A Simple Preparation for (η⁶-Arene)(η⁴-cyclo-octa-1,5-diene)ruthenium-(0) Complexes and their Conversion into the Corresponding Arene–Dichlororuthenium(II) Complexes

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A series of (η⁶-arene)(η⁴-cyclo-octa-1,5-diene)ruthenium(0) complexes have been readily prepared by reaction of (η⁴-cyclo-octa-1,5-diene)(η⁶-cyclo-octa-1,3,5-triene)ruthenium(0) with arene compounds, under 1 atm H_2 [arene = C_6H_6, $CH_3C_6H_5$, 1,4-$Me_2C_6H_4$, 1,3,5-$Me_3C_6H_3$, $C_2H_5C_6H_5$, $Me_2CHC_6H_5$, $Et_2CHC_6H_5$, $C_6H_5(CH_2)_3$-C_6H_5, $C_6H_5C_6H_5$, $C_2H_5CH(Me)C_6H_5$, $Me_2CHCH(Me)C_6H_5$, $NH_2CH(Me)C_6H_5$, $CH_3OC_6H_5$, or $CH_3COC_6H_5$]. These complexes react with aqueous HCl to give in almost quantitative yield the corresponding (η⁶-arene)-dichlororuthenium(II) complexes.

ZEROVALENT arene–olefin complexes of ruthenium, analogues of the well known carbonyl–olefin complexes,[1] are receiving increasing attention as potential catalysts and as models for oxidative-addition reactions.[2] Despite this interest, only a few synthetic methods have been reported.[3] The first example of these compounds, [Ru(η⁶-C_6H_6)(η⁴-C_8H_{12})] (C_8H_{12} = cyclo-octa-1,5-diene), was prepared by reaction of [{RuCl₂(η⁶-C_6H_6)}₂] and C_8H_{12}, in the presence of a Grignard reagent.[4] More recently, it has been obtained in good yields by heating a benzene solution of [RuH(C_8H_{12})(NH_2NMe_2)₃][BPh₄].[5] Reaction of C_8H_{12} with [{RuCl₂(η⁶-arene)}₂] (arene = C_6H_6, 1,3,5-$Me_3C_6H_3$, or C_6Me_6) in the presence of reducing agents gives the corresponding [Ru(η⁶-arene)(η⁴-C_8H_{12})] complex,[6] but this method is limited by the availability of the starting ruthenium complex.[7]

We report here the reaction of [Ru(η⁶-C_8H_{10})(η⁴-C_8H_{12})] (1) (C_8H_{10} = cyclo-octa-1,3,5-triene) with arenes under atmospheric pressure of H_2 to form a large number of [Ru(η⁶-arene)(η⁴-C_8H_{12})] complexes, (2). Reaction of (2) with aqueous HCl gives, in almost quantitative yields, the corresponding [{RuCl₂(η⁶-arene)}₂] complexes, many of which cannot be prepared in other ways.[7] Some aspects of this work have appeared in a preliminary communication.[8]

RESULTS AND DISCUSSION

Complex (1) is an important starting material in the preparative chemistry of ruthenium complexes [9] and its ready availability by reaction of $RuCl_3 \cdot xH_2O$ and C_8H_{12} in the presence of zinc dust [10] stimulated new interest in the preparation of ruthenium(0) complexes.

Complex (1) reacts readily with arenes, under 1 atm † of hydrogen and at room temperature, to give a wide range of [Ru(η⁶-arene)(η⁴-C_8H_{12})] complexes, (2), including those containing arenes with bulky or functional groups (Scheme 1). Yellow solutions of (1) and arene, in liquid arene or in solvents (n-pentane or tetrahydrofuran), readily become brown in the presence of H_2.

† Throughout this paper: 1 atm = 101 325 Pa; 1 mmHg ≈ 13.6 × 9.8 Pa.

