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Recent advances in the chemistry of arene complexes of ruthenium(0) and ruthenium(II)

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Contents

Abstract

Aspects of the chemistry of arene complexes of ruthenium and osmium in zero and +2 oxidation states are reviewed, with emphasis on the formation of isomeric *endo*- and *exo*-*o*-xylylene complexes of ruthenium(0) and osmium(0) from 1,2-dimethylarene complexes of the divalent metals, and on the stoichiometric and catalytic chemistry of a labile naphthalene complex of ruthenium(0). © 1997 Elsevier Science S.A.

1. Introduction

The organometallic chemistry of mononuclear ruthenium and osmium is dominated by compounds in which the metal atoms have the oxidation states M(0)(d^8), M(II)(d^6) and M(IV)(d^4) [1,2]. There is an enormous range of half-sandwich, 18-electron compounds of Ru(II), and to a lesser extent Os(II), containing cyclopentadienyl and substituted cyclopentadienyl (commonly C_5Me_5) ligands; when halide, hydride, alkyl or η^3-allyl ligands are also present, complexes containing the tetravalent metal can either be prepared or generated as likely intermediates in catalytic cycles [3]. In contrast, the somewhat less extensive chemistry of the arene complexes derives much of its interest from the existence and interconversions of stable 18-electron compounds of both M(0) and M(II).

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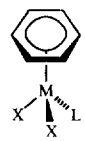
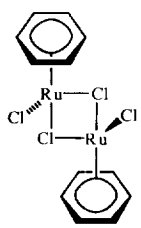
This review focuses on aspects of our past and current research in Canberra on this topic. Although detailed recent reviews are available [4,5], it is appropriate first to provide a brief background. *Hexahapto*-arene complexes of ruthenium(II) of the type $[Ru(\eta^6\text{-arene})_2]^{2+}$ were first made in 1957 by the classic Fischer–Hafner reducing Friedel–Crafts procedure from anhydrous $RuCl_3$ [6–8], but these are not convenient precursors to the half-sandwich arene complexes. Winkhaus et al. [9] made the important discovery that 1,3-cyclohexadiene undergoes dehydrogenation on reaction with aqueous ethanolic $RuCl_3$ to give the insoluble benzene complex $[RuCl_2(C_6H_6)]_n$ and with $OsCl_3$ in the presence of I_2 to give $[OsI_2(C_6H_6)]_n$ [10]. They also demonstrated the formation of 1:1 adducts of these compounds with tri-*n*-butylphosphine, and subsequently Zelonka and Baird [11,12] and we [13,14] showed independently that these should be formulated as monomeric, half-sandwich complexes containing *hexahapto*-benzene (**1**). Other 1,3-cyclohexadienes, such as α-phellandrene and 1,4-cyclohexadienes (available from the Birch reduction of arenes) react similarly with $RuCl_3$ to give the corresponding $[RuCl_2(\eta^6\text{-arene})]_2$ derivatives (**2**) [14]. The *p*-cymene complex, $[RuCl_2(\eta^6\text{-1,4-MeC}_6H_4CHMe_2)]_2$, is more soluble in organic solvents than the benzene compound and is a useful precursor to other members of the series containing methyl-substituted arenes, such as $[RuCl_2(\eta^6\text{-}C_6Me_6)]_2$ [15]. In these compounds, the arene is more resistant to displacement than is the case for the benzene complex.



M = Ru, Os; X = Cl, Br, I

1

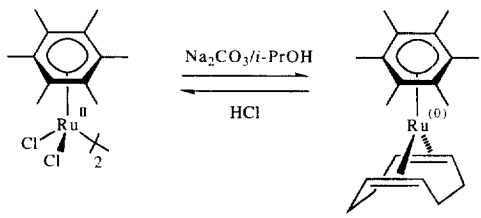


2

The arene metal dihalides are key starting materials for the formation of a wide range of conventional neutral and cationic ligand derivatives as well as hydride, alkyl, allyl, carbene and vinylidene complexes [1,4,5]. They are also useful precursors to homogeneous catalysts for the asymmetric hydrogenation of a range of unsaturated organic compounds [16–20] and for ring-opening metathesis polymerization [21].

Arene–ruthenium(0) and –osmium(0) complexes are also readily accessible

from the corresponding divalent metal precursors. It was shown early that $[Ru(\eta^6\text{-}C_6H_6)_2]^{2+}$ is reduced by $NaBH_4$ in THF to the 1,3-cyclohexadiene–ruthenium(0) complex $Ru(\eta^6\text{-}C_6H_6)(\eta^4\text{-}1,3\text{-}C_6H_8)$ [22] and that $[Ru(\eta^6\text{-}C_6Me_6)_2]^{2+}$ is reduced by Na/NH_3 to the ruthenium(0) species $Ru(\eta^6\text{-}C_6Me_6)(\eta^4\text{-}C_6Me_6)$ in which the two arene functions exchange hapticity rapidly on the NMR time scale at room temperature [8,23]. The arene metal dihalides are also readily reduced to arene metal(0) complexes by heating with various 1,3-dienes, 1,5-cyclooctadiene and ethylene in the presence of anhydrous Na_2CO_3 in ethanol and 2-propanol (Eq. (1)) [24–27]. These reactions undoubtedly proceed via arene ruthenium(II) hydrido-intermediates similarly to the corresponding reductions of the η^5-pentamethylcyclopentadienyl dihalides of rhodium(III) and iridium(III) to diene complexes of rhodium(I) and iridium(I) studied by Maitlis et al. [28–31]. The reactions are reversible, and, for example, treatment of $Ru(\eta^6\text{-arene})(\eta^4\text{-}1,5\text{-}C_8H_{12})$ with HCl regenerates $[RuCl_2(\eta^6\text{-arene})]_2$ [32].

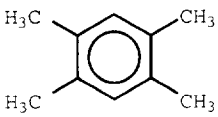
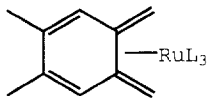
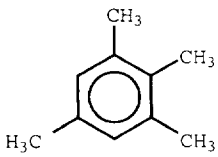
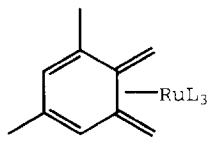
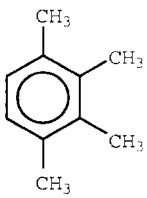
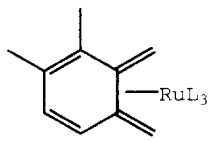
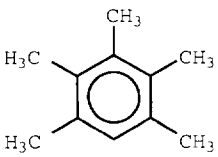
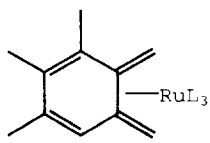
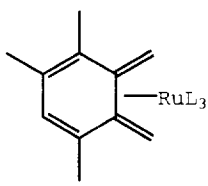
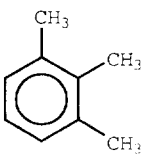
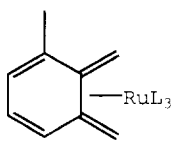
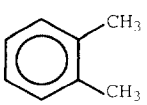
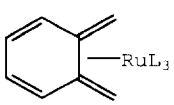


(1)

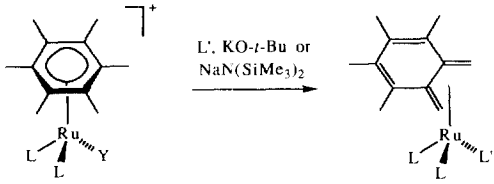
2. Formation and reactivity of *o*-xylylene complexes of ruthenium(0)

The enhanced acidity of benzylic protons in η^6-arenes coordinated to $Cr(CO)_3$ and $Fe(\eta^5\text{-}C_5H_5)$ units is well established [33]. We discovered the facile deprotonation of C_6Me_6 coordinated to ruthenium(II) accidentally, when we attempted to prepare the zerovalent metal complex $Ru\{P(OMe)_3\}_2(\eta^6\text{-}C_6Me_6)$ by potassium-amalgam reduction of $[Ru(ONO_2)\{P(OMe)_3\}_2(\eta^6\text{-}C_6Me_6)]NO_3$ and unexpectedly obtained small amounts of a solid of apparent formula $Ru\{P(OMe)_3\}_3(C_6Me_6)$. It soon became clear that the C_6Me_6 had undergone double deprotonation, probably induced by traces of KOH. We found that treatment of a series of nitrato or trifluoroacetato salts $[Ru(ONO_2)L_2(\eta^6\text{-}C_6Me_6)]NO_3$ or $[Ru(O_2CCF_3)L_2(\eta^6\text{-}C_6Me_6)]PF_6$ with a strong base such as KO-*t*-Bu or $(Me_3Si)_2NNa$ in the presence of an added tertiary phosphine or phosphite gives good yields of *exo*-tetramethyl-*o*-xylylene complexes of ruthenium(0) (Eq. (2)) [34,35]. Other η^6-1,2-dimethylarene complexes $[Ru(O_2CCF_3)L_2(\eta^6\text{-arene})]^+$ react similarly with base in the presence of L (PMe_2Ph, $PMePh_2$) to give the corresponding *exo*-η^4-*o*-xylylene complexes (Eq. (3) and Table 1), but the reaction fails for the corresponding osmium systems. Deprotonation of coordinated 1,2,3,4-tetramethylbenzene under these conditions occurs exclusively at the outer pair of methyl groups to give the 3,4-dimethyl-*o*-xylylene complex, whereas 1,2,3,4,5-pentamethylbenzene is deprotonated at both the inner and outer pairs of

Table 1
Formation of RuL_3(*o*-xylylene) complexes from cationic η^6-1,2-dimethylarene complexes of ruthenium(II)

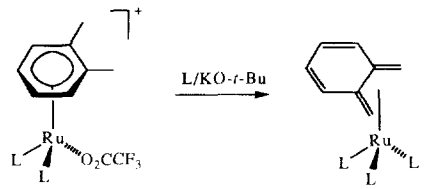
Arene	*o*-Xylylene complex	Tertiary phosphine
		PMe_2Ph, $PMePh_2$
		PMe_2Ph
		PMe_2Ph
		PMe_2Ph
		PMe_2Ph
		PMe_2Ph
		PMe_2Ph, $PMePh_2$

methyl groups to give a mixture of 3,4,5- and 3,4,6-*o*-xylylene complexes [36].



(2)

Y = ONO_2, O_2CCF_3
L_2 = $2PMe_2Ph$, $2PMePh_2$, $2P(OMe)_3$, $2P(OCH_2)_3CMe$, $Ph_2PCH_2CH_2PPh_2$, Z-$Ph_2PCH{=}CHPPh_2$
L' = PMe_2Ph, $PMePh_2$, $P(OMe)_3$, $P(OCH_2)_3CMe$



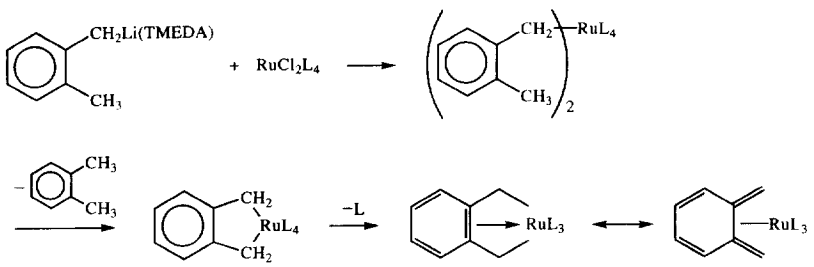
(3)

L = PMe_2Ph

An X-ray study of $Ru(PMe_2Ph)_3\{\eta^4\text{-}exo\text{-}(CH_2)_2C_6H_4\}$ has shown that the molecule is approximately square pyramidal, if the midpoints of the exocyclic double bonds are assumed to be the coordination centres, with one PMe_2Ph ligand occupying the axial site and the diene occupying two basal sites [37]. The geometry is very similar to that of the well-known $Fe(CO)_3(\eta^4\text{-}1,3\text{-diene})$ complexes, the *o*-xylylene unit being almost planar.

