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A Simple Preparation for  $(\eta^6$ -Arene) $(\eta^4$ -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  $(\eta^{6}\text{-arene})(\eta^{4}\text{-cyclo-octa-1,5-diene})$  ruthenium(0) complexes have been readily prepared by reaction of  $(\eta^{4}\text{-cyclo-octa-1,5-diene})(\eta^{6}\text{-cyclo-octa-1,3,5-triene})$  ruthenium(0) with arene compounds, under 1 atm H<sub>2</sub> [arene = C<sub>6</sub>H<sub>6</sub>, CH<sub>3</sub>C<sub>6</sub>H<sub>5</sub>, 1,4-Me<sub>2</sub>C<sub>6</sub>H<sub>4</sub>, 1,3,5-Me<sub>3</sub>C<sub>6</sub>H<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>C<sub>6</sub>H<sub>5</sub>, Me<sub>2</sub>CHC<sub>6</sub>H<sub>5</sub>, Et<sub>2</sub>CHC<sub>6</sub>H<sub>5</sub>, C<sub>6</sub>H<sub>5</sub>(CH<sub>2</sub>)<sub>3</sub>-C<sub>6</sub>H<sub>5</sub>, C<sub>6</sub>H<sub>5</sub>C<sub>6</sub>H<sub>5</sub>, C<sub>2</sub>H<sub>5</sub>CH(Me)C<sub>6</sub>H<sub>5</sub>, Me<sub>2</sub>CHCH(Me)C<sub>6</sub>H<sub>5</sub>, NH<sub>2</sub>CH(Me)C<sub>6</sub>H<sub>5</sub>, CH<sub>3</sub>OC<sub>6</sub>H<sub>5</sub>, or CH<sub>3</sub>COC<sub>6</sub>H<sub>5</sub>]. These complexes react with aqueous HCI to give in almost quantitative yield the corresponding ( $\eta^{6}\text{-arene}$ )-dichlororuthenium(II) complexes.

ZEROVALENT arene-olefin complexes of ruthenium, analogues of the well known carbonyl-olefin complexes,<sup>1</sup> are receiving increasing attention as potential catalysts and as models for oxidative-addition reactions.<sup>2</sup> Despite this interest, only a few synthetic methods have been reported.<sup>3</sup> The first example of these compounds,  $[\operatorname{Ru}(\eta^{6}-\operatorname{C}_{6}H_{6})(\eta^{4}-\operatorname{C}_{8}H_{12})]$  (C<sub>8</sub>H<sub>12</sub> = cyclo-octa-1,5-diene), was prepared by reaction of  $[{RuCl_2(\eta^6-C_6H_6)}_2]$  and  $C_8H_{12}$ , in the presence of a Grignard reagent.<sup>4</sup> More recently, it has been obtained in good yields by heating a benzene solution of [RuH(C<sub>8</sub>H<sub>12</sub>)(NH<sub>2</sub>NMe<sub>2</sub>)<sub>3</sub>][BPh<sub>4</sub>].<sup>5</sup> Reaction of  $C_8H_{12}$  with  $[{RuCl_2(\eta^6-arene)}_2]$  (arene =  $C_6H_6$ , 1,3,5-Me<sub>3</sub> $C_6H_3$ , or  $C_6Me_6$ ) in the presence of reducing agents gives the corresponding  $[Ru(\eta^{6}-arene)(\eta^{4}-C_{8}H_{12})]$ complex,<sup>6</sup> but this method is limited by the availability of the starting ruthenium complex.7

We report here the reaction of  $[\operatorname{Ru}(\eta^6-C_8H_{10})(\eta^4-C_8H_{12})]$  (1)  $(C_8H_{10} = \operatorname{cyclo-octa-1,3,5-triene})$  with arenes under atmospheric pressure of H<sub>2</sub> to form a large number of  $[\operatorname{Ru}(\eta^6-\operatorname{arene})(\eta^4-C_8H_{12})]$  complexes, (2). Reaction of (2) with aqueous HCl gives, in almost quantitative yields, the corresponding  $[{\operatorname{RuCl}_2(\eta^6-\operatorname{arene})}_2]$  complexes, many of which cannot be prepared in other ways.<sup>7</sup> Some aspects of this work have appeared in a preliminary communication.<sup>8</sup>

