Arene Ligand Exchange Reactions in (η^4-Cyclo-octa-1,5-diene)(η^6-naphthalene)ruthenium(o): A Convenient Route to New Ruthenium(o) Complexes

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The reaction of (η^4-cyclo-octa-1-5-diene)(η^6-cyclo-octa-1,3,5-triene)ruthenium with naphthalene, under H_2, affords the complex (η^4-cyclo-octa-1,5-diene)(η^6-naphthalene)ruthenium which easily undergoes arene exchange reactions in the presence of MeCN.

The exchange of arene ligands between free and bound states is of relevance in the aromatic hydrocarbon chemistry of transition metals.[1] Exchange phenomena have been studied extensively in many arene complexes: *e.g.* (η^6-arene)tricarbonylmetal (Cr, Mo, and W), (η^6-arene)dichloro(phosphine)ruthenium, and (η^6-arene)(diene)metal (Ru, Ir^I).[2,3] Only in a few cases, however, has the exchange reaction been employed as a convenient route for preparing new arene complexes. The complexes $[RuCl_2(PR_3)(arene)]$ (arene = benzene or *p*-cymene, R = Bu^n or Ph) undergo thermally and photochemically induced arene exchange, but the reaction conditions are so severe that extensive decomposition takes place simultaneously.[4] Arenes having electron-withdrawing substituents such as Cl, F, or CO_2Et fail to displace any arene ligands in such complexes. (η^6-Benzene)(η^4-cyclo-octa-1,5-diene)ruthenium gives no detectable arene exchange up to the temperature where the complex undergoes thermal decomposition, even in the presence of Lewis bases.[3] Complexes containing polycyclic aromatic hydrocarbons as ligands are expected to have a higher reactivity compared to the corresponding benzene compounds in view of the lower aromatic delocalization energy per ring.[5] We prepared (η^4-cyclo-octa-1,5-diene)(η^6-naphthalene)ruthenium according to a procedure previously described[6] and we report here some results on the arene ligand exchange reaction and reactivity in this complex.

Experimental

All manipulations were performed under a dry 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. Hydrogen-1 n.m.r. spectra were recorded on a Varian XL 100 spectrometer. Microanalyses were by the laboratorio di Microanalisi, Facoltà di Farmacia, Università di Pisa.

Preparation of $[Ru(\eta^6\text{-}C_{10}H_8)(\eta^4\text{-}C_8H_{12})]$ (1).—Naphthalene, $C_{10}H_8$ (175 mg, 1.36 mmol), was added to a solution of $[Ru(\eta^6\text{-}C_8H_{10})(\eta^4\text{-}C_8H_{12})]$ (215 mg, 0.68 mmol) (C_8H_{10} = cyclo-octa-1,3,5-triene), in n-pentane (10 cm^3) and the reaction mixture stirred at room temperature for *ca.* 6 h, under 1 atm (*ca.* 10^5 Pa) of H_2. The solvent was evaporated under reduced pressure and the excess naphthalene removed by sublimation at 40 °C and 0.01 mmHg (*ca.* 1.3 Pa). n-Pentane (30 cm^3) was added to the solid residue and the orange solution obtained was filtered and evaporated to dryness. Recrystallization of the crude product from n-pentane gives (1) as red-brown crystals (182 mg, 0.544 mmol, *ca.* 80%).

Exchange Reactions: Preparation of $[Ru(\eta^6\text{-arene})(\eta^4\text{-}C_8H_{12})]$ (2).—Only the preparation of $[Ru(\eta^6\text{-}C_6H_5Cl)(\eta^4\text{-}C_8H_{12})]$ (2f) is described in detail, the experimental procedure being substantially the same for all other complexes (2) (Scheme 1).

Complex (1) (0.1 g, 0.29 mmol) was dissolved in chlorobenzene (5 cm^3) containing acetonitrile (0.05 cm^3, 0.9 mmol) and the mixture stirred at room temperature for *ca.* 24 h. Evaporation of the excess chlorobenzene under vacuum, followed by addition of n-pentane (30 cm^3) resulted in a yellow solution which was filtered on alumina and evaporated to dryness. Recrystallization from n-pentane at −78 °C gave $[Ru(\eta^6\text{-}C_5H_6Cl)(\eta^4\text{-}C_8H_{12})]$ (2f) as pale yellow crystals (0.084 g, yield *ca.* 90%).