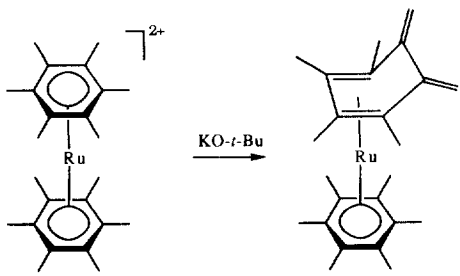
Similar compounds to those in Table 1 have been prepared independently by Cole-Hamilton and coworkers [37,38], who have treated $RuCl_2L_4$ ($L = PMe_3$, PMe_2Ph, $PMePh_2$, PEt_3) with the appropriate *o*-methylbenzyl-magnesium or, better, -lithium reagent; the reaction probably proceeds as shown in Scheme 1. The initially formed, undetected bis(*o*-methylbenzyl)ruthenium(II) complex is assumed to undergo a δ-elimination of *o*-xylene to give the chelate, σ-bonded xylene -1,2-diyl or κ^2-*o*-xylylene complex. In the final step, a ligand L is displaced by the formal 1,2-double bond of the aromatic ring. It is of interest that, under these conditions, 1,2,3,4-tetramethylbenzene gives a mixture of the 3,4- and 3,6-dimethyl-*o*-xylylene complexes, in contrast to the regiospecific formation of the former by deprotonation of the arene ruthenium(II) complex (Table 1).

The formation of *exo*-*o*-xylylene complexes by reactions of the type shown in Eq. (2) and Table 1 is intriguing because, as Gladfelter and coworkers have shown [39,40], base-promoted deprotonation of dicationic bis(η^6-1,2-dimethylarene) complexes of ruthenium(II) affords exclusively *endo*-*o*-xylylene complexes of ruthenium(0) (Eq. (4)). Similarly, we have found [41] that treatment of the dications $[ML_3(\eta^6\text{-}o\text{-}C_6H_4Me_2)]^{2+}$ ($M = Ru$, Os; $L = PMe_3$, PMe_2Ph) with KO-*t*-Bu gives only

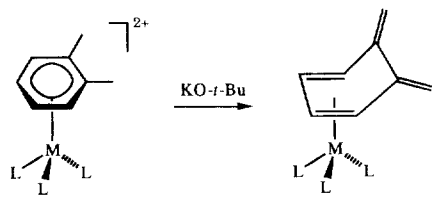


Scheme 1. Formation of $RuL_3\{\eta^4\text{-}exo\text{-}o\text{-}C_6H_4(CH_2)_2\}$ from $RuCl_2L_4$ ($L = PMe_3$, PMe_2Ph, $PMePh_2$, PEt_3).

endo-η^4-isomers of $ML_3\{o\text{-}C_6H_4(CH_2)_2\}$, no *exo*-isomers being detected (Eq. (5)).



(4)

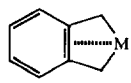


(5)

M = Ru, Os; L = PMe_3, PMe_2Ph

In the X-ray structures of the PMe_2Ph compounds, the geometry about the metal atom is similar to that in the *exo*-Ru isomer, but the xylylene unit is now markedly non-planar, being bent away from the metal centre at the terminal carbon atoms of the coordinated diene. The dihedral angles are 37.0°(Ru) and 39.5°(Os), cf. 33.8° in $Ru(\eta^6\text{-}C_6Me_6)\{\eta^4\text{-}endo\text{-}o\text{-}(CH_2)_2C_6Me_4\}$ [39]. This distortion arises from the usual disrotatory motion of substituents at the carbon termini of 1,3-diene complexes, which allows better overlap of the diene π-orbitals with the metal orbitals. According to density functional calculations on the model system $Ru(PH_3)_3$(*o*-xylylene), the *exo*-isomer is about 60 kJ mol^{-1} more stable than the *endo*-isomer [42]. This accords with qualitative expectation, because of the two limiting resonance forms **3** and **4**, only that from the *exo*-isomer (**3**) allows aromatic stabilization of the six-membered ring.

Despite the thermodynamic preference, *endo*- to *exo*-isomerization is not rapid



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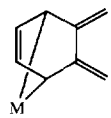
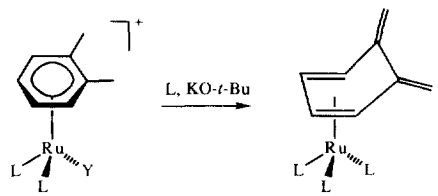


4

and, in the case of $Ru(PMe_2Ph)_3\{\eta^4$-*endo*-*o*-$C_6H_4(CH_2)_2\}$, requires heating of the molten compound. Since the *endo*-isomer clearly cannot be an intermediate in the formation of *exo*-$Ru(PMe_2Ph)_3\{\eta^4$-$(CH_2)_2C_6H_4\}$ in Eq. (3), we suggested [35] that rapid deprotonation of $[Ru(O_2CCF_3)(PMe_2Ph)_2(\eta^6$-*o*-$C_6H_4Me_2)]PF_6$ gives initially a coordinatively unsaturated *o*-xylylene species, $Ru(PMe_2Ph)_2\{\eta^4$-*endo*-$C_6H_4(CH_2)_2\}$. The electronic unsaturation can be relieved by additional coordination to one of the *exo*-double bonds, which could allow the metal fragment to migrate rapidly from the *endo*- to the *exo*-site; coordination of the added PMe_2Ph then completes the process (Scheme 2). In contrast with this behaviour, however, treatment of the bis(trimethylphosphine) complex $[Ru(O_2CCF_3)(PMe_3)_2(\eta^6$-*o*-$C_6H_4Me_2)]PF_6$ with KO-*t*-Bu in the presence of PMe_3 gives exclusively the *endo*-*o*-xylylene complex (Eq. (6)). The reason for this difference is not known; presumably the presumed intermediate $Ru(PMe_3)_2\{\eta^4$-*endo*-$C_6H_4(CH_2)_2\}$ is attacked rapidly by PMe_3 before the *endo*- to *exo*-migration occurs.

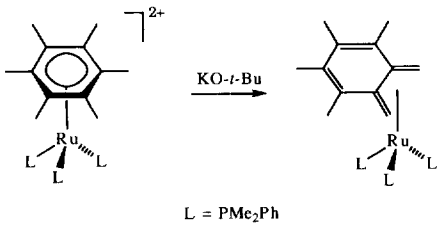


Y = O_2CCF_3; L = PMe_3

(6)

The presence of methyl substituents on the inner diene fragment favours formation of the *exo*-*o*-xylylene isomer, probably owing to steric hindrance to coordination. Thus, in contrast with the behaviour described in Eq. (5), deprotonation of $[Ru(PMe_2Ph)_3(\eta^6$-$C_6Me_6)]^{2+}$ gives exclusively the *exo*-tetramethyl-*o*-xylylene complex (Eq. (7)). Deprotonation of $[Ru(PMe_3)_3(\eta^6$-$C_6Me_6)]^{2+}$ and of $[OsL_3(\eta^6$-$C_6Me_6)]^{2+}$ (L = PMe_3, PMe_2Ph) gives exclusively the *endo*-tetramethyl-*o*-xylylene complexes, but these isomerize quantitatively in refluxing toluene to the corresponding *exo*-isomers (Scheme 3). The kinetics of these isomerizations are being studied by ^1H NMR spectroscopy in the range 65 to 110 °C [36]. They are cleanly first-order in complex and are retarded by addition of free tertiary phosphine, although the osmium systems are complicated by a rapid reaction of the formed *exo*-isomer with the tertiary phosphine (Eq. (8)). In this reaction, the

η^4-tetramethyl-*o*-xylylene is converted into a κ^2-tetramethyl-*o*-xylylene by displacement of the formal double bond of the aromatic ring. For $L = PMe_2Ph$, the reaction is reversible and the adduct can be detected only by its ^1H NMR spectrum; in contrast, for $L = PMe_3$, the reaction is irreversible and the adduct has been structurally characterized by X-ray crystallography.



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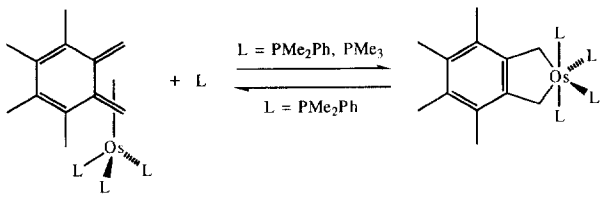


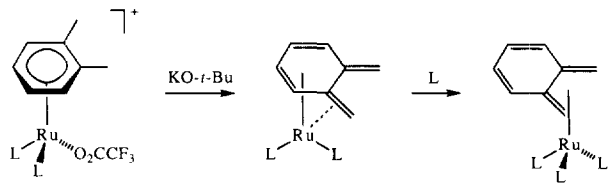
(8)

Our kinetic data point to the existence of two independent routes for *endo*- to *exo*-isomerization in the tetramethyl-*o*-xylylene complexes of ruthenium(0) and osmium(0). In one pathway, a tertiary phosphine ligand dissociates to generate a 16-electron intermediate in which migration can occur, as discussed above and shown in Scheme 4. However, there is also a pathway that is independent of added tertiary phosphine, indicating that isomerization can also take place in the original 18-electron complex. The *endo*- to *exo*-migration is closely related to the haptotropic rearrangements that occur, for example, in 1,3,5-cycloheptatriene iron tricarbonyl [43] and in acyclic polyene iron tricarbonyls [44–48], (e.g. Eq. (9)), which are slow on the NMR time scale at room temperature.

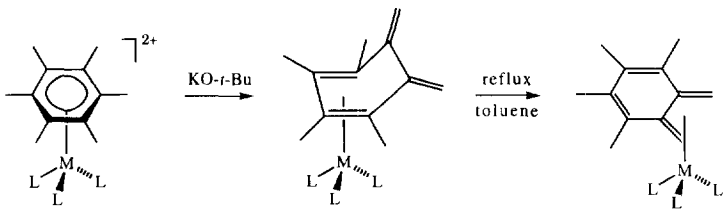
(9)

As expected, substitution of methyl groups on the outer diene fragment favours formation of the *endo-o*-xylylene complex. Thus, deprotonation of both 1,2-diethylbenzene complexes $[Ru(PMe_2Ph)_3(\eta^6\text{-}o\text{-}C_6H_4Et_2)]^{2+}$ or $[Ru(O_2CCF_3)(PMe_2Ph)_2(\eta^6\text{-}o\text{-}C_6H_4Et_2)]PF_6$ in the presence of PMe_2Ph gives the same η^4-*endo*-dimethyl-*o*-xylylene complex (Scheme 5) [36]; it is not yet clear whether this is a kinetic product or whether it is thermodynamically more stable than the

exo-isomer. Attempts to deprotonate the 1,2-diisopropylbenzene complex $[Ru(O_2CCF_3)(PMe_2Ph)_2(\eta^6\text{-}o\text{-}C_6H_4\text{-}i\text{-}Pr_2)]PF_6$ with KO-*t*-Bu/PMe_2Ph have been unsuccessful. In contrast, the complex $[Ru(PMe_3)_3(\eta^6\text{-indane})]^{2+}$ is readily deprotonated to give an *exo*-η^4-isoindene species, presumably formed via its undetected *endo*-isomer. On heating, the former loses PMe_3 and hydride migrates from the methylene carbon atom to the metal to give a stable η^5-indenyl hydrido-complex as the final product (Scheme 6).

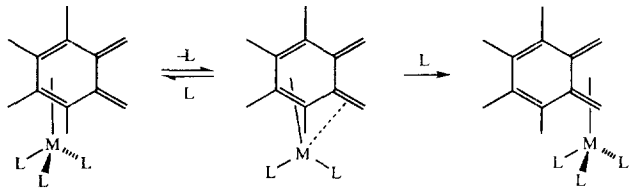


Scheme 2. Possible mechanism of formation of $RuL_3\{\eta^4\text{-}exo\text{-}o\text{-}C_6H_4(CH_2)_2\}$.