## **RESULTS AND DISCUSSION**

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

Complex (1) reacts readily with arenes, under 1 atm  $\dagger$  of hydrogen and at room temperature, to give a wide range of  $[\operatorname{Ru}(\eta^{6}\operatorname{-arene})(\eta^{4}\operatorname{-C}_{8}\operatorname{H}_{12})]$  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<sub>2</sub>.

Evaporation of the solvent and recrystallization from npentane 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



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  $C_6H_5(CH_2)_3$ - $C_6H_5$ , <sup>1</sup>H n.m.r. spectroscopy has shown that only one ring is co-ordinated to the ruthenium atom.

In agreement with data for other arene-transitionmetal complexes,<sup>2,11</sup> a large upfield shift of the aromatic proton resonances (ca. 2.5 p.p.m.) has been observed in the <sup>1</sup>H 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,  $\Delta \delta = \delta$  (free ligand) –  $\delta$ (complex)], in (2j) are 2.52,3.16 p.p.m. for the ortho-protons H<sup>1</sup>,H<sup>5</sup>, 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  $\Delta\delta$  values of the protons H<sup>1</sup>,-H<sup>4</sup>, and H<sup>2</sup>, H<sup>5</sup> ( $\Delta\delta$ H<sup>1</sup> =  $\Delta\delta$ H<sup>4</sup>;  $\Delta\delta$ H<sup>2</sup> =  $\Delta\delta$ H<sup>5</sup>). As far as complex (21) is concerned, the  $\Delta\delta$  values are 1.94,3.31 p.p.m. for the H<sup>1</sup>,H<sup>5</sup> protons and 3.26,2.47 for the H<sup>2</sup>,-H<sup>4</sup> protons. The low value of  $\Delta \delta H^1$  indicates the proximity of H<sup>1</sup> to the NH<sub>2</sub> group.

<sup>†</sup> Throughout this paper: 1 atm = 101 325 Pa; 1 mmHg  $\approx$  13.6  $\times$  9.8 Pa.

TABLE 1	
Analytical and spectroscopic data for $[Ru(\eta^{6}-arene)(\eta^{4}-C_{8}H_{12})]$ com	plexes