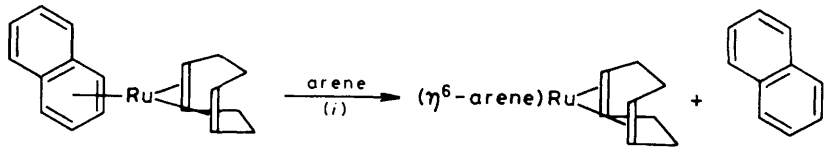
Results and Discussion

The reaction of naphthalene, under H_2, with $[Ru(\eta^6\text{-}C_8H_{10})(\eta^4\text{-}C_8H_{12})]$ (easily obtained by the reaction of $RuCl_3{\cdot}xH_2O$ and C_8H_{12} in the presence of Zn[7]) affords complex (1), as red-brown crystals, in yields of *ca.* 80% (Scheme 2).

Complex (1) is air sensitive and soluble in common organic solvents; it has been characterized by elemental analysis and spectroscopic measurements (Table). In agreement with literature reports, upfield shifts of the aromatic proton resonances and sharp, discrete signals for the free and coordinated ring sections of the naphthalene ligand have been observed in the ^1H n.m.r. spectrum of (1). Complex (1) easily undergoes exchange reactions with arenes in the presence of MeCN. The naphthalene is completely removed by the new arene ligand and the corresponding $[Ru(\eta^6\text{-arene})(\eta^4\text{-}C_8H_{12})]$ complexes (2) are formed in almost quantitative yields (Scheme 1). This reaction enables the types of arenes that can be complexed to ruthenium to be greatly extended.

Complexes (2) are pale yellow crystalline compounds which have been characterized by elemental analysis and spectroscopic measurements (Table), as well as by comparison with authentic samples for (2a)—(2e).[6] The upfield shift of the aromatic proton resonances observed in the ^1H n.m.r. spectra of the complexes is very large (*ca.* 2.5 p.p.m.). However, no correlation of the magnitude of the upfield shift and the stability of the arene complex is discernible. The complexes of benzene, methyl-substituted benzenes, and anisole, (2a)—(2e), react considerably faster than those of arenes containing electron-withdrawing groups, (2f) and (2g), suggesting that electronic factors may strongly operate in this exchange process.

Exchange reactions can be greatly catalysed by simple Lewis bases. Acetonitrile has proved to be a very good



(1) (2)

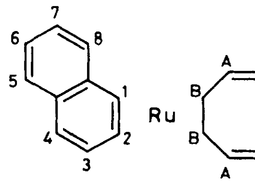
Scheme 1. (*i*) MeCN, room temperature, 4—22 h; molar ratio MeCN : (1), 3 : 1. Arene = C_6H_6 (2a), C_6H_5Me (2b), $C_6H_4Me_2$-1,4 (2c), $C_6H_3Me_3$-1,3,5 (2d), C_6H_5OMe (2e), C_6H_5Cl (2f), C_6H_5CHO (2g)

$$2RuCl_3 + 6C_8H_{12} + 3Zn \xrightarrow{EtOH} 2[Ru(\eta^6\text{-}C_8H_{10})(\eta^4\text{-}C_8H_{12})] + 2C_8H_{14} + 3ZnCl_2$$

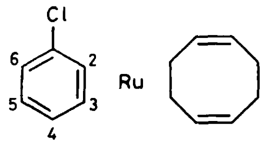
$$[Ru(\eta^6\text{-}C_8H_{10})(\eta^4\text{-}C_8H_{12})] + C_{10}H_8 \xrightarrow{2H_2} \underset{(1)}{[Ru(\eta^6\text{-}C_{10}H_8)(\eta^4\text{-}C_8H_{12})]} + C_8H_{14}$$

Scheme 2.

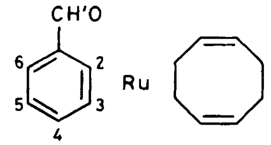
Table. Analytical and spectroscopic data for $[Ru(\eta^6\text{-arene})(\eta^4\text{-}C_8H_{12})]$ complexes



(1)



(2f)



(2g)