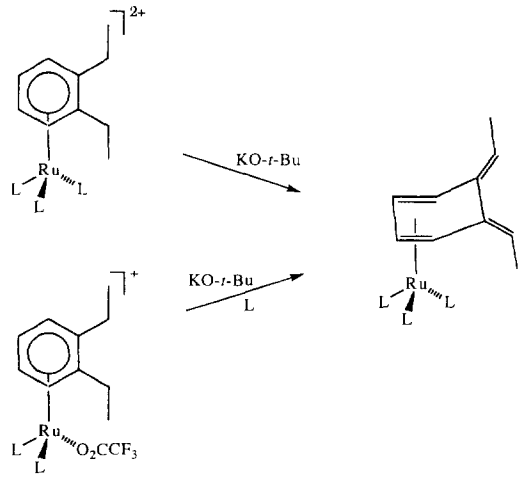
M = Ru, L = PMe_3; M = Os, L = PMe_3, PMe_2Ph

Scheme 3. Successive formation of *endo*- and *exo*-isomers of $ML_3\{o\text{-}C_6Me_4(CH_2)_2\}$.

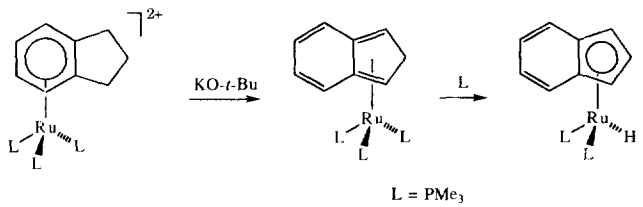


Scheme 4. Dissociative pathway for formation of *exo*- $ML_3\{o\text{-}C_6Me_4(CH_2)_2\}$ from its *endo*-precursor.

Like other 1,3-diene complexes of the zerovalent d^8 metals, the *o*-xylylene complexes of ruthenium(0) and osmium(0) are readily protonated, a process that occurs in two steps. Careful treatment of the *exo*-tetramethyl-*o*-xylylene complexes with 60% aqueous HPF_6 precipitates PF_6 salts of η^3-benzyl-ruthenium(II) cations **5**–**7** resulting from addition of a proton to one of the terminal diene carbon atoms (Eq. (10)). The X-ray structures of **6** and **7** have been determined. In **6** the formal electron-deficiency at the 16-electron Ru(II) centre is relieved in a now familiar way by the formation of a three-centre, two-electron Ru–H–C bond (an agostic interaction) [*r*(Ru–H) 1.92 Å, *r*(C–H) 1.01(5) Å, C–Ĥ–Ru 107(3)°], similar to those found in $[Fe\{P(OMe)_3\}_3(\eta^3\text{-}C_8H_{13})]^+$ [49], $Mn(CO)_3(\eta^3\text{-}C_7H_{11})$ [50,51],

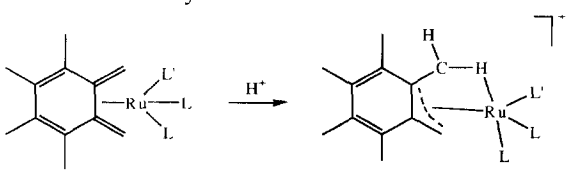


Scheme 5. Deprotonation of η^6-1,2-diethylbenzene ruthenium (II) complexes.



Scheme 6. Deprotonation of η^6-indane ruthenium (II) complexes.

$Ru(PMe_2Ph)_3(\eta^3\text{-}C_4H_7)$ [52] and $[Ru\{P(OMe)Ph_2\}_3(\eta^3\text{-}C_8H_{13})]$ [53]. The structure of **7** is probably similar, but appears to be an average in which the proton has added to either of the benzylic carbon atoms.



(10)

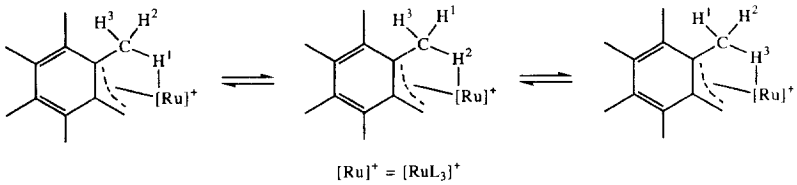
$L_2 = Ph_2PCH_2CH_2PPh_2$; $L' = PMe_2Ph$ **(5)**
$L_2 = Z\text{-}Ph_2PCH{=}CHPPh_2$; $L' = PMe_2Ph$ **(6)**
$L = L' = PMe_2Ph$ **(7)**

The η^3-benzyl cations are highly fluxional in solution. Three processes have been proposed [35] to account for the observed behaviour:

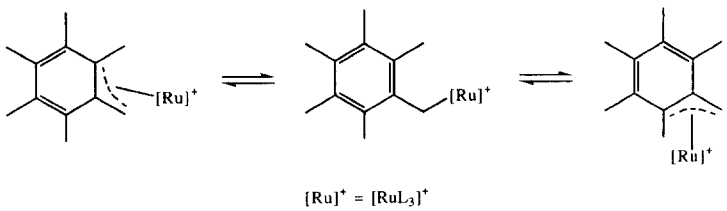
(1) reversible exchange of the agostic methyl protons, probably by reversible Ru H bond breaking (Scheme 7);

(2) an $\eta^3 \leftrightarrow \eta^1$ interconversion of the benzyl group arising from reversible removal of the formal double bond of the arene ring (Scheme 8);

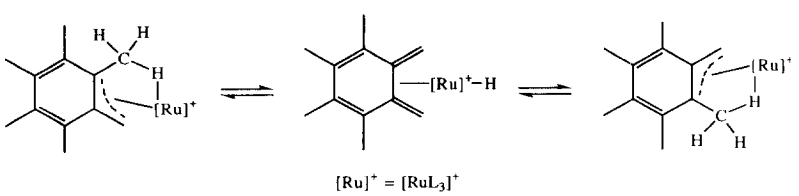
(3) reversible C–H bond cleavage of the Ru–H–C interaction via a diene-hydride intermediate (Scheme 9).



Scheme 7. Reversible exchange of agostic methyl protons.



Scheme 8. Reversible *trihapto*-to *monohapto*-benzyl interconversion.

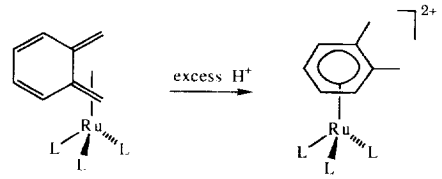


Scheme 9. Reversible C-H bond cleavage.

The operation of all three processes in the hexamethylbenzyl system enables the RuL_3 fragment to migrate round the six-membered ring.

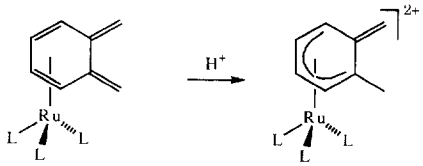
Reaction of the *exo*-*o*-xylylene complexes with an excess of CF_3SO_3H or HPF_6 cleaves the initially formed metal–benzyl bond to give dicationic arene–ruthenium(II) salts. $[RuL_3(\eta^6\text{-}1,2\text{-dimethylarene})]^{2+}$ (Eq. (11)). Since these species are sometimes difficult to prepare directly by reaction of L with $[Ru(O_2CCF_3)L_2(\eta^6\text{-}1,2\text{-dimethylarene})]^+$ owing to competing loss of the coordinated arene, this often represents a convenient alternative route. Moreover, as discussed above, deprotonation of the dications generally gives an *endo*-*o*-xylylene complex, so this procedure can be used to convert *exo*-η^4-*o*-xylylene complexes into their *endo*-isomers. In contrast to $[Ru(PMe_2Ph)_3(\eta^6\text{-}o\text{-}C_6H_4Me_2)]^{2+}$, dications containing four or more methyl groups on the arene, such as $[Ru(PMe_2Ph)_3(\eta^6\text{-}C_6Me_6)]^{2+}$, readily lose the arene in solution. This is the reverse of the normal stability trend in arene–ruthenium(II) complexes, and is probably a consequence of steric crowding in the coordination sphere. Thus, protonation of the *exo*-isomers of either $Ru(PMe_2Ph)_3\{C_6Me_4(CH_2)_2\}$ or $Ru(PMe_2Ph)_3\{3,4\text{-}$

$C_6H_2Me_2(CH_2)_2\}$ with an excess of CF_3SO_3H(TfOH) gives $[Ru_2(\mu\text{-}OTf)_2(PMe_2Ph)_6](OTf)_2$ [36].

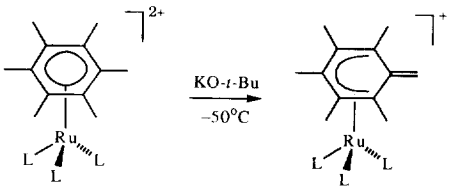


(11)

Protonation of the *endo-o*-xylylene complexes gives initially monocations that have not yet been fully characterized, but probably contain the η^5-methylbenzyl ligand (Eq. (12)). The corresponding η^5-pentamethylbenzylruthenium(II) cation can be detected as an intermediate in the deprotonation of $[Ru(PMe_2Ph)_3(\eta^6\text{-}C_6Me_6)]^{2+}$ with KO-*t*-Bu at −50 °C (Eq. (13)). Loss of the second proton occurs when this species is allowed to come to room temperature in the presence of KO-*t*-Bu to give $Ru(PMe_2Ph)_3\{exo\text{-}\eta^4\text{-}(CH_2)_2C_6Me_4\}$; the expected *endo*-isomer could not be detected (cf. Scheme 3).



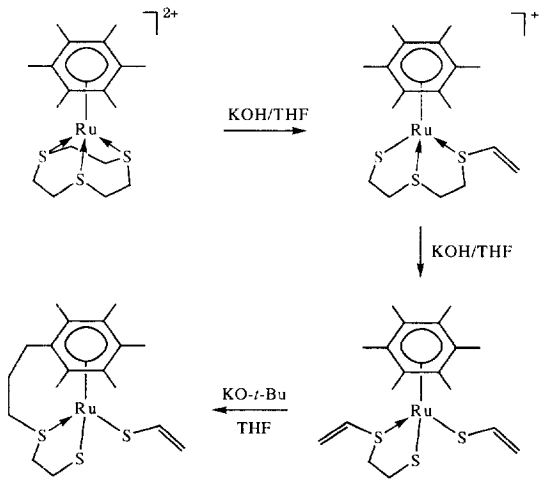
(12)



(13)

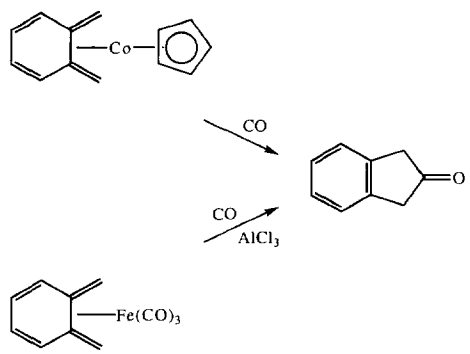
In summary, *o*-xylylene complexes of ruthenium(0) and osmium(0) can be generated by treatment of readily accessible arene complexes of ruthenium(II) and osmium(II) with KO-*t*-Bu under mild conditions. Whether the metal fragment is coordinated to the *exo*- or *endo*-double bonds in the resulting complex depends on the metal, the other ligands, and the arene substituents. These results led us to expect that deprotonation of $[RuL_3(\eta^6\text{-}C_6Me_6)]^{2+}$, where L_3 is a tridentate ligand, should give an *endo*-η^4-tetramethyl-*o*-xylylene ruthenium(0) complex $RuL_3\{\eta^4\text{-}C_6Me_4(CH_2)_2\}$ and thus seemed to offer a possible route to ruthenium(0) complexes containing thioether ligands instead of the usual tertiary phosphines. When L_3 is the tridentate sulphur donor 1,4,7-trithiacyclononane (abbreviated [9]aneS_3), however, the base reaction takes a different course because the CH_2 protons in α-position to sulphur are deprotonated before the arene methyl protons. On treatment with KOH, $[Ru\{[9]aneS_3\}(\eta^6\text{-}C_6Me_6)]^{2+}$ undergoes two successive

deprotonations of this type, which lead to cleavage of C–S bonds as shown in Scheme 10 [54,55]. The first isolated product contains a tridentate open-chain, mono-anionic vinyl thioether-thiolate ligand, $\bar{S}CH_2CH_2SCH_2CH_2SCH{=}CH_2$, and the second contains a bidentate vinyl thioether/thiolate ligand $\bar{S}CH_2CH_2SCH{=}CH_2$ as well as ethenethiolate. Only in the final step, when KO-*t*-Bu is used as base, is one of the C_6Me_6 methyl groups deprotonated. The resulting carbanion adds to the vinyl group of $\bar{S}CH_2CH_2SCH{=}CH_2$ to give, after uptake of one proton, an unusual η^6-arene-thioether-thiolate ligand (Scheme 10).