			Analysis <sup>ø</sup> (%)		<sup>1</sup> H N.m.r. data •		
		Vield			Aromatic	ligand	
	Compound <sup>a</sup>	(%)	C	Н	Arene protons <sup>d</sup>	Others	C <sub>8</sub> H <sub>12</sub> <sup>a</sup>
(2a)	$[\mathrm{Ru}(\mathrm{C_6H_6})(\mathrm{C_8H_{12}})]$	95	58.5 (58.3)	6.60 (6.20)	4.95 (s, 6 H)		3.6 (m, 4 H, CH), 24 (m 8 H CH)
(2b)	$[\mathrm{Ru}(\mathrm{CH}_{3}\mathrm{C}_{6}\mathrm{H}_{5})(\mathrm{C}_{8}\mathrm{H}_{12})]$	95	59.8	6.70	4.9 (m, 5 H)	1.8 (s, 3 H, CH <sub>3</sub> )	3.5 (m, 4 H),
(2c)	$[\mathrm{Ru}(1,4\text{-}\mathrm{Me_2C_6H_4})(\mathrm{C_8H_{12}})]$	95	(59.6) 61.1 (62.2)	(6.60) 6.95 (6.95)	4.8 (s, 4 H)	1.8 (s, 6 H, CH <sub>3</sub> )	2.4 (m, 8 H) 3.4 (m, 4 H), 2.4 (m, 8 H)
(2d)	$[\mathrm{Ru}(1,3,5\mathrm{-Me}_{3}\mathrm{C}_{6}\mathrm{H}_{3})(\mathrm{C}_{8}\mathrm{H}_{12})]$	95	61.0	7.50	4.85 (s, 3 H)	1.75 (s, 9 H, CH <sub>3</sub> )	3.1 (m, 4 H),
(2e)	$[{\rm Ru}({\rm C_2H_5C_6H_5})({\rm C_8H_{12}})]$	75	(62.0) 61.3 (60.95)	(7.30) 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),	2.3 (m, 8 H) 3.5 (m, 4 H), 2.4 (m, 8 H)
(2f)	$[\mathrm{Ru}(\mathrm{Me_2CHC_6H_5})(\mathrm{C_8H_{12}})]$	70	62.15 (62.0)	7.40 (7.30)	5.35 (m, 1 H, $H_p$ ), 4.6 (m, 4 H, $H_o + H_m$ )	1.1 (t, 3 H, $CH_3$ ) 2.4 (1 H, $CH$ ), $e$ 1.2 (d, 6 H, $CH_3$ ,	3.5 (m, 4 H), 2.4 (m, 8 H)
(2g)	$[\mathrm{Ru}(\mathrm{Et_2CHC}_6\mathrm{H}_{\delta})(\mathrm{C}_8\mathrm{H}_{12})]$	65	63.4 (63.8)	7.65 (7.85)	5.35 (m, 1 H, H <sub>p</sub> ), 4.55 (m, 4 H, H <sub>o</sub> + H <sub>m</sub> )	f = 7) 2.3 (1 H, CH), <sup>e</sup> 1.48 (m, 4 H, CH <sub>2</sub> ), 0.88 (t, 6 H, CH <sub>3</sub> ,	3.35 (m, 4 H), 2.31 (m, 8 H)
(2h)	$[Ru\{C_{6}H_{5}(CH_{2})_{3}C_{6}H_{5}\}(C_{8}H_{12})]$	70	67.9 (68.1)	6.80 (6.90)	7.25 (m, 5 H, $C_6H_5$ ), <sup>f</sup> 5.4 (m, 1 H, $H_p$ ), 5.1 (m, 4 H, $H_o + H_m$ )	J = 7) 2.7 (t, 2 H, $C_{6}H_{5}-CH_{2}, J = 7$ ), <sup>g</sup> 2.25 (m, 2 H, $C_{6}H_{5}-CH_{2}$ ), <sup>h</sup> 2.0 (2 H, CH <sub>2</sub> )	3.3 (m, 4 H), 2.1 (m, 8 H)
(2i)	$[\mathrm{Ru}(\mathrm{C_6H_5C_6H_5})(\mathrm{C_8H_{12}})]$	60	$\begin{array}{c} 65.8 \\ \mathbf{(66.1)} \end{array}$	5.90 (6.05)	7.6—7.1 (m, 5 H, $C_{6}H_{5}$ ), $f$ 5.4—4.7 (m, 5 H, C H)	2.0 (2 11, 0112)	3.5 (m, 4 H), 2.3 (m, 8 H)
(2j)	$[\mathbf{Ru}\{\mathbf{C_2H_5CH(Me)C_6H_5}\}(\mathbf{C_8H_{12}})]$	35	62.5 (62.95)	7.40 (7.60)	$\begin{array}{c} C_{6} H_{5} \\ 5.18 \ (t, 1 \ H, \ H_{p}, \\ J_{mp} = J_{m'p} = 6), \\ 4.69 \ (t, 1 \ H, \ H_{m'}, \\ J_{o'm'} = 6), \\ 4.68 \ (d, 1 \ H, \ H_{o}, \\ J_{om} = 6), \\ 4.09 \ (t, 1 \ H, \ H_{m'}), \\ 4.04 \ (t, 1 \ H, \ H_{m'}), \end{array}$	2.3 (1 H, CH), $e$ 1.45 (m, 2 H, CH <sub>2</sub> ), 1.25 (d, 3 H, CH-CH <sub>3</sub> , J = 7), 0.86 (t, 3 H, CH <sub>2</sub> -CH <sub>3</sub> , J = 7)	3.5 (m, 4 H), 2.36 (m, 8 H)
(2k)	[Ru{Me <sub>2</sub> CHCH(Me)C <sub>6</sub> H <sub>5</sub> }(C <sub>8</sub> H <sub>12</sub> )]	35	63.7 (63.85)	7.30 (7.85)	4.04 (d, 1 H, $H_{p}$ , 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,	2.5—1.5 (br m, 2 H, CH– $CH$ ), 1.3 (d, 3 H, $CH$ – $CH_3$ , $J = 7$ ), 0.8 [d, 6 H, $CH$ – $(CH_3)_2$ , $J = 7$ ]	3.5 (m, 4 H), 2.4 (m, 8 H)
(21)	[Ru{NH <sub>2</sub> CH(Me)C <sub>6</sub> H <sub>5</sub> }(C <sub>8</sub> H <sub>12</sub> )] <sup>j</sup>	60	58.55 (58.15)	6.55 (6.95)	$\begin{array}{l} H_m + H_{n'} \\ 5.26 & (d, 1 H, H_o, \\ J_{om} = 6), {}^t \\ 5.08 & (t, 1 H, H_p, \\ J_{mp} = J_{m'p} = 6), \\ 4.73 & (t, 1 H, H_{m'}, \\ J_{m'o'} = 6), \\ 3.93 & (t, 1 H, H_m), \end{array}$	3.5 (1 H, CH) $e$ 1.2 (d, 3 H, CH <sub>3</sub> , J = 7), 1.2 (2 H, NH <sub>2</sub> ) $*$	3.5 (m, 4 H), 2.3 (m, 8 H)
(2m)	$[\operatorname{Ru}(\operatorname{CH}_3\operatorname{OC}_6\operatorname{H}_5)(\operatorname{C}_8\operatorname{H}_{12})]$	75	56.05	6.00	3.89 (d, 1 H, H <sub>o</sub> ) 4.8 (m, 5 H)	3.4 (s, 3 H, CH <sub>a</sub> )	3.5 (m, 4 H),
(9-1)		75	(65.75)	(6.30) 5 00	5 95 (J 9 H H	98 (e 9H CH)	2.4 (m, 8 H) 3.5 (m, 4 H)
(211)	[Ru(CI13COC6n5/(C6n12/]	79	(58.35)	(6.10)	$J_{om} = 6),  5.3 (t, 1 H, H_p,  J_{mp} = 6),l  4.6 (t, 2 H, H_m)$	2.0 (3, 0 11, 0113)	2.2 (m, 8 H)