	Analysis ^{a} (%)		^1H N.m.r. data ^{b} (δ) Aromatic ligand		
Complex	C	H	Arene protons	Others	C_8H_{12} ligand
(1)	63.85 (64.1)	5.70 (5.95)	5.4 (m, 2 H, $H^{1,4}$) 4.1 (m, 2 H, $H^{2,3}$)	6.95 (m, 4 H, $H^{5,8}$ + $H^{6,7}$)	3.4 (m, 4 H, H^A) 1.8 (m, 8 H, H^B)
(2f)	52.2 (52.35)	5.35 (5.30)	5.0 [d, 2 H, $H^{2,6}$, $J(H^{2,6}H^{3,5}) = 6$] 4.6 [t, 2 H, $H^{3,5}$, $J(H^{3,5}H^4) = J(H^{3,5}H^{2,6}) = 6$] 4.0 (t, 1 H, H^4)		3.2 (m, 4 H, H^A) 2.0 (m, 8 H, H^B)
(2g)	57.3 (57.15)	5.65 (5.70)	4.9 (m, 3 H, $H^{2,6}$ + H^4) 4.3 [t, 2 H, $H^{3,5}$, $J(H^{3,5}H^4) = J(H^{3,5}H^{2,6}) = 6$]	9.4 (s, 1 H, H′)	3.3 (m, 4 H, H^A) 2.0 (m, 8 H, H^B)

^{a} Calculated values are given in parentheses. ^{b} Spectra were measured at 100 MHz in C_6D_6 using $SiMe_4$ as internal standard; *J* values are in Hz.

catalyst in this case, while diethyl ether or acetone do not work, probably because of a weaker interaction with the Ru^0 centre. As in the isoelectronic $[Ir(\eta^6\text{-arene})(\eta^4\text{-}C_8H_{12})]^+$ systems,[8] it seems reasonable to suppose that in the exchange reaction, displacement of naphthalene by a Lewis base and subsequent reaction on an incoming arene with a co-ordinatively unsaturated Lewis base complex, to generate the new arene complex, are operative. Complex (1) can be strongly distinguished from all reported ruthenium arene compounds by this high lability of the co-ordinated aromatic ring. It is suggested that the easy displacement of an η^6-co-ordinated naphthalene probably derives from its great ability to adopt $\eta^4 : \eta^2$ bonding modes, thus allowing co-ordination of incoming ligands at the metal centre.[5,9] Extended-Hückel calculations on $[Cr(CO)_3(\eta^6\text{-}C_{10}H_8)]$, which undergoes arene exchange reactions more readily than $[Cr(CO)_3(\eta^6\text{-}C_6H_6)]$, have shown that it requires *ca.* 100 kJ mol^{-1} for the former to attain an η^2 geometry while the corresponding value for the latter is *ca.* 146 kJ mol^{-1}.[10]

Displacement of the arene ring by donor molecules also takes place easily in complex (1): preliminary experiments have shown that (1) reacts under mild conditions with ligands L = CO or $P(OMe)_3$ to give $[Ru(\eta^4\text{-}C_8H_{12})L_3]$ derivatives in good yields.

The exchange and displacement reactions in complex (1), which can be easily obtained according to Scheme 2, thus appear to provide a very convenient route to a wide range of new Ru^0 compounds.

References

1 See, for example, M. F. Farona, in 'Organometallic Reactions and Synthesis,' eds. E. Becker and M. Tsusui, Plenum Press, New York, 1977, vol. 6, p. 223.

2 W. Strohmeier and R. Müller, *Z. Phys. Chem.* (*Frankfurt*), 1964, **40**, 85.

3 E. L. Muetterties, J. R. Bleeke, and A. C. Sievert, *J. Organomet. Chem.*, 1979, **178**, 197.

4 M. A. Bennett and A. K. Smith, *J. Chem. Soc., Dalton Trans.*, 1974, 233.

5 E. P. Kundig and P. L. Timms, *J. Chem. Soc., Chem. Commun.*, 1977, 912; *J. Chem. Soc., Dalton Trans.*, 1980, 991.

6 P. Pertici, G. Vitulli, R. Lazzaroni, P. Salvadori, and P. L. Barili, *J. Chem. Soc., Dalton Trans.*, 1982, 1019.

7 P. Pertici, G. Vitulli, M. Paci, and L. Porri, *J. Chem. Soc., Dalton Trans.*, 1980, 1961.

8 A. C. Sievert and E. L. Muetterties, *Inorg. Chem.*, 1981, **20**, 489.

9 M. P. Garcia, M. Green, F. G. A. Stone, R. Somerville, and A. J. Welch, *J. Chem. Soc., Chem. Commun.*, 1981, 871.

10 E. L. Muetterties, J. R. Bleeke, E. J. Wucherer, and T. A. Albright, *Chem. Rev.*, 1982, 499.

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