca.* 60%.

Further elution of the column with acetone–water (3 : 1) gave a second yellow band. This was collected and the acetone was removed under reduced pressure, giving yellow crystals. Comparison of its i.r. and ^1H n.m.r. spectra with those of a separately prepared and fully characterised sample showed the *complex* to be [Co(η-C_5H_5)(PMe_3)$_3$][PF_6]$_2$, *ca.* 10%.

(η-Cyclopentadienyl)(η-1-methylallyl)(trimethylphosphine)cobalt Hexafluorophosphate, (8).—This complex was prepared in a similar manner to that of the η-allyl analogue from [Co(η-C_5H_5)(PMe_3)(CO)] (1.4 g, 6.14 mmol) and but-2-enyl bromide (1.4 g, 11.1 mmol). From the resulting precipitate, two *complexes* were isolated by chromatography: [Co(η-C_5H_5)(PMe_3)$_3$][PF_6]$_2$ (7), identified by comparison of its i.r. and ^1H n.m.r. spectra with those of a separately prepared and fully characterised sample, yield *ca.* 30%; and [Co(η-C_5H_5)(η-1-MeC_3H_4)(PMe_3)][PF_6], *ca.* 25%.

If the mother liquor was left for 15 d at r.t. more of the initial orange precipitate was formed, together with a few black crystals. These were extracted with toluene, the toluene solution concentrated *in vacuo* and light petroleum (b.p. 100—120 °C) was added. Cooling to −40 °C for 12 h gave black *crystals* of the neutral complex [Co(η-C_5H_5)(η-1-MeC_3H_4)Br] (9), *ca.* 10%.

(η-Cyclopentadienyl)(η-2-methylallyl)(trimethylphosphine)cobalt Hexafluorophosphate.—Complex (4) (0.5 g, 1.6 mmol) in acetone (30 cm^3) was treated with PMe_3 (1 g, 13.15 mmol). An orange precipitate was formed immediately. It was extracted with water and addition of [NH_4][PF_6] (1 g in 10 cm^3) gave an orange precipitate which was recrystallised from acetone–water as orange microcrystals of [Co(η-C_5H_5)(η-2-MeC_3H_4)(PMe_3)][PF_6], *ca.* 75%.

(η-Cyclopentadienyl)(η-2-methylallyl)pyridinecobalt Hexafluorophosphate.—Complex (4) (0.2 g, 0.76 mmol) in acetone (20 cm^3) was treated with pyridine (0.978 g, 12.4 mmol). The mixture was heated for 10 min at 60 °C. Then aqueous [NH_4][PF_6] (1 g in 10 cm^3) was added giving a red precipitate. This was crystallised from acetone–water and then recrystallised from hot methanol to give red *needles* of [Co(η-C_5H_5)(η-2-MeC_3H_4)(py)][PF_6], *ca.* 75%.

Ammine(η-cyclopentadienyl)(η-2-methylallyl)cobalt Hexafluorophosphate.—Complex (4) (0.3 g, 0.98 mmol) in acetone (20 cm^3) was treated with NH_3 (0.88 g, 6.29 mmol). The acetone was partially removed under reduced pressure and addition of aqueous [NH_4][PF_6] (1 g in 10 cm^3) gave a red precipitate, which was crystallised from acetone–water to give red *crystals* of [Co(η-C_5H_5)(η-2-MeC_3H_4)(NH_3)][PF_6], *ca.* 75%.

(η-Cyclopentadienyl)(dimethylphenylphosphine)di-iodocobalt, (10).—This complex was prepared by the method of King.[6] Thus [Co(η-C_5H_5)(CO)I_2] (2.4 g, 5.91 mmol) in dry methylene chloride (50 cm^3) was treated dropwise with PMe_2Ph (1 g, 7.25 mmol) in dry methylene chloride (30 cm^3). After 12 h the solvent was partially removed under reduced pressure, and hexane (50 cm^3) was added to give very deep purple *crystals* of [Co(η-C_5H_5)(PMe_2Ph)I_2], *ca.* 95%.