<sup>a</sup> C<sub>8</sub>H<sub>12</sub> = Cyclo-octa-1,5-diene. <sup>b</sup> Calculated values are given in parentheses. <sup>c</sup> Unless otherwise noted, spectra were measured at 60 MHz in [<sup>2</sup>H<sub>6</sub>]benzene solution, using SiMe<sub>4</sub> as internal standard;  $\delta$  scale; coupling constants, J, are in Hz; s =singlet, d =doublet, t =triplet, q =quartet, m =multiplet, br =broad. <sup>d</sup> o =ortho, m =meta, p =para. <sup>e</sup> Observed by double resonance. <sup>f</sup> Aromatic ring not co-ordinated to ruthenium. <sup>e</sup> CH<sub>2</sub> group bonded to free aromatic ring. <sup>b</sup> CH<sub>2</sub> group bonded to aromatic ring co-ordinated to ruthenium. <sup>e</sup> MHz; for details see the Figure;  $H^1 = H_o$ ,  $H^2 = H_m$ ,  $H^3 = H_p$ ,  $H^4 = H_m$ ,  $H^5 = H_o$ . <sup>f</sup> Analysis (%): N = 4.00 (4.25). <sup>k</sup> Observed by integration. <sup>f</sup> Partially obscured by H<sub>o</sub> 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. Since 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