Evaporation of the solvent and recrystallization from n-pentane affords (2) in yields ranging from 35% for complexes (2j) and (2k), to 95% for complexes (2a) and (2b). The relatively low yields (35%) observed for complexes (2j) and (2k), containing chiral arene ligands, may be related to the low arene : Ru molar ratio (ca. 10 : 1) used in the preparation. Complexes (2) are yellow crystalline compounds, soluble in common organic solvents. They
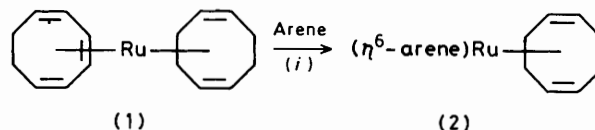
SCHEME 1 (i) Under H_2, room temperature, 8 h; arene = C_6H_6 (a), $CH_3C_6H_5$ (b), 1,4-$Me_2C_6H_4$ (c), 1,3,5-$Me_3C_6H_3$ (d), $C_2H_5C_6H_5$ (e), $Me_2CHC_6H_5$ (f), $Et_2CHC_6H_5$ (g), $C_6H_5(CH_2)_3C_6H_5$ (h), $C_6H_5C_6H_5$ (i), $C_2H_5CH(Me)C_6H_5$ (j), $Me_2CHCH(Me)C_6H_5$ (k), $NH_2CH(Me)C_6H_5$ (l), $CH_3OC_6H_5$ (m), or $CH_3COC_6H_5$ (n)

have been identified by elemental analysis and spectroscopic measurements (Table 1). With ligands containing two aromatic rings, e.g. $C_6H_5C_6H_5$ and $C_6H_5(CH_2)_3$-C_6H_5, ¹H n.m.r. spectroscopy has shown that only one ring is co-ordinated to the ruthenium atom.

In agreement with data for other arene–transition-metal complexes,[2,11] a large upfield shift of the aromatic proton resonances (ca. 2.5 p.p.m.) has been observed in the ¹H n.m.r. spectra of complexes (2). In addition, the complexes (2j), (2k), and (2l) containing chiral arene ligands show a significant anisochronicity of both the ortho- and meta-protons of the arene ring. For example, the upfield shifts on co-ordination, Δδ [Δδ = δ(free ligand) − δ(complex)], in (2j) are 2.52,3.16 p.p.m. for the ortho-protons H^1,H^5, and 3.11,2.51 p.p.m. for the meta-protons H^2,H^4 [Figure (a)]. Very similar behaviour is shown by the aromatic protons of the complex (2k), including the unexpected Δδ values of the protons H^1,-H^4, and H^2,H^5 (ΔδH^1 = ΔδH^4; ΔδH^2 = ΔδH^5). As far as complex (2l) is concerned, the Δδ values are 1.94,3.31 p.p.m. for the H^1,H^5 protons and 3.26,2.47 for the H^2,-H^4 protons. The low value of ΔδH^1 indicates the proximity of H^1 to the NH_2 group.

TABLE 1

Analytical and spectroscopic data for $[Ru(\eta^6\text{-arene})(\eta^4\text{-}C_8H_{12})]$ complexes