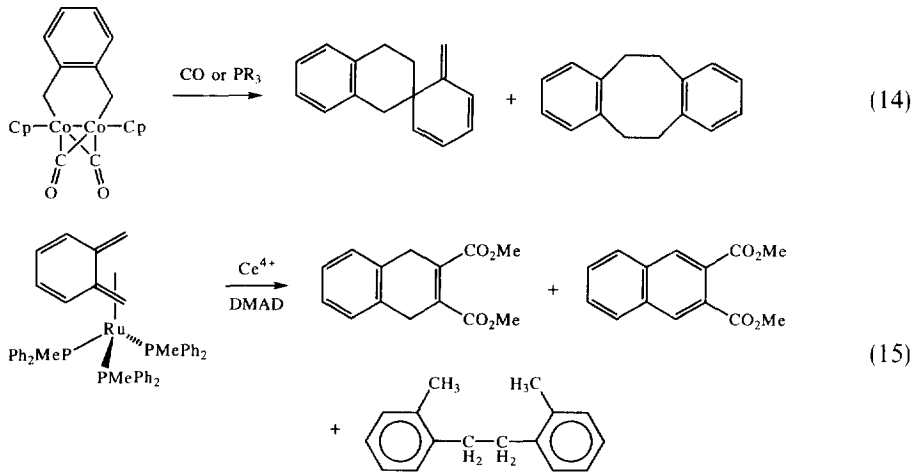
Scheme 10. Fragmentation of [9]aneS$_3$ coordinated to $[Ru(\eta^6\text{-}C_6Me_6)]^{2+}$.

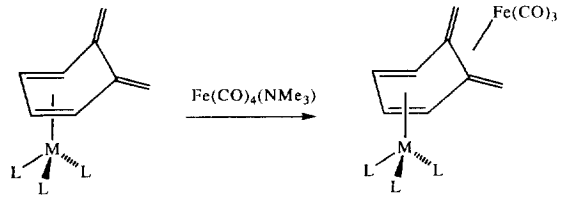
Although short-lived in the free state, *o*-xylylenes readily undergo [4+2]-cycloadditions at the *exo*-double bonds, a reaction that has found extensive application in organic synthesis [56]. The organic chemistry of the metal complexes has proved so far to be disappointingly limited. The *exo*-*o*-xylylene complexes of $Co(\eta^5\text{-}C_5H_5)$ and $Fe(CO)_3$ react with CO to give 2-indanone (in the latter case $AlCl_3$ is required as a catalyst) (Scheme 11) [57,58], and the bridging η^1, η^1-*o*-xylylene dicobalt dicarbonyl complex shown in Eq. (14) readily releases *o*-xylylene, isolated as its dimers, on treatment with CO or tertiary phosphines [59]. Cole-Hamilton and coworkers [60] have shown that *o*-xylylene can be liberated from $RuL_3\{\eta^4\text{-}exo\text{-}(CH_2)_2C_6H_4\}$ ($L = PMe_2Ph$, $PMePh_2$) by ceric ion oxidation and trapped with dimethyl acetylenedicarboxylate ($MeO_2CC_2CO_2Me$, DMAD) to give the expected [4+2]cycloadduct (Eq. (15)). The yield was only 14%, however, and the corresponding naphthalene and 2,2′-dimethylbibenzyl were also formed; the less reactive dienophile MeC_2CO_2Me failed to give any Diels–Alder adduct. As expected, the *endo*-*o*-xylylene complexes are more reactive than their *exo*-isomers. Thus, the *endo*-*o*-xylylene complexes $Ru(\eta^6\text{-}C_6Me_6)\{\eta^4\text{-}C_6Me_4(CH_2)_2\}$ and $M(PMe_2Ph)_3\{\eta^4\text{-}C_6H_4(CH_2)_2\}$ ($M = Ru$, Os) form iron carbonyl adducts by complexation with the *exo*-double bonds, the two metal-containing fragments being transoid; (Eqs. (16) and (17)) [40,41]; the *exo*-isomers are unreactive. Either or both of the *exo*-double



Scheme 11. Carbonylation of *exo*-*o*-xylylene complexes.

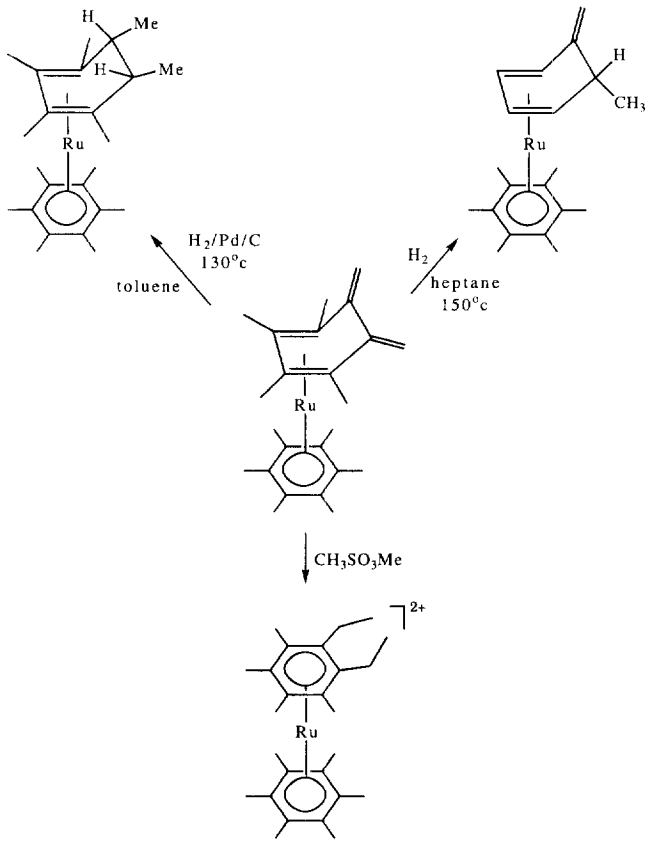
bonds in $Ru(\eta^6\text{-}C_6Me_6)\{\eta^4\text{-}C_6Me_4(CH_2)_2\}$ can also be hydrogenated, and the *exo*-methylene groups are readily protonated by acid and alkylated by methyl triflate (Scheme 12) [40]. Although electron-deficient olefins do react with the *endo*-*o*-xylylene complexes $Ru(\eta^6\text{-}C_6Me_6)\{\eta^4\text{-}C_6Me_4(CH_2)_2\}$ and $Ru(PMe_2Ph)_3\{\eta^4\text{-}C_6H_4(CH_2)_2\}$, the products have not yet been identified.





(17)

M = Ru, Os; L = PMe_2Ph



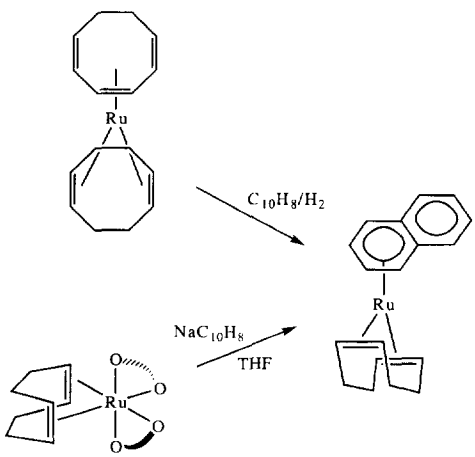
Scheme 12. Reactions of $Ru(\eta^6\text{-}C_6Me_6)\{\eta^4\text{-}endo\text{-}C_6Me_4(CH_2)_2\}$.

3. A labile arene–ruthenium(0) complex: (η^6-naphthalene)(η^4-1,5-cyclooctadiene)ruthenium(0), Ru(NAP)(COD)

A useful precursor for synthesis and catalysis in zerovalent ruthenium chemistry is the 18-electron complex $Ru(\eta^6\text{-}1,3,5\text{-}C_8H_{10})(\eta^4\text{-}1,5\text{-}C_8H_{12})$ or Ru(COD)(COT), where COT = 1,3,5-cyclooctatriene (C_8H_{10}) and COD = 1,5-cyclooctadiene (C_8H_{12})

[5,61]. This can be made in ca. 50% yield by reducing hydrated $RuCl_3$ with zinc dust in the presence of 1,5-cyclooctadiene [62–65]. The COT ligand is labilized under hydrogen, probably because addition of hydrogen generates a labile 16-electron species $Ru(\eta^4\text{-}1,3\text{-}C_8H_{12})(\eta^4\text{-}1,5\text{-}C_8H_{12})$. Thus, Ru(COD)(COT) reacts under hydrogen (1 atm) with arenes to give $Ru(\eta^6\text{-arene})(\eta^4\text{-}1,5\text{-}C_8H_{12})$ [32], which can be readily converted by HCl into $[RuCl_2(\eta^6\text{-arene})]_2$. This methodology provides an alternative route to these complexes that is complementary to that mentioned in Section 2. It is especially valuable for functionalized arenes, such as acetophenone, whose dihydroarene derivatives are not conveniently available by Birch reduction.

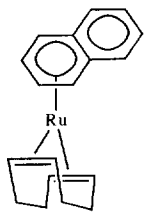
Although the benzene and mesitylene complexes of the type $Ru(\eta^6\text{-arene})(\eta^4\text{-}1,5\text{-}C_8H_{12})$ catalyse the hydrogenation of monoalkenes such as 1-pentene, 1-hexene and cyclohexene at room temperature [66], the ligands in these complexes are, in general, not particularly labile. For example, the benzene complex does not exchange with free arenes on heating to 97 °C, although there is slow exchange with C_6D_6 in the presence of acetonitrile at 50 °C [67]. The naphthalene complex $Ru(\eta^6\text{-}C_{10}H_8)(\eta^4\text{-}1,5\text{-}C_8H_{12})$[Ru(NAP)(COD)] is, however, much more labile. This compound was made first from the reaction of Ru(COD)(COT) with naphthalene under hydrogen in ca. 80% yield [68], but is more conveniently prepared on a larger scale in ca. 60% yield by sodium naphthalide reduction of the bis(acetylacetonato) complex $Ru(acac)_2(1,5\text{-}C_8H_{12})$ (Scheme 13) [69]. The corresponding reaction of $LiC_{10}H_8$ with $[RuCl_2(1,5\text{-}C_8H_{12})]_n$ gives only ca. 10–20% yield [70], probably owing to the insolubility of the polymeric ruthenium(II) complex in the reaction medium.



Scheme 13. Preparation of Ru(NAP)(COD).

In the presence of acetonitrile (ca. 3 mol per mol of complex), naphthalene is displaced from Ru(NAP)(COD) by a wide range of arenes, including those bearing functional groups, to give the corresponding $Ru(\eta^6\text{-arene})(\eta^4\text{-}1,5\text{-}C_8H_{12})$ complexes (Eq. (18)). The reaction usually takes periods of hours to days at room temperature, being slower for arenes containing three or four methyl groups. Mesitylene reacts

especially slowly, requiring 4–5 days at 40–50 °C, and hexamethylbenzene fails to react. The Ru(η⁶-arene)(η⁴-1,5-C_8H_{12}) complexes are probably formed more rapidly from Ru(COD)(COT)/H_2 than from Ru(NAP)(COD)/CH_3CN, which is an advantage for complexes of limited thermal stability. On the other hand, olefinic substituents are hydrogenated to some extent in the presence of Ru(COD)(COT)/H_2, whereas the Ru(NAP)(COD)/CH_3CN system can be used to make the otherwise inaccessible η⁶-styrene complex [69].