Proton n.m.r. spectra (aromatic protons) of complexes (2j) (a) and (2l) (b) at 270 MHz. Values (p. p. m.) from internal SiMe<sub>4</sub> are: (a) H<sup>1</sup> 4.68, H<sup>2</sup> 4.09, H<sup>3</sup> 5.18, H<sup>4</sup> 4.69, H<sup>5</sup> 4.04, J(H-H) =5.6 ± 0.2 Hz; (b) H<sup>1</sup> 5.26, H<sup>2</sup> 3.93, H<sup>3</sup> 5.08, H<sup>4</sup> 4.73, H<sup>5</sup> 3.89,  $J(H-H) = 5.6 \pm 0.2$  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-1,3,5triene ligand bonded to ruthenium in the starting complex (1), perhaps via enyl-Ru hydride species,<sup>12</sup> probably takes place, giving a co-ordinatively unsaturated ruthenium complex which undergoes ligand exchange in the presence of arene compounds (Scheme 2). <sup>1</sup>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.





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 areneruthenium compounds as hydrogenation catalysts.<sup>2</sup> Complexes (3) are reported to be active in the catalytic hydrogenation of olefins <sup>13</sup> and preliminary experiments show that complexes (2) can also be used in catalytic double-bond hydrogenation under mild conditions (25 °C, H<sub>2</sub> pressure = 25 atm).<sup>14</sup> 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.

$$(\eta^6 - \text{arene}) \text{Ru}$$
 + 2HCl  $\xrightarrow{(i)} \frac{1}{2} [\{\text{RuCl}_2(\eta^6 - \text{arene})\}_2] +$ 

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  $[{RuCl_2(\eta^6-arene)}_2]$  compounds, (3), as crystalline precipitates (Scheme 3). No  $[{RuCl_2(\eta^4-C_8H_{12})}_n]$  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

## 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.<sup>15</sup> The complex [Ru( $\eta^{6}$ -C<sub>8</sub>H<sub>10</sub>)( $\eta^{4}$ -C<sub>8</sub>H<sub>12</sub>)] was prepared as recently reported.<sup>10</sup> Hydrogen-1 n.m.r. spectra were recorded on a Varian T-60 spectrometer and a Bruker

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

TABLE 2 Analytical and <sup>1</sup>H n.m.r. data for  $[{RuCl_2(\eta^6-arene)}_2]$  complexes

<sup>a</sup> Calculated values are given in parentheses. <sup>b</sup> Measured at 60 MHz in  $[{}^{2}H_{6}]$  dimethyl sulphoxide solution, using SiMe<sub>4</sub> as internal standard;  $\delta$  scale; coupling constants, J, are in Hz. <sup>c</sup> o = ortho, m = meta, p = para.

270-MHz spectrometer, for complexes (2) and (2). 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.— $[Ru(\eta^{6}-arene)(\eta^{4}-C_{8}H_{12})]$  (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.

 $[Ru(\eta^{6}-C_{6}H_{5}C_{6}H_{5})(\eta^{4}-C_{8}H_{12})]$  (2i). Biphenyl,  $C_{6}H_{5}C_{6}H_{5}$ (500 mg, 3.24 mmol), was added to a solution of [Ru( $\eta^{6}$ - $C_8H_{10}/(\eta^4-C_8H_{12})]$ , (1) (100 mg, 0.32 mmol), in n-pentane (10 cm<sup>3</sup>) 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<sup>3</sup>) was added to the solid residue and the yellow solution obtained was chromatographed on alumina (activity II-III) using pentane-benzene (l: lv/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).

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

Reaction of  $[Ru(\eta^{6}-arene)(\eta^{4}-C_{8}H_{12})]$  with Hydrochloric

Acid.-In a typical experiment, a freshly prepared acetone solution of 36% aqueous HCl (0.2 cm<sup>3</sup>) was syringed dropwise onto an acetone solution of  $[Ru\{\eta^{6}-C_{2}H_{5}CH(Me)C_{6}H_{5}\}$ - $(\eta^4-C_8H_{12})$ ], (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  $[\{RuCl_2[\eta^6-C_2H_5CH(Me)C_6H_5]\}_2]$ , (3d), which precipitated were collected and washed with acetone and n-pentane (125 mg, 0.40 mmol).

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