Compound[a]	Yield (%)	Analysis[b] (%) C	H	Arene protons[d]	Others	C_8H_{12}[a]
(2a) $[Ru(C_6H_6)(C_8H_{12})]$	95	58.5 (58.3)	6.60 (6.20)	4.95 (s, 6 H)		3.6 (m, 4 H, CH), 2.4 (m, 8 H, CH_2)
(2b) $[Ru(CH_3C_6H_5)(C_8H_{12})]$	95	59.8 (59.6)	6.70 (6.60)	4.9 (m, 5 H)	1.8 (s, 3 H, CH_3)	3.5 (m, 4 H), 2.4 (m, 8 H)
(2c) $[Ru(1,4\text{-}Me_2C_6H_4)(C_8H_{12})]$	95	61.1 (62.3)	6.95 (6.95)	4.8 (s, 4 H)	1.8 (s, 6 H, CH_3)	3.4 (m, 4 H), 2.4 (m, 8 H)
(2d) $[Ru(1,3,5\text{-}Me_3C_6H_3)(C_8H_{12})]$	95	61.0 (62.0)	7.50 (7.30)	4.85 (s, 3 H)	1.75 (s, 9 H, CH_3)	3.1 (m, 4 H), 2.3 (m, 8 H)
(2e) $[Ru(C_2H_5C_6H_5)(C_8H_{12})]$	75	61.3 (60.95)	6.35 (7.00)	5.1 (m, 1 H, H_p), 4.7 (m, 4 H, $H_o + H_m$)	2.1 (q, 2 H, CH_2, $J = 7$), 1.1 (t, 3 H, CH_3)	3.5 (m, 4 H), 2.4 (m, 8 H)
(2f) $[Ru(Me_2CHC_6H_5)(C_8H_{12})]$	70	62.15 (62.0)	7.40 (7.30)	5.35 (m, 1 H, H_p), 4.6 (m, 4 H, $H_o + H_m$)	2.4 (1 H, CH),[e] 1.2 (d, 6 H, CH_3, $J = 7$)	3.5 (m, 4 H), 2.4 (m, 8 H)
(2g) $[Ru(Et_2CHC_6H_5)(C_8H_{12})]$	65	63.4 (63.8)	7.65 (7.85)	5.35 (m, 1 H, H_p), 4.55 (m, 4 H, $H_o + H_m$)	2.3 (1 H, CH),[e] 1.48 (m, 4 H, CH_2), 0.88 (t, 6 H, CH_3, $J = 7$)	3.35 (m, 4 H), 2.31 (m, 8 H)
(2h) $[Ru\{C_6H_5(CH_2)_3C_6H_5\}(C_8H_{12})]$	70	67.9 (68.1)	6.80 (6.90)	7.25 (m, 5 H, C_6H_5),[f] 5.4 (m, 1 H, H_p), 5.1 (m, 4 H, $H_o + H_m$)	2.7 (t, 2 H, $C_6H_5\text{-}CH_2$, $J = 7$),[g] 2.25 (m, 2 H, $C_6H_5\text{-}CH_2$),[h] 2.0 (2 H, CH_2)	3.3 (m, 4 H), 2.1 (m, 8 H)
(2i) $[Ru(C_6H_5C_6H_5)(C_8H_{12})]$	60	65.8 (66.1)	5.90 (6.05)	7.6—7.1 (m, 5 H, C_6H_5),[f] 5.4—4.7 (m, 5 H, C_6H_5)		3.5 (m, 4 H), 2.3 (m, 8 H)
(2j) $[Ru\{C_2H_5CH(Me)C_6H_5\}(C_8H_{12})]$	35	62.5 (62.95)	7.40 (7.60)	5.18 (t, 1 H, H_p, $J_{mp} = J_{m'p} = 6$),[i] 4.69 (t, 1 H, $H_{m'}$, $J_{o'm'} = 6$), 4.68 (d, 1 H, H_o, $J_{om} = 6$), 4.09 (t, 1 H, $H_{m'}$), 4.04 (d, 1 H, $H_{o'}$)	2.3 (1 H, CH),[e] 1.45 (m, 2 H, CH_2), 1.25 (d, 3 H, $CH\text{-}CH_3$, $J = 7$), 0.86 (t, 3 H, $CH_2\text{-}CH_3$, $J = 7$)	3.5 (m, 4 H), 2.36 (m, 8 H)
(2k) $[Ru\{Me_2CHCH(Me)C_6H_5\}(C_8H_{12})]$	35	63.7 (63.85)	7.30 (7.85)	5.5 (t, 1 H, H_p, $J_{mp} = J_{m'p} = 6$), 5.35 (t + d, 2 H, $H_{m'} + H_o$, $J_{m'o'} = J_{om} = 6$), 4.11 (t + d, 2 H, $H_m + H_{o'}$)	2.5—1.5 (br m, 2 H, $CH\text{-}CH$), 1.3 (d, 3 H, $CH\text{-}CH_3$, $J = 7$), 0.8 [d, 6 H, $CH\text{-}(CH_3)_2$, $J = 7$]	3.5 (m, 4 H), 2.4 (m, 8 H)
(2l) $[Ru\{NH_2CH(Me)C_6H_5\}(C_8H_{12})]$[j]	60	58.55 (58.15)	6.55 (6.95)	5.26 (d, 1 H, H_o, $J_{om} = 6$),[i] 5.08 (t, 1 H, H_p, $J_{mp} = J_{m'p} = 6$), 4.73 (t, 1 H, $H_{m'}$, $J_{m'o'} = 6$), 3.93 (t, 1 H, H_m), 3.89 (d, 1 H, $H_{o'}$)	3.5 (1 H, CH)[e] 1.2 (d, 3 H, CH_3, $J = 7$), 1.2 (2 H, NH_2)[k]	3.5 (m, 4 H), 2.3 (m, 8 H)
(2m) $[Ru(CH_3OC_6H_5)(C_8H_{12})]$	75	56.05 (65.75)	6.00 (6.30)	4.8 (m, 5 H)	3.4 (s, 3 H, CH_3)	3.5 (m, 4 H), 2.4 (m, 8 H)
(2n) $[Ru(CH_3COC_6H_5)(C_8H_{12})]$	75	57.5 (58.35)	5.90 (6.10)	5.35 (d, 2 H, H_o, $J_{om} = 6$), 5.3 (t, 1 H, H_p, $J_{mp} = 6$),[i] 4.6 (t, 2 H, H_m)	2.8 (s, 3 H, CH_3)	3.5 (m, 4 H), 2.2 (m, 8 H)