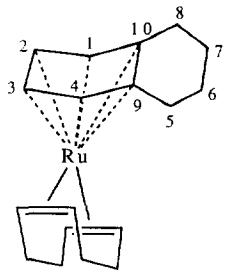


$$+ \text{ arene} \xrightarrow{CH_3CN} \text{Ru}(\eta^6\text{-arene})(\eta^4\text{-1,5-}C_8H_{12}) + C_{10}H_8 \quad (18)$$

arene = C_6H_6, $C_6H_5CH_3$, $C_6H_4(CH_3)_2$-1,4, $C_6H_3(CH_3)_3$-1,2,4, $C_6H_3(CH_3)_3$-1,3,5, $C_6H_2(CH_3)_4$-1,2,3,4, C_6H_5OMe, C_6H_5Cl, C_6H_5CHO, C_6H_5CN, $C_6H_5CH{=}CH_2$, C_6H_4-1-Me-4-$CH_2{=}CMe$, *E*-$C_6H_5CH{=}CHC_6H_5$, $(C_6H_5)_3As$, $(2\text{-}CH_3C_6H_4)_3P$

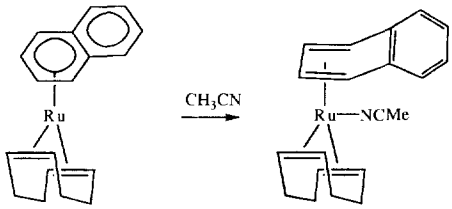
It is well known that η⁵-indenyl complexes generally undergo substitution reactions at the metal centre more readily than the corresponding η⁵-cyclopentadienyls (the so-called "indenyl effect"). This is thought to be a consequence of the stabilization of η³- and η¹-indenyl intermediates resulting from the recovery of full aromatic character in the uncomplexed six-membered ring [71–76]. Related to this is the well-established lability of complexes of naphthalene and of other polycyclic arenes. For example, the coordinated arene is displaced more easily by CO or tertiary phosphines from $Cr(CO)_3(\eta^6\text{-}C_{10}H_8)$ and $Cr(\eta^6\text{-}C_{10}H_8)_2$ than from $Cr(CO)_3(\eta^6\text{-}C_6H_6)$ and $Cr(\eta^6\text{-}C_6H_6)_2$ [77–82]. Similar observations have been made for complexes of the type $[Ir(\eta^6\text{-arene})(\eta^4\text{-1,5-}C_8H_{12})]^+$ [83,84] and $[Ru(\eta^5\text{-}C_5R_5)(\eta^6\text{-arene})]^+$ (R = H, Me) [85]. Extended Hückel MO calculations on ring slippage in $Cr(CO)_3(\eta^6\text{-}C_{10}H_8)$ and $Mn(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_{10}H_8)$ suggest that an η⁶- to η²- path should be most favourable, without a discrete η⁴- intermediate [86]. On the other hand, IR-spectroscopic evidence has been provided for an intermediate $Cr(CO)_3(\eta^4\text{-}C_{10}H_8)(THF)$ in the displacement of naphthalene from $Cr(CO)_3(\eta^6\text{-}C_{10}H_8)$ by THF [87].

The displacement of naphthalene from Ru(NAP)(COD) by benzene and other arenes is first-order in complex and approximately first-order in acetonitrile provided the ratio $[CH_3CN]/[Ru(NAP)(COD)]$ does not exceed ca. 3. The kinetic data are consistent with the reversible formation of an η⁴-naphthalene complex that is stabilized by coordination of acetonitrile (Eq. (19)), i.e. acetonitrile assists the first step in the displacement of naphthalene by the entering arene. Other potential donors such as THF and ketones do not promote the displacement of naphthalene from Ru(NAP)(COD), although they do catalyse arene exchange in $Cr(CO)_3(\eta^6\text{-arene})$ complexes [88].



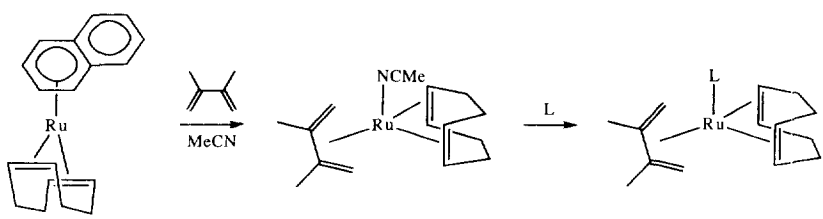
Ru–C(1)	2.221(2)	Ru–C(2)	2.276(3)
Ru–C(3)	2.262(3)	Ru–C(4)	2.205(3)
Ru–C(5)	2.346(3)	Ru–C(10)	2.338(2)

Fig. 1. Metal carbon bond lengths to *hexahapto*-naphthalene in Ru(NAP)(COD) [70].



(19)

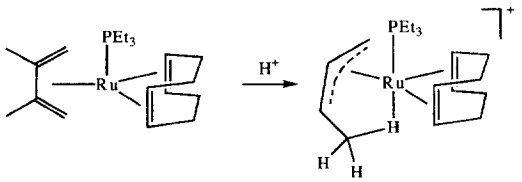
The tendency toward *tetrahapto*-coordination is already evident in the ground state structure of Ru(NAP)(COD) [70]. The bound six-membered ring is distinctly non-planar (Fig. 1); the dihedral angle between the planes C(1)–C(2)–C(3)–C(4) and C(1)–C(4)–C(5)–C(10) is about 8° and carbon atoms C(1)–C(4) are significantly closer to the metal atom (average Ru–C 2.241 Å) than are carbon atoms C(5) and C(10) (average Ru–C 2.342 Å). Similar effects have been observed for other η^6-naphthalene complexes, including $Cr(CO)_3(\eta^6\text{-}C_{10}H_8)$ [89]. It seems reasonable to suppose that the more weakly bound carbon atoms will be readily displaced by a ligand such as acetonitrile. Moreover, in the presence of acetonitrile, naphthalene is displaced from Ru(NAP)(COD) by 1,3-dienes such as 2,3-dimethylbutadiene, 3-methyl-1,3-pentadiene and isoprene to give labile but isolable complexes of the type Ru(NCMe)(η^4-1,3-diene)(η^4-1,5-C_8H_{12}), which are direct analogues of the intermediate proposed in Eq. (19). The coordinated acetonitrile exchanges rapidly with free acetonitrile and is easily replaced by CO, other nitriles (*t*-BuCN, PhCN), isonitriles (*t*-BuNC) and Group 15 donors [PPh_3, PEt_3, P-*n*-Bu_3, $P(OMe)_3$] to give



L = *t*-BuCN, PhCN, CO, *t*-BuNC, PPh_3, PEt_3, P-*n*-Bu_3, $P(OMe)_3$

Scheme 14. Reaction of Ru(NAP)(COD) with 2,3-dimethylbutadiene.

thermally more stable derivatives Ru(L)(η^4-1,3-diene)(η^4-1,5-C_8H_{12}) (Scheme 14) [90]. Like the *o*-xylylene complexes discussed in Section 2 and the closely related $ML_3(\eta^4$-1,3-diene) (M = Fe, Ru) complexes, these compounds readily form agostic mono-protonated derivatives on treatment with 60% aqueous HPF_6 (Eq. (20)).



(20)

Ligands that are stronger π-acceptors than acetonitrile, such as tertiary phosphines, phosphites and isocyanides, react at low temperature with Ru(NAP)(COD) to give isolable *tetrahapto*-naphthalene complexes Ru(L)(η^4-$C_{10}H_8$)(η^4-1,5-C_8H_{12}) [L = $P(OMe)_3$, PMe_3, PEt_3, *t*-BuNC], several of which have been characterized by X-ray crystallography [91]. The structure of the PMe_3 derivative is shown in Fig. 2. The η^4-naphthalene ligand shows the non-planarity expected for an η^4-1,3-cyclic diene, the hinge angle between the planes C(1)–C(2)–C(3)–C(4) and C(1)–C(4)–C(5)–C(10) being 41°, similar to those observed for the η^4-arenes in Ru(η^6-C_6Me_6)(η^4-C_6Me_6) [92], Ru(η^6-C_6Me_6)(η^4-$C_{10}Me_8$) [93] and

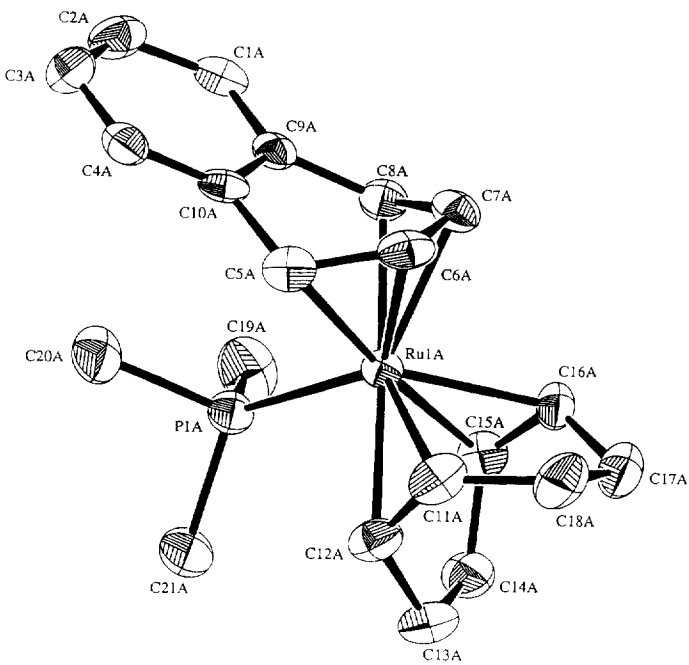


Fig. 2. X-ray structure of Ru(PMe_3)(η^4-$C_{10}H_8$)(η^4-1,5-C_8H_{12}) (hydrogen atoms omitted for clarity). The hinge angle of η^4-naphthalene is 41°.

$Fe(\eta^6\text{-}C_6Me_6)(\eta^4\text{-}C_{10}H_8)$ [94]. The coordination geometry can be described as approximately square pyramidal, with the midpoints of the double bonds of η^4-naphthalene and 1,5-COD occupying the basal sites and the added ligand in the apical site. The ruthenium(0) complexes $Ru\{P(OMe)_3\}(1\text{-}4\eta\text{-}1,3,5\text{-}C_8H_{10})(\eta^4\text{-}1,5\text{-}C_8H_{12})$ [95], $Ru(L)(1\text{-}4\eta\text{-}C_8H_8)(1,2,5,6\eta\text{-}C_8H_8)$ (L = CO, *t*-BuNC, PMe_3] [96] and $Ru\{P(OMe)_3\}(E,E\text{-}MeO_2CCH{=}CHCH{=}CHCO_2Me)_2$ [97] show similar geometries. The complexes are unstable in solution and, in some cases, form binuclear complexes $(\eta^4\text{-}1,5\text{-}C_8H_{12})Ru(\mu\text{-}\eta^6,\eta^4\text{-}C_{10}H_8)Ru(L)(\eta^4\text{-}1,5\text{-}C_8H_{12})$ [L = $P(OMe)_3$, PEt_3] in which an additional Ru(COD) unit is attached to the second ring of the naphthalene, the two metal centres being mutually *trans* [98]. Complexes of this type can also be isolated by careful treatment of Ru(NAP)(COD) with slightly less than one equivalent of L. Fig. 3 shows the X-ray structure of the derivative with L = PEt_3; the conformation of the naphthalene ligand is almost identical to that in the mononuclear complexes. Treatment of Ru(NAP)(COD) with an excess of Group 15 donor ligands or isocyanides gives $RuL_3(\eta^4\text{-}1,5\text{-}C_8H_{12})$.

