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RUTHENIUM AND OSMIUM COMPLEXES CONTAINING CYCLOPENTADIENYL AND RELATED PENTA *HAPTO* DIENYL LIGANDS

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CONTENTS

ABBREVIATIONS

acac	acetylacetonate
Ar	arene
bipy	2,2′-bipyridine
BSTFA	*N,N*-bis(trimethylsilyl)trifluoroacetamide
Bu	butyl
CHT	cyclohepta-1,3,5-triene

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COD	cycloocta-1,5-diene
COT	cyclooctatetraene
Cp	cyclopentadienyl
diphos	bidentate phosphine ligand
DME	1,2-dimethoxyethane
DMSO	dimethylsulfoxide
dppb	1,4-bis(diphenylphosphino)butane
dppe	1,2-bis(diphenylphosphino)ethane
dppm	bis(diphenylphosphino)methane
dppp	1,3-bis(diphenylphosphino)propane
Et	ethyl
L	two electron donor ligand (unless otherwise indicated)
Me	methyl
NBD	norbornadiene (bicyclo[2.2.1]hepta-2,5-diene)
NOE	nuclear Overhauser effect
n-, *i*-, *t*-	normal, iso, tertiary
Ph	phenyl
phen	1,10-phenanthroline
Pr	propyl
py	pyridine
R	alkyl or aryl (unless otherwise indicated)
TCNE	tetracyanoethylene
THF	tetrahydrofuran
X	halide (unless otherwise indicated)

A. INTRODUCTION

The coordination chemistry of cyclopentadienyl and related ligand systems forms one of the cornerstones of transition metal organometallic chemistry. These ligand systems, in all their different forms and variations, have been widely employed as stabilizing groups in transition metal complexes, allowing, to date, the development of a remarkably diverse and rich chemistry. In this regard the cyclopentadienyl ligand is probably unique, especially considering the wide range of properties which can be tailored at the metal centre simply by adjustments to the cyclopentadienyl moiety, and the ability of the ligand to coordinate strongly to metal centres, very often apparently regardless of the oxidation state of the metal and of the surrounding ligand environment.

These considerations are particularly relevant to much of the organometallic chemistry of ruthenium and osmium, and the advent of a number of significant recent developments in the cyclopentadienyl chemistry of these elements has prompted us to survey this area before the conflicting demands of critical evaluation, correlation and coverage become overwhelming.

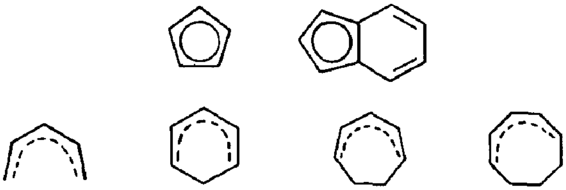


Fig. 1.

It is a fact that the vast majority of penta-*hapto*-coordinated hydrocarbon ligands in transition metal chemistry are of the cyclopentadienyl variety. There remain, however, a small but important class of penta-*hapto* (η^5) ligands which are based on acyclic fragments, and on larger ring systems, whose chemistry is formally related to that of the cyclopentadienyl type but may indeed be quite different. Both classes of ligand systems coordinated to ruthenium and osmium, are considered in this survey. The most prominent types of penta-*hapto* ligands covered in this survey are summarized in Fig. 1.

This survey has been broadly sub-divided into the chemistry of ruthenium and osmium metallocenes, the chemistry of half-sandwich compounds, and of dinuclear and polynuclear metal centres. Within these sub-divisions, further classification is introduced only to distinguish major trends and to facilitate the collation of data.

The last major surveys of ruthenium and osmium cyclopentadienyl chemistry included coverage to mid-1981 [1–6]. This survey covers the literature from then up to and including 1985.

B. METALLOCENES

Although the chemistry of ferrocene has been rapidly developed since its discovery in 1951, that of ruthenocene has received relatively little attention [7] and the chemistry of osmocene remains virtually unexplored [8]. This may largely be attributed to the lack of suitable synthetic routes which produce these complexes both in high yields and in substantial amounts. It is thus significant that a number of general, high yield synthetic procedures, easily adaptable to give large quantities of compound have recently been reported.

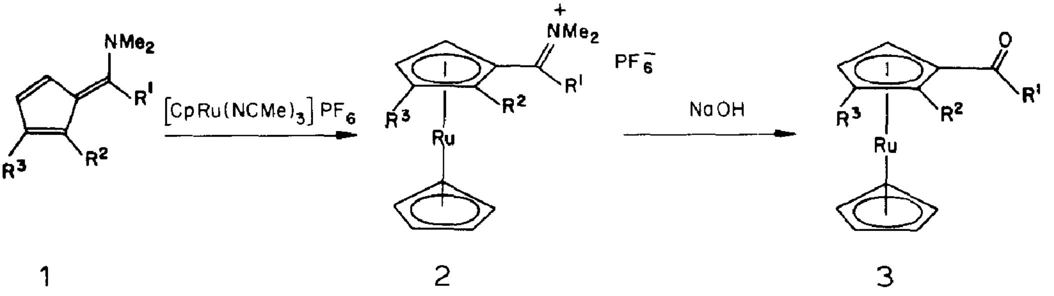
In a modification of the original Vitulli synthesis involving zinc reduction of ruthenium trichloride in the presence of cyclopentadiene [9], Vol'kenau and co-workers [10] have obtained ruthenocene in 95% yield in 10 g batches by carrying out the reaction under carefully controlled reaction conditions. Another high yield synthesis of ruthenocene is based on the treatment of $[RuCl_2(DMSO)_4]$ with a three-fold excess of NaC_5H_5 in DME [11]. Ruthenocene and mixed ligand ruthenocenes are obtained in good yield by the treatment of the complexes [(η-C_5R_5)Ru(COD)X] (R = H, alkyl; COD = cycloocta-1,5-diene; X = halide) with cyclopentadienyl anions in THF [12–14]. Decamethylruthenocene is obtained in low yield (18%) via the zinc reduction of ruthenium trichloride in the presence of pentamethylcyclopentadiene [15], and also by the direct reaction between ruthenium trichloride and pentamethylcyclopentadiene in ethanol or methanol (yield 10%) [16]. However, the most efficient route to this complex reported to date involves the treatment of the polymeric material [{$RuCl_2$(COD)}$_x$] (COD = cycloocta-1,5-diene) in ethanol with [$Bu^n_3Sn(C_5Me_5)$] (yields in excess of 70%, 5–10 g batches) [14,17]. (Ruthenocene has also been synthesized in high yield by this route but utilizing instead the reagent [$Bu^n_3Sn(C_5H_5)$].) The X-ray crystal structure of decamethylruthenocene has been determined at 303 K [14,17]. The complex has crystallographic mirror symmetry with