[a] C_8H_{12} = Cyclo-octa-1,5-diene. [b] Calculated values are given in parentheses. [c] Unless otherwise noted, spectra were measured at 60 MHz in $[^2H_6]$benzene solution, using $SiMe_4$ as internal standard; δ scale; coupling constants, J, are in Hz; s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. [d] o = ortho, m = meta, p = para. [e] Observed by double resonance. [f] Aromatic ring not co-ordinated to ruthenium. [g] CH_2 group bonded to free aromatic ring. [h] CH_2 group bonded to aromatic ring co-ordinated to ruthenium. [i] Measured at 270 MHz; for details see the Figure; $H^1 = H_o$, $H^2 = H_m$, $H^3 = H_p$, $H^4 = H_{m'}$, $H^5 = H_{o'}$. [j] Analysis (%): N = 4.00 (4.25). [k] Observed by integration. [l] Partially obscured by H_o doublet.

Further investigations are in progress to determine the reason for the observed $\Delta\delta$ values $(\Delta\delta H^1 = \Delta\delta H^4$; $\Delta\delta H^2 = \Delta\delta H^5)$. However, at present we assume that the anisochronicity of the *ortho*- and *meta*-protons is related to the presence of the asymmetric substituent on the aromatic ligand. Si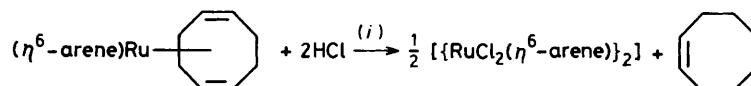nce no anisochronicity has been observed in the chiral $[\{RuCl_2(\eta^6\text{-arene})\}_2]$ complexes, the cyclo-octa-1,5-diene ligand must play an important role in determining the observed effects, perhaps by a preferential orientation with respect to the arene ligand or a favoured twisted conformation.

The reaction between (1) and arene does not occur in

(a)

(b)
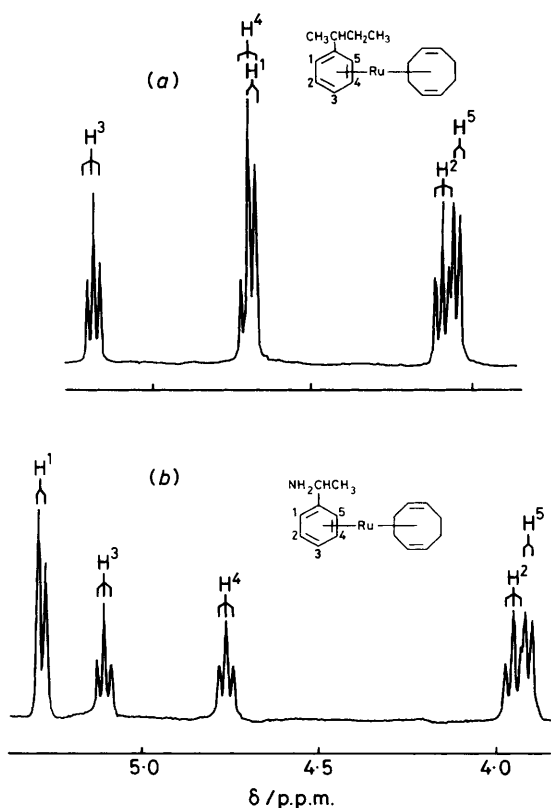
Proton n.m.r. spectra (aromatic protons) of complexes (2j) (a) and (2l) (b) at 270 MHz. Values (p.p.m.) from internal $SiMe_4$ are: (a) H^1 4.68, H^2 4.09, H^3 5.18, H^4 4.69, H^5 4.04, J(H–H) = 5.6 ± 0.2 Hz; (b) H^1 5.26, H^2 3.93, H^3 5.08, H^4 4.73, H^5 3.89, J(H–H) = 5.6 ± 0.2 Hz