The η^4-naphthalene in the $Ru(L)(\eta^4\text{-}C_{10}H_8)(\eta^4\text{-}1,5\text{-}C_8H_{12})$ complexes is very labile. For example, it is replaced at room temperature by 1,3-dienes, thus providing an alternative route to the compounds shown in Scheme 14. Aromatic compounds such as styrene, methyl cinnamate and 2-vinylnaphthalene also react to give η^4-diene complexes **8**–**10** in which one formal double bond of the ring is attached to ruthenium [98]. Similar complexes **11** and **12** are formed by acyclic α,β-unsatu-

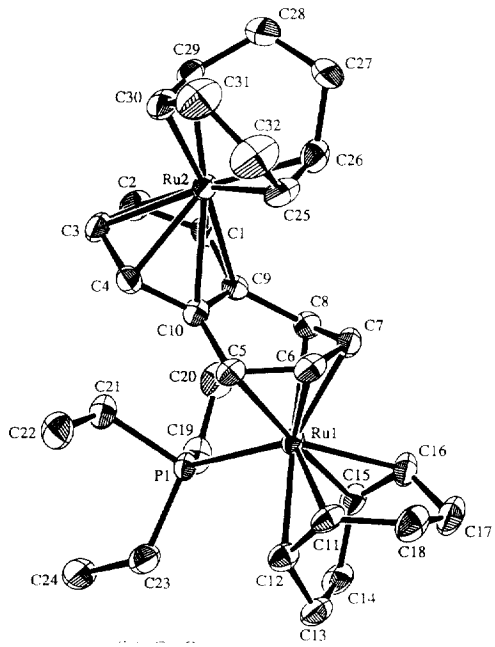
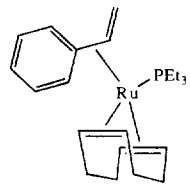


Fig. 3. X-ray structure of $(\eta^4\text{-}1,5\text{-}C_8H_{12})Ru(\mu\text{-}\eta^6,\eta^4\text{-}C_{10}H_8)Ru(PEt_3)(\eta^4\text{-}5\text{-}C_8H_{12})$ (hydrogen atoms omitted for clarity). The hinge angle of η^4-naphthalene is 39°.

rated ketones and aldehydes, such as *trans*-chalcone and mesityl oxide, and by aromatic ketones, such as 2-naphthone (**13**). Even dimethyl fumarate forms an η^4- complex (**14**) with $Ru\{P(OMe)_3\}(\eta^4\text{-}1,5\text{-}C_8H_{12})$ in which one of the ester C=O groups is side-bonded to the metal atom [99]. The $Ru(L)(1,5\text{-}C_8H_{12})$ fragment clearly has a high affinity for conjugated systems and, to an even greater extent than its close relative $Fe(CO)_3$, is capable of overcoming the aromaticity of a benzene ring [100–103].



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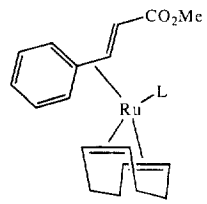
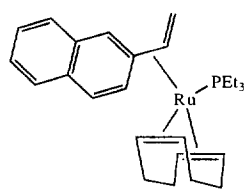


9: L = $P(OMe)_3$, PMe_3



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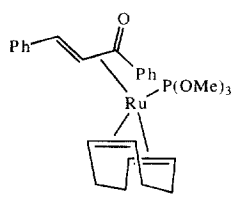

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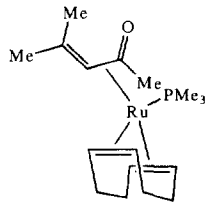
Although the displacement of naphthalene from Ru(NAP)(COD) by most arenes requires the assistance of acetonitrile, this is not the case for olefinic ligands such as cycloheptatriene, styrene and *trans*-stilbene. Moreover, styrene catalyses the displacement of naphthalene by benzene [104]. It seems likely that the ability of styrene to



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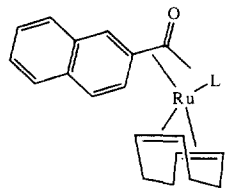

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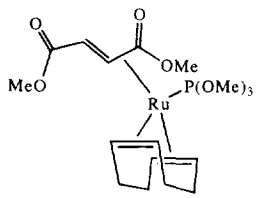

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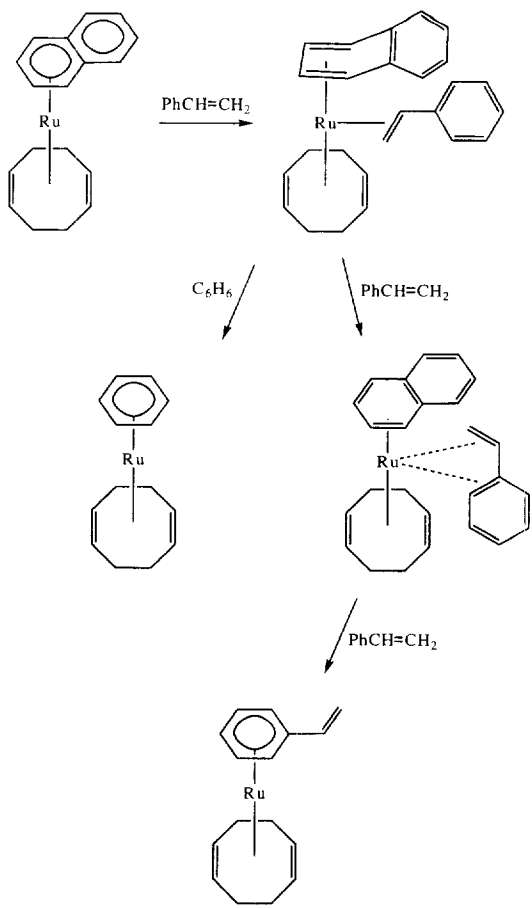
act as an η^2- and η^4-donor to ruthenium(0) may help to generate η^4- and η^2-naphthalene intermediates, as shown in Scheme 15.

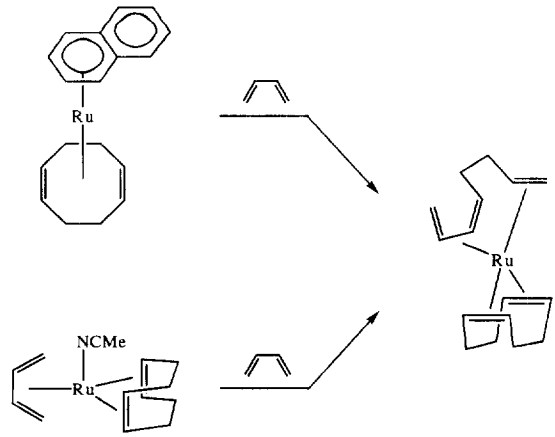
Butadiene also reacts rapidly with Ru(NAP)(COD) in benzene, hexane or THF to give brown, thermally labile crystals of formula $Ru(C_4H_6)_2(COD)$, which, according to the ^1H and ^{13}C NMR spectra, may be a ruthenium(0) complex containing 1,3,7-octatriene, a linear dimer of butadiene [104]. The same compound is formed, though less rapidly, by treatment of the isolated acetonitrile complex, $Ru(NCMe)(\eta^4\text{-}C_4H_6)(\eta^4\text{-}1,5\text{-}C_8H_{12})$, with butadiene (Scheme 16). Isoprene reacts more slowly than butadiene to generate the corresponding 3,7-dimethyl-1,3,7-octatriene complex as a brown oil. 2,3-Dimethylbutadiene is unreactive, but treatment of its acetonitrile complex $Ru(NCMe)(\eta^4\text{-}2,3\text{-}C_4H_4Me_2)(\eta^4\text{-}1,5\text{-}C_8H_{12})$ with butadiene yields the coupled product containing 2,3-dimethyl-1,3,7-octatriene (Scheme 17). This stoichiometric coupling depends on the lability of acetonitrile, since there is no reaction between butadiene and the trimethylphosphite complex $Ru\{P(OMe)_3\}(\eta^4\text{-}2,3\text{-}C_6H_4Me_2)(\eta^4\text{-}1,5\text{-}C_8H_{12})$. Although many systems are capable of catalysing the linear dimerization and oligomerization of 1,3-dienes [105,106], intermediates have rarely been isolated. Further study of the ruthenium(0) systems may provide insight into the mechanism of these C–C coupling reactions.

There has been considerable recent interest in the use of organoruthenium(0) and organoruthenium(II) complexes to catalyse C–C coupling reactions [107–112] and

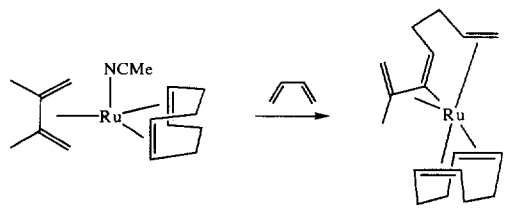


Scheme 15. Reaction or Ru(NAP)(COD) with styrene.

the lability of Ru(NAP)(COD) suggests that this complex could also be a useful catalyst for this and other types of reaction of interest in organic chemistry. In the presence of acetonitrile at 20 C, Ru(NAP)(COD) is an active catalyst for olefin isomerization. For example, 1,5-cyclooctadiene is converted into 1,3-cyclooctadiene and 1-hexene into a mixture of *E*- and *Z*-2-hexenes [113], and at 65 C allyl ethers and acetals are converted into the corresponding vinyl derivatives [114]. Terminal and internal olefins are readily hydrogenated in the presence of Ru(NAP)(COD)/CH_3CN [69]. In the presence of acetonitrile at 140 C in THF or *N*-methyl-2-pyrrolidinone, Ru(NAP)(COD) selectively catalyses tail-to-tail dimerization of methyl acrylate (CH_2=$CHCO_2Me$) to *Z*-dimethyl-2-hexenedioate (MeO_2CCH=$CHCH_2CH_2CO_2Me$) [115]. In all these reactions, monocyclic arene-ruthenium(0) complexes, such as Ru(η^6-*p*-cymene)(η^4-1,5-C_8H_{12}), are inactive or much less active, and the presence of acetonitrile is essential for catalytic activity.



Scheme 16. Coupling of butadiene units promoted by Ru(NAP)(COD).

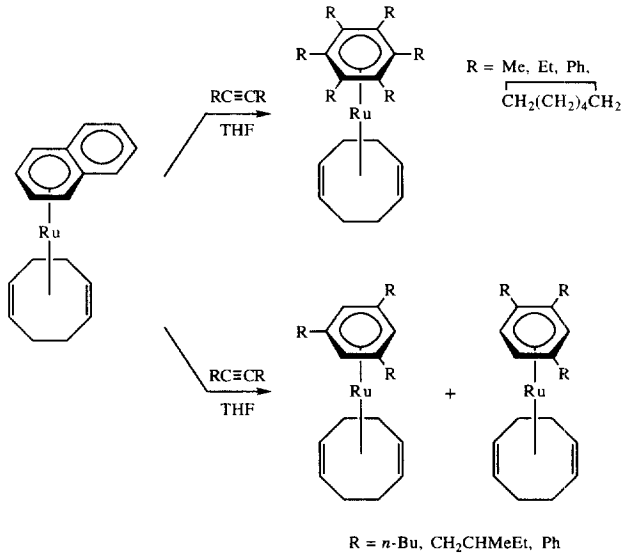


Scheme 17. Coupling of 2,3-dimethylbutadiene and butadiene promoted by Ru(NAP)(COD).

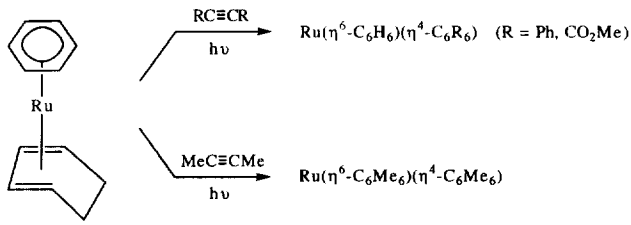
In the acrylate dimerization, the acetonitrile does not fulfil its usual function of assisting displacement of naphthalene, since methyl acrylate does this in the absence of acetonitrile, even at −30 °C. The acetonitrile may serve in this case rather to promote the reductive coupling and elimination of the acrylate units on ruthenium. Like Ru(COD)(COT) [111,112], Ru(NAP)(COD) catalyses the codimerization of diphenylacetylene with methyl acrylate to give methyl (2*E*,4*Z*)-4,5-diphenyl-2,4-pentadienoate, $PhCH{=}C(Ph){-}CH{=}CHCO_2Me$, and the codimerization of isoprene with methyl acrylate in the presence of *N*-methylpiperidine, though the products in the latter reaction have not yet been conclusively identified [116].