(η-Cyclopentadienyl)tris(trimethylphosphine)cobalt Bis(hexafluorophosphate), (7).—The complex [Co(η-C_5H_5)(CO)I_2] (7.5 g, 18.47 mmol) in dry methylene chloride (50 cm^3) was treated with PMe_3 (5 g, 67.5 mmol). A yellow precipitate was immediately formed and a gas evolved. The yellow precipitate was extracted with water and addition of aqueous [NH_4][PF_6] (3.5 g, 215 mmol) gave a yellow precipitate which was crystallised from acetone–water giving [Co(η-C_5H_5)(PMe_3)$_3$][PF_6]$_2$, *ca.* 70%.

Reactions of [Co(η-C_5H_5)(η-CHRCR′CH_2)L][PF_6] (L = PMe_3 *or* CO; R, R′ = H *or* Me) *with* Na[AlH_2(OCH_2CH_2OMe)$_2$].—A typical reaction is described. The complex [Co(η-C_5H_5)(η-C_3H_5)(CO)][PF_6] (50 mg, 0.15 mol) suspended in dry toluene (1 cm^3) at *ca.* −20 °C was treated with an excess of Na[AlH_2(OCH_2CH_2OMe)$_2$]. The solid reacted readily giving a red solution. The reaction mixture was allowed to warm to room temperature and the solution became brown. The gaseous products evolved in the reaction were investigated by gas–liquid chromatography (g.l.c.) using columns of polyethylene glycol on Chromosorb P and 10% KCl on alumina. The product was shown to be propene. After 15 d the gaseous products from the same reaction vessels were again investigated, and they were shown to be mainly propane and trace amounts of propene. Attempts to isolate any tractable organometallic products failed.

Reaction of [Co(η-C_5H_5)(η-CHRCR′CH_2)L](PF_6) (L = PMe_3 *or* CO; R, R′ = Me *or* H) *with* LiMe.—A typical reaction is described. The complex [Co(η-C_5H_5)(η-C_3H_5)(CO)][PF_6] (50 mg, 0.15 mmol) suspended in dry diethyl ether at *ca.* −20 °C was treated with an excess of LiMe (1 cm^3 of 2 mol dm^{-3}, 2 mmol). The solid reacted rapidly giving a brownish solution. The mixture was allowed to warm to r.t. and the gaseous products were examined by g.l.c. using columns of silver nitrate–polyethylene glycol on Chromosorb P and 10% KCl on alumina. The product was shown to be propene.

(η-Cyclopentadienyl)bis(dimethylphenylphosphine)hydridocobalt Hexafluorophosphate, (13).—Complex (10) (0.5 g, 0.97 mmol) in dry tetrahydrofuran (50 cm^3) was cooled to −30 °C and treated with isopropylmagnesium bromide (3.0 cm^3 of a 2 mol dm^{-3} solution in OEt_2, 6 mmol). The colour of the mixture changed from the original purple to orange after *ca.* 1 min. After 10 min the mixture was cooled to −10 °C and ethanol was added. The solvent was removed under reduced pressure and the residue extracted

with water. Addition of aqueous $[NH_4][PF_6]$ (1 g in 10 cm^3) gave a yellow precipitate, which was recrystallised from acetone–water to give yellow *crystals* of $[Co(\eta\text{-}C_5H_5)(PMe_2Ph)_2H][PF_6]$, *ca.* 70%.

(η-Cyclopentadienyl)dimethyl(trimethylphosphine)cobalt, (12).—Complex (7) (1 g, 1.56 mmol) suspended in dry diethyl ether (20 cm^3) was treated with LiMe (3 cm^3 of a 2 mol dm^{-3} solution in OEt_2, 6 mmol) and rapid reaction gave an orange solution. The mixture was cooled to −10 °C and water was added. The diethyl ether layer was decanted off and the solvent removed giving an orange oil. This was chromatographed on an alumina column made up in light petroleum (b.p. 60—80 °C). Light petroleum eluted an orange band. This was collected, concentrated, then cooled to −78 °C. Orange needles of pure $[Co(\eta\text{-}C_5H_5)(PMe_3)Me_2]$ separated, *ca.* 70%.

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