the absence of molecular H_2 and in the mother-liquor of this reaction only cyclo-octene has been found with no detectable amounts of cyclo-octatriene. This suggests that selective hydrogenation of the cyclo-octa-1,3,5-triene ligand bonded to ruthenium in the starting complex (1), perhaps via enyl–Ru hydride species,[12] probably takes place, giving a co-ordinatively unsaturated ruthenium complex which undergoes ligand exchange in the presence of arene compounds (Scheme 2).
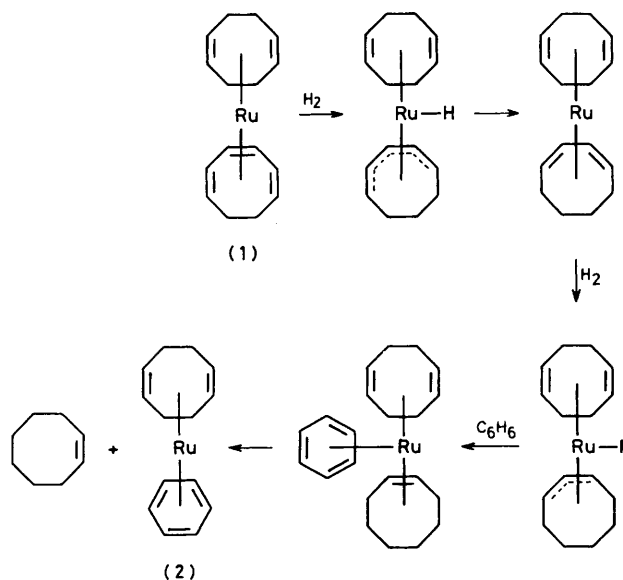
^{1}H n.m.r. spectra of all complexes show an upfield shift of the arene protons of ca. 1.2 p.p.m. and complex (3d), containing the chiral ligand $C_2H_5CH(Me)C_6H_5$, does not show any anisochronicity of the ortho- and meta-protons.

(1)

(2)

Scheme 2   Proposed mechanism of formation of complexes (2) from (1)

This route to complexes (3) from (2) can be applied generally and represents a convenient alternative route to such complexes.

There is increasing interest in the chemistry of arene–ruthenium compounds as hydrogenation catalysts.[2] Complexes (3) are reported to be active in the catalytic hydrogenation of olefins [13] and preliminary experiments show that complexes (2) can also be used in catalytic double-bond hydrogenation under mild conditions (25 °C, H_2 pressure = 25 atm).[14] The ability to obtain readily arene–ruthenium complexes containing chiral arenes suggests that they should now be tested as catalysts in the asymmetric hydrogenation of prochiral olefins.

Complexes (2) are convenient starting materials for the preparation of new arene–ruthenium complexes. Yellow solutions of (2) in acetone or tetrahydrofuran readily turn red on addition of HCl giving [{RuCl₂(η⁶-arene)}₂] compounds, (3), as crystalline precipitates (Scheme 3). No [{RuCl₂(η⁴-C₈H₁₂)}ₙ] is obtained as by-product and only cyclo-octene is detected in the mother-liquor of the reaction.

Complexes (3) have been characterized by elemental analysis and spectroscopic measurements as well as by comparison with authentic samples [7] (Table 2). The

Scheme 3   (i) Room temperature, acetone or tetrahydrofuran as solvents; arene = C_6H_6, 1,4-$Me_2C_6H_4$, 1,3,5-$Me_3C_6H_3$, $C_2H_5CH(Me)C_6H_5$, $Et_2CHC_6H_5$, or $CH_3OC_6H_5$

EXPERIMENTAL

All the reactions described were carried out under a dry oxygen-free nitrogen atmosphere, using conventional Schlenk-tube techniques. Solvents were purified by conventional methods, distilled, and stored under nitrogen. Arene ligands (Farmitalia–Carlo Erba products) were distilled or recrystallized, when solid, prior to use. 1,3-Diphenylpropane was prepared as described in the literature.[15] The complex [Ru(η⁶-C₈H₁₀)(η⁴-C₈H₁₂)] was prepared as recently reported.[10] Hydrogen-1 n.m.r. spectra were recorded on a Varian T-60 spectrometer and a Bruker