Alkynes undergo stoichiometric cyclotrimerization on reaction with Ru(NAP)(COD) in THF at room temperature, thus providing another useful route into Ru(η^6-arene)(η^4-1,5-C_8H_{12}) complexes (Scheme 18) [117,118]. For example, 3-hexyne and cyclooctyne give the η^6-hexaethylbenzene and tris(cyclooctenо)benzene complexes respectively, whereas terminal alkynes give inseparable mixtures of the η^6-1,3,5-arene and η^6-1,2,4-arene complexes. The proportions of the isomers are ca. 7:3 from aliphatic acetylenes and 1:4 from phenylacetylene, indicating the importance of electronic effects in the reaction pathway. These reactions are related to the reported formation of bis(arene)ruthenium(0) complexes by UV irradiation of Ru(η^6-C_6H_6)(η^4-1,3-C_6H_8) with disubstituted alkynes (Scheme 19) [119]. Treatment

of $Ru(\eta^6\text{-arene})(\eta^4\text{-}1,5\text{-}C_8H_{12})$ [arene = C_6Et_6, $C_6(C_8H_{12})_3$] with HCl gives the corresponding dichlororuthenium(II) dimers, which, unlike $[RuCl_2(\eta^6\text{-}C_6Me_6)]_2$, are not accessible by fusion of the free arenes with $[RuCl_2(p\text{-cymene})]_2$, presumably because the arenes are too hindered sterically.

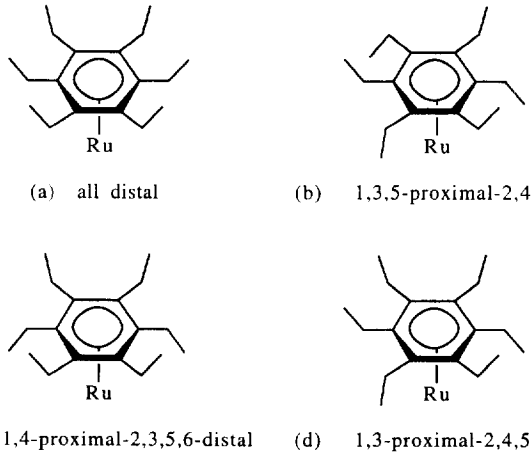


Scheme 18. Alkyne cyclotrimerization promoted by Ru(NAP)(COD).



Scheme 19. Alkyne cyclotrimerization promoted by $Ru(\eta^6\text{-}C_6H_6)(\eta^4\text{-}1,3\text{-}C_6H_8)$.

An interesting feature of the hexaethylbenzene complexes is the conformation adopted by the ethyl groups. The general problems of conformational preferences and dynamic processes in sterically crowded arene complexes have attracted considerable attention, mainly in the case of the readily accessible $Cr(CO)_3$ complexes [120]. The conformations observed in the ruthenium complexes are summarized in Fig. 4 and Table 2. In crystalline $Ru(\eta^6\text{-}C_6Et_6)(\eta^4\text{-}1,5\text{-}C_8H_{12})$, the 1,4-ethyl groups point towards the metal atom (proximal), while the 2,3,5,6-ethyl groups point away from it (distal) [conformation (c) in Fig. 4]; the aromatic carbon atoms bearing the distal groups eclipse the olefinic carbon atoms of COD, an arrangement that presumably minimizes steric interactions with the proximal groups. In solution at room temperature, all the ethyl groups are equivalent on the NMR time scale owing to rapid



(a) all distal (b) 1,3,5-proximal-2,4,6-distal

(c) 1,4-proximal-2,3,5,6-distal (d) 1,3-proximal-2,4,5,6-distal

Fig. 4. Conformations of ethyl groups observed in hexaethylbenzene–ruthenium complexes.

Table 2
Conformations of ethyl groups in crystalline Ru–C_6Et_6 complexes[a]

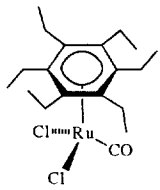
Entry	Complex	Conformation
1	$Ru(\eta^6\text{-}C_6Et_6)(\eta^4\text{-}1,5\text{-}C_8H_{12})$	1,4-Proximal-2,3,5,6-distal (c)
2	$[RuCl_2(\eta^6\text{-}C_6Et_6)]_2$	All distal (a)
3	$[Ru_2Cl_3(\eta^6\text{-}C_6Et_6)_2]PF_6$	1,3,5-Proximal-2,4,6-distal (b)
4	$RuCl_2(L)(\eta^6\text{-}C_6Et_6)$ (L = PMe_3, PPh_3)	All distal (a)
5	$RuCl_2(L)(\eta^6\text{-}C_6Et_6)$ (L = CO, *t*-BuNC)	1,3,5-Proximal-2,4,6-distal (b)
6	$RuH_2(PMe_3)(\eta^6\text{-}C_6Et_6)$	1,3-Proximal-2,4,5,6-distal (d)
7	$RuCl(CH_3)(PMe_3)(\eta^6\text{-}C_6Et_6)$	All distal (a) 1,3-Proximal-2,4,5,6-distal (d)

[a] See Fig. 4.

rotation about the ethyl C–C bonds, but at −100 °C they appear as two sets of signals in a 2:1 ratio, consistent with the solid-state structure [118]. In $[RuCl_2(\eta^6\text{-}C_6Et_6)]_2$ and its derived salt $[Ru_2(\mu\text{-}Cl)_3(\eta^6\text{-}C_6Et_6)_2]PF_6$, the ethyl groups adopt different conformations, viz. all distal, (a), in the former, alternating proximal/distal, (b), in the latter. However, in CH_2Cl_2 solution at −100 °C, both compounds show a 1:1 ratio of ethyl resonances consistent with (b). Clearly, the various conformations differ little in energy, so for a given complex they may also differ between solid and solution; however, it is also possible that $[RuCl_2(\eta^6\text{-}C_6Et_6)]_2$ exists predominantly as an ion-pair, $[Ru_2(\mu\text{-}Cl)_3(\eta^6\text{-}C_6Et_6)_2]^+Cl^-$, in CH_2Cl_2.

Comparison of entry 4 with entries 5 and 6 in Table 2 shows, as expected, that conformation (b) having three proximal groups is favoured by the presence of smaller ligands (H smaller than Cl; CO and *t*-BuNC smaller than PMe_3, PPh_3). The small difference in the energies of the various conformations is also illustrated by the fact that the unit cell of $RuCl(CH_3)(PMe_3)(\eta^6\text{-}C_6Et_6)$ (entry 7), contains two

molecules with the all-distal conformation (a) and two molecules with the 1,3-proximal–2,4,5,6-distal conformation (d). In general, the only dynamic process observed in the variable temperature NMR spectra of the hexaethylbenzene-ruthenium compounds is rotation about the C–C bonds of the ethyl groups. However, in the case of $RuCl_2(CO)(\eta^6\text{-}C_6Et_6)$, it appears that a lower energy process can also be frozen out, presumably rotation of the arene about the metal–ring axis. At −100 °C four sets of aromatic carbon resonances in a 1:2:2:1 ratio are observed, consistent with a 1,3,5-proximal–2,4,6-distal arrangement (**15**) which is frozen into an eclipsed conformation relative to the tripod of ligands beneath the ruthenium atom.



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References

[1] Articles on organoruthenium chemistry by M.A. Bennett, M.I. Bruce and T.W. Matheson and on organoosmium chemistry by R.D. Adams and J.P. Selegue, in: G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, vol. 4, Pergamon Press, Oxford, 1982, pp. 651–965, 967–1064.
[2] M.I. Bruce, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, vol. 7, Pergamon Press, Oxford, 1995, p. 291.
[3] M.A. Bennett, K. Khan, E. Wenger, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, vol. 7, Pergamon Press, Oxford, 1995, p. 473.
[4] H. Le Bozec, D. Touchard, P.H. Dixneuf, Adv. Organomet. Chem. 29 (1989) 163.
[5] M.A. Bennett, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, vol. 7, Pergamon Press, Oxford, 1995, p. 549.
[6] E.O. Fischer, R. Böttcher, Z. anorg. allgem. Chem. 291 (1957) 305.
[7] E.O. Fischer, C. Elschenbroich, C.G. Kreiter, J. Organomet. Chem. 7 (1967) 481.
[8] E.O. Fischer, C. Elschenbroich, Chem. Ber. 103 (1970) 162.
[9] G. Winkhaus, H. Singer, J. Organomet. Chem. 7 (1967) 487.
[10] G. Winkhaus, H. Singer, M. Kricke, Z. Naturforsch. Sect. B 21 (1966) 1109.