TABLE 2

Analytical and ^{1}H n.m.r. data for $[\{RuCl_2(\eta^6\text{-arene})\}_2]$ complexes

	Analysis (%) [a]			^{1}H N.m.r. data [b]	
Compound	C	H	Cl	Arene protons	Others
(3a) $[\{RuCl_2(C_6H_6)\}_2]$	28.1 (28.8)	2.20 (2.40)	27.9 (28.4)	6.0 (s)	
(3b) $[\{RuCl_2(1,4\text{-}Me_2C_6H_4)\}_2]$	34.2 (34.55)	3.80 (3.60)	25.75 (25.5)	5.9 (s, 4 H)	2.1 (s, 6 H, CH_3)
(3c) $[\{RuCl_2(1,3,5\text{-}Me_3C_6H_3)\}_2]$	36.2 (37.0)	4.00 (4.10)	23.75 (24.3)	6.0 (s, 3 H)	2.1 (s, 9 H, CH_3)
(3d) $[\{RuCl_2[C_2H_5CH(Me)C_6H_5]\}_2]$	38.95 (39.2)	4.40 (4.55)	23.0 (23.2)	5.8 (m, 5 H)	2.3 (m, 1 H, CH), 1.5 (m, 2 H, CH_2), 1.2 (d, 3 H, CH–CH_3, $J = 7$), 0.8 (t, 3 H, CH_2–CH_3, $J = 7$)
(3e) $[\{RuCl_2(Et_2CHC_6H_5)\}_2]$	41.55 (41.25)	5.35 (5.05)	22.0 (22.15)	5.9 (m, 5 H)	2.4 (m, 1 H, CH), 1.6 (m, 4 H, CH_2), 0.8 (t, 6 H, CH_3),
(3f) $[\{RuCl_2(CH_3OC_6H_5)\}_2]$	29.3 (30.0)	2.55 (2.85)	24.9 (25.3)	6.1 (t, 2 H, H_m, $J_{om} = J_{op} = 6$) [c] 5.5 (d, 2 H, H_o) 5.3 (t, 1 H, H_p)	3.9 (s, 3 H, CH_3)

[a] Calculated values are given in parentheses. [b] Measured at 60 MHz in $[^2H_6]$dimethyl sulphoxide solution, using $SiMe_4$ as internal standard; δ scale; coupling constants, J, are in Hz. [c] $o = ortho$, $m = meta$, $p = para$.

270-MHz spectrometer, for complexes (2j) and (2l). Mass spectra were measured on a Varian MAT CH7 spectrometer. Gas–liquid chromatographic analysis was carried out using a Perkin-Elmer F 30 instrument, with a 2-m column packed with 8% Carbowax 20 and 2% KOH on Chromosorb W (80—100 mesh). Melting or decomposition points (uncorrected) were measured on a Kofler hot-stage apparatus. Microanalyses were by the Laboratorio di Microanalisi, Istituto di Chimica Organica, Facoltà di Farmacia, Università di Pisa.

Preparation of Complexes.—$[Ru(\eta^6\text{-arene})(\eta^4\text{-}C_8H_{12})]$ (2). Only the preparation of compounds (2i) and (2m), prepared from solid and liquid arene respectively, are described in detail, the experimental procedure being substantially the same for all other compounds of the same type.

$[Ru(\eta^6\text{-}C_6H_5C_6H_5)(\eta^4\text{-}C_8H_{12})]$ (2i). Biphenyl, $C_6H_5C_6H_5$ (500 mg, 3.24 mmol), was added to a solution of $[Ru(\eta^6\text{-}C_8H_{10})(\eta^4\text{-}C_8H_{12})]$, (1) (100 mg, 0.32 mmol), in n-pentane (10 cm^3) and the reaction mixture stirred at room temperature for *ca.* 8 h, under 1 atm of H_2. The solvent was evaporated under reduced pressure and the excess of biphenyl removed by sublimation at 40 °C and 0.01 mmHg. n-Pentane (30 cm^3) was added to the solid residue and the yellow solution obtained was chromatographed on alumina (activity II—III) using pentane–benzene (1 : 1 v/v) as eluant. The yellow fraction was evaporated to dryness and the crude solid recrystallized from n-pentane at −78 °C, giving light yellow crystals of (2i) (70 mg, 0.19 mmol; $M = 364$).

$[Ru(\eta^6\text{-}CH_3OC_6H_5)(\eta^4\text{-}C_8H_{12})]$ (2m). A solution of $[Ru(\eta^6\text{-}C_8H_{10})(\eta^4\text{-}C_8H_{12})]$, (1) (150 mg, 0.47 mmol), in methyl phenyl ether, $CH_3OC_6H_5$ (5 cm^3), was stirred at room temperature for *ca.* 8 h, under 1 atm H_2. The excess of methyl phenyl ether was removed at reduced pressure and n-pentane (30 cm^3) was added to the solid residue. The yellow solution obtained was chromatographed on alumina, using n-pentane–benzene (1 : 1 v/v) as eluant, and the yellow fraction evaporated to dryness *in vacuo*. Recrystallization from n-pentane at −78 °C gives (2m) (108 mg, 0.34 mmol) as light yellow crystals ($M = 318$).

Reaction of $[Ru(\eta^6\text{-arene})(\eta^4\text{-}C_8H_{12})]$ *with Hydrochloric*

Acid.—In a typical experiment, a freshly prepared acetone solution of 36% aqueous HCl (0.2 cm^3) was syringed dropwise onto an acetone solution of $[Ru\{\eta^6\text{-}C_2H_5CH(Me)C_6H_5\}\text{-}(\eta^4\text{-}C_8H_{12})]$, (2j) (150 mg, 0.40 mmol). The resulting dark red solution was stirred at room temperature for 30 min and the red-brown crystals of $[\{RuCl_2[\eta^6\text{-}C_2H_5CH(Me)C_6H_5]\}_2]$, (3d), which precipitated were collected and washed with acetone and n-pentane (125 mg, 0.40 mmol).

REFERENCES

[1] G. Deganello, ' Transition Metal Complexes of Cyclic Polyolefins,' Academic Press, London, 1978.
[2] R. G. Gastinger and K. J. Klabunde, *Transition Met. Chem.,* 1979, **4**, 1.
[3] P. M. Maitlis, *Chem. Soc. Rev.,* 1981, **10**, 1.
[4] E. O. Fischer and J. Muller, *J. Organomet. Chem.,* 1966, **5**, 275; J. Muller, C. G. Kreiter, B. Mertschenk, and S. Schmitt, *Chem. Ber.,* 1975, **108**, 273.
[5] T. V. Ashowork, M. G. Nolte, R. H. Reimann, and E. Singleton, *J. Chem. Soc., Chem. Commun.,* 1977, 937.
[6] M. A. Bennett and T. Matheson, *J. Organomet. Chem.,* 1978, **153**, C25.
[7] G. Winkaus and H. Singer, *J. Organomet. Chem.,* 1967, **7**, 487; R. A. Zelonka and M. C. Baird, *Can. J. Chem.,* 1972, **50**, 3063; M. A. Bennett and A. K. Smith, *J. Chem. Soc., Dalton Trans.,* 1974, 233.
[8] P. Pertici, G. P. Simonelli, G. Vitulli, G. Deganello, P. L. Sandrini, and A. Mantovani, *J. Chem. Soc., Chem. Commun.,* 1977, 123.
[9] P. Pertici, G. Vitulli, W. Porzio, and M. Zocchi, *Inorg. Chim. Acta Lett.,* 1979, **37**, L521.
[10] P. Pertici, G. Vitulli, M. Paci, and L. Porri, *J. Chem. Soc., Dalton Trans.,* 1980, 1961.
[11] V. Graves and J. J. Lagowski, *J. Organomet. Chem.,* 1976, **120**, 397.
[12] M. Airoldi, G. Deganello, G. Dia, and G. Gennaro, *J. Organomet. Chem.,* 1980, **187**, 391.
[13] I. Ogata, R. Iwata, and Y. Ikeda, *Tetrahedron Lett.,* 1970, 3011; R. Iwata and I. Ogata, *Tetrahedron,* 1973, **29**, 2753; A. G. Hinze, *Recl. Trav. Chim. Pays-Bas,* 1973, **92**, 542.
[14] P. Pertici, G. Vitulli, R. Lazzaroni, and P. Salvadori, XIVth National Congress of the Italian Chemical Society, Catania, Italy, 21—25 September, 1981, p. 413.
[15] Huang-Minlon, *J. Am. Chem. Soc.,* 1946, **68**, 2487; D. J. Cram and H. Steinberg, *ibid.,* 1951, **73**, 5691.