[11] R.A. Zelonka, M.C. Baird, J. Organomet. Chem. 35 (1972) C43.
[12] R.A. Zelonka, M.C. Baird, Can. J. Chem. 50 (1972) 3063.
[13] M.A. Bennett, G.B. Robertson, A.K. Smith, J. Organomet. Chem. 43 (1972) C41.
[14] M.A. Bennett, A.K. Smith, J. Chem. Soc. Dalton Trans. (1974) 233.
[15] M.A. Bennett, T.-N. Huang, T.W. Matheson, A.K. Smith, Inorganic Syntheses 21 (1982) 74.
[16] K. Mashima, K. Kusano, T. Ohta, R. Noyori, H. Takaya, J. Chem. Soc. Chem. Commun. (1989) 1208.
[17] K. Mashima, Y. Matsumura, K. Kusano, H. Kumobayashi, N. Sayo, Y. Hori, T. Ishizaki, S. Akutagawa, H. Takaya, J. Chem. Soc. Chem. Commun. (1991) 609.
[18] K. Mashima, K. Kusano, N. Sato, Y. Matsumura, K. Nozaki, H. Kumobayashi, N. Sayo, Y. Hori, T. Ishizaki, S. Akutagawa, H. Takaya, J. Org. Chem. 59 (1994) 3064.
[19] S. Hashiguchi, A. Fujii, J. Takehara, T. Ikariya, R. Noyori, J. Am. Chem. Soc. 117 (1995) 7562.
[20] A. Fujii, S. Hashiguchi, N. Uematsu, T. Ikariya, R. Noyori, J. Am. Chem. Soc. 118 (1996) 2521.
[21] A.W. Stumpf, E. Saive, A. Demonceau, A.F. Noels, J. Chem. Soc. Chem. Commun. (1995) 1127.
[22] D. Jones, L. Pratt, G. Wilkinson, J. Chem. Soc. (1962) 4458.
[23] M.Y. Darensbourg, E.L. Muetterties, J. Am. Chem. Soc. 100 (1978) 7425.
[24] M.A. Bennett, T.W. Matheson, J. Organomet. Chem. 153 (1978) C25.
[25] M.A. Bennett, I.J. McMahon, S. Pelling, J. Organomet. Chem. 382 (1990) 175.
[26] M.A. Bennett, I.J. McMahon, S. Pelling, G.B. Robertson, W.A. Wickramasinghe, Organometallics 4 (1985) 754.
[27] M.A. Bennett, I.J. McMahon, S. Pelling, M. Brookhart, D.M. Lincoln, Organometallics 11 (1992) 127.
[28] K. Moseley, J.W. Kang, P.M. Maitlis, J. Chem. Soc. A (1970) 2875.
[29] K. Moseley, P.M. Maitlis, J. Chem. Soc. A (1970) 2884.
[30] H.-B. Lee, P.M. Maitlis, J. Chem. Soc. Dalton Trans. (1975) 2316.
[31] H.-B. Lee, K. Moseley, C. White, P.M. Maitlis, J. Chem. Soc. Dalton Trans. (1975) 2322.
[32] P. Pertici, G. Vitulli, R. Lazzaroni, P. Salvadori, P.L. Barili, J. Chem. Soc. Dalton Trans. (1982) 1019.
[33] F. Moulines, D. Astruc, J. Chem. Soc. Chem. Commun. (1989) 614, and references cited therein.
[34] M.A. Bennett, I.J. McMahon, T.W. Turney, Angew. Chem. Int. Ed. Engl. 21 (1982) 379.
[35] M.A. Bennett, L.Y. Goh, I.J. McMahon, T.R.B. Mitchell, G.B. Robertson, T.W. Turney, W.A. Wickramasinghe, Organometallics 11 (1992) 3069.
[36] M.A. Bennett, M. Bown, unpublished work.
[37] S.D. Chappell, D.J. Cole-Hamilton, A.M.R. Galas, M.B. Hursthouse, J. Chem. Soc. Dalton Trans. (1982) 1867.
[38] N.J. Simpson, D.J. Cole-Hamilton, J. Chem. Soc. Dalton Trans. (1990) 1329.
[39] J.W. Hull Jr.., W.L. Gladfelter, Organometallics 1 (1982) 1716.
[40] J.W. Hull Jr.., C. Mann, W.L. Gladfelter, Organometallics 11 (1992) 3117.
[41] M.A. Bennett, M. Bown, L.Y. Goh, D.C.R. Hockless, T.R.B. Mitchell, Organometallics 14 (1995) 1000.
[42] J.E. McGrady, R. Stranger, M. Bown, M.A. Bennett, Organometallics 15 (1996) 3109.
[43] K.J. Karel, T.A. Albright, M. Brookhart, Organometallics 1 (1982) 419.
[44] H.W. Whitlock, Y.N. Chuah, J. Am. Chem. Soc. 87 (1965) 3605.
[45] H.W. Whitlock, C. Reich, W.D. Woessner, J. Am. Chem. Soc. 93 (1971) 2483.
[46] H.W. Whitlock, R.L. Markezich, J. Am. Chem. Soc. 93 (1971) 5290.
[47] H.W. Whitlock, R.L. Markezich, J. Am. Chem. Soc. 93 (1971) 5291.
[48] Z. Goldschmidt, Y. Bakal, J. Organomet. Chem. 269 (1984) 191.
[49] R.K. Brown, J.M. Williams, A.J. Schultz, G.D. Stucky, S.D. Ittel, R.L. Harlow, J. Am. Chem. Soc. 102 (1980) 981.
[50] M. Brookhart, W. Lamanna, M.B. Humphrey, J. Am. Chem. Soc. 104 (1982) 2117.
[51] A.J. Schultz, R.G. Teller, M.A. Beno, M. Brookhart, W. Lamanna, M.B. Humphrey, Science 220 (1983) 197.
[52] T.V. Ashworth, D.C. Liles, E. Singleton, Organometallics 3 (1984) 1851.

[53] T.V. Ashworth, A.A. Chalmers, E. Meintjes, H. Oosthuizen, E. Singleton, J. Organomet. Chem. 286 (1985) 237.
[54] M.A. Bennett, L.Y. Goh, A.C. Willis, J. Chem. Soc. Chem. Commun. (1992) 1180.
[55] M.A. Bennett, L.Y. Goh, A.C. Willis, J. Am. Chem. Soc. 118 (1996) 4984.
[56] W. Oppolzer, in: B.M. Trost, I. Fleming, L.A. Paquette (Eds.), Comprehensive Organic Synthesis, vol. 5, Pergamon Press, Oxford, 1991, pp. 385–396.
[57] W.H. Hersh, F.J. Hollander, R.G. Bergman, J. Am. Chem. Soc. 105 (1983) 5834.
[58] B.F.G. Johnson, J. Lewis, D.J. Thompson, Tetrahedron Lett. (1974) 3789.
[59] W.H. Hersh, R.G. Bergman, J. Am. Chem. Soc. 105 (1983) 5846.
[60] C.L. Skerratt, S.D. Chappell, R.D. Bowen, R.C. Storr, D.J. Cole-Hamilton, Polyhedron 5 (1986) 1035.
[61] P. Pertici, G. Vitulli, Comments Inorg. Chem. 11 (1991) 175.
[62] P. Pertici, G. Vitulli, M. Paci, L. Porri, J. Chem. Soc. Dalton Trans. (1980) 1961.
[63] P. Pertici, G. Vitulli, Inorg. Synth. 22 (1983) 176.
[64] K. Itoh, H. Nagashima, T. Ohshima, N. Oshima, H. Nishiyama, J. Organomet. Chem. 272 (1984) 179.
[65] K.-M. Frosin, L. Dahlenburg, Inorg. Chim. Acta 167 (1990) 83.
[66] P. Pertici, G. Vitulli, C. Bigelli, R. Lazzaroni, J. Organomet. Chem. 275 (1984) 113.
[67] E.L. Muetterties, J.R. Bleeke, A.C. Sievert, J. Organomet. Chem. 178 (1979) 197.
[68] G. Vitulli, P. Pertici, P. Salvadori, J. Chem. Soc. Dalton Trans. (1984) 2255.
[69] M.A. Bennett, H. Neumann, M. Thomas, X.Q. Wang, P. Pertici, P. Salvadori, G. Vitulli, Organometallics 10 (1991) 3238.
[70] M. Crocker, M. Green, J.A.K. Howard, N.C. Norman, D.M. Thomas, J. Chem. Soc. Dalton Trans. (1990) 2299.
[71] See, for example: A.J. Hart-Davis, R.J. Mawby, J. Chem. Soc. A. (1969) 2403.
[72] See, for example: C. White, R.J. Mawby, Inorg. Chim. Acta 4 (1970) 261.
[73] See, for example: C. White, R.J. Mawby, Inorg. Chim. Acta 4 (1970) 441.
[74] See, for example: M.E. Rerek, F. Basolo, J. Am. Chem. Soc. 106 (1984) 5908.
[75] See, for example: L.-N. Ji, M.E. Rerek, F. Basolo, Organometallics 3 (1984) 740.
[76] See, for example: T.B. Marder, J.C. Calabrese, T.H. Tulip, Organometallics 6 (1987) 2012.
[77] G. Yagupsky, M. Cais, Inorg. Chim. Acta 12 (1975) L27.
[78] M. Cais, D. Fraenkel, K. Weidenbaum, Coord. Chem. Rev. 16 (1975) 27.
[79] C. Elschenbroich, R. Möckel, Angew. Chem. Int. Ed. Engl. 16 (1977) 870.
[80] E.P. Kündig, P.L. Timms, J. Chem. Soc. Dalton Trans. (1980) 991.
[81] E.P. Kündig, C. Perret, S. Spichiger, G. Bernardinelli, J. Organomet. Chem. 286 (1985) 183.
[82] B.F. Bush, V.M. Lynch, J.J. Lagowski, Organometallics 6 (1987) 1267.
[83] C. White, S.J. Thompson, P.M. Maitlis, J. Chem. Soc. Dalton Trans. (1977) 1654.
[84] A.C. Sievert, E.L. Muetterties, Inorg. Chem. 20 (1981) 489.
[85] A.M. McNair, K.R. Mann, Inorg. Chem. 25 (1986) 2519.
[86] J.A.S. Howell, N.F. Ashford, D.T. Dixon, J.C. Kola, T.A. Albright, S.K. Kang, Organometallics 10 (1991) 1852.
[87] R. Dabard, G. Jaouen, G. Simonneaux, M. Cais, D.H. Kohn, A. Lapid, D. Tatarsky, J. Organomet. Chem. 184 (1980) 91.
[88] T.G. Traylor, K.J. Stewart, M.J. Goldberg, J. Am. Chem. Soc. 106 (1984) 4445, and references cited therein.
[89] V. Kunz, W. Nowacki, Helv. Chim. Acta 50 (1967) 1052.
[90] M.A. Bennett, X.Q. Wang, J. Organomet. Chem. 428 (1992) C17.
[91] M.A. Bennett, D.C.R. Hockless, Z.B. Lu, X.Q. Wang, unpublished work.
[92] G. Huttner, S. Lange, Acta Cryst. B 28 (1972) 2049.
[93] J.W. Hull Jr., W.L. Gladfelter, Organometallics 3 (1984) 605.
[94] C. Brodt, S. Niu, H. Pritzkow, M. Stephan, U. Zenneck, J. Organomet. Chem. 459 (1993) 283.
[95] P. Pertici, G. Vitulli, W. Porzio, M. Zocchi, P. Barili, G. Deganello, J. Chem. Soc. Dalton Trans. (1983) 1553.

[96] M.A. Bennett, H. Neumann, A.C. Willis, V. Ballantini, P. Pertici, B.E. Mann, Organometallics 16 (1997) 2868.
[97] R.J. McKinney, M.C. Colton, Organometallics 5 (1986) 1080.
[98] M.A. Bennett, M. Bown, D.C.R. Hockless, Z.B. Lu, X.Q. Wang, unpublished work.
[99] M.A. Bennett, D.C.R. Hockless, Z.B. Lu, work in progress.
[100] R. Davis, R. Pettit, J. Am. Chem. Soc. 92 (1970) 716.
[101] R. Victor, R. Ben-Shoshan, S. Sarel, J. Chem. Soc. Chem. Commun. (1970) 1680.
[102] R. Victor, R. Ben-Shoshan, S. Sarel, Tetrahedron Lett. (1970) 4257.
[103] R. Victor, R. Ben-Shoshan, S. Sarel, J. Org. Chem. 37 (1972) 1930.
[104] X.Q. Wang, Ph.D. thesis, Australian National University, 1992.
[105] W. Keim, A. Behr, M. Röper, in: G. Wilkinson, F.G. A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, vol. 8, Pergamon Press, Oxford, 1982, p. 371.
[106] J.P. Collman, L.S. Hegedus, J.R. Norton, R.G. Finke, Principles and Applications of Organotransition Metal Chemistry, University Science Books, Mill Valley, CA, 1987, pp. 597–608.
[107] T. Mitsudo, Y. Hori, Y. Watanabe, J. Organomet. Chem. 334 (1987) 157, and references cited therein.
[108] H. Butenschön, Angew. Chem. Int. Ed. Engl. 33 (1994) 636, and references cited therein.
[109] T. Mitsudo, H. Naruse, T. Kondo, Y. Ozaki, Y. Watanabe, Angew. Chem. Int. Ed. Engl. 33 (1994) 580.
[110] B.M. Trost, A.F. Indolese, T.J.J. Müller, B. Treptow, J. Am. Chem. Soc. 117 (1995) 615.
[111] T. Mitsudo, S.W. Zhang, M. Nagao, Y. Watanabe, J. Chem. Soc. Chem. Commun. (1991) 598.
[112] T. Mitsudo, S.W. Zhang, T. Kondo, Y. Watanabe, Tetrahedron Lett. 33 (1992) 341.
[113] P. Pertici, G. Uccello Barretta, F. Burzagli, P. Salvadori, M.A. Bennett, J. Organomet. Chem. 413 (1991) 303.
[114] P. Pertici, C. Malanga, A. Giuntoli, G. Vitulli, G. Martra, Gazz. Chim. Ital. 126 (1996) 587.
[115] P. Pertici, V. Ballantini, P. Salvadori, M.A. Bennett, Organometallics 14 (1995) 2565.
[116] M.A. Bennett, Z.B. Lu, work in progress.
[117] P. Pertici, A. Verrazzani, G. Vitulli, R. Baldwin, M.A. Bennett, J. Organomet. Chem. in press.
[118] P. Pertici, A. Verrazzani, G. Uccello Barretta, F. Marchetti, P. Salvadori, R. Baldwin, M.A. Bennett, D.C.R. Hockless, unpublished work.
[119] A. Lucherini, L. Porri, J. Organomet. Chem. 155 (1978) C45.
[120] M.J. McGlinchey, Adv. Organomet. Chem. 34 (1992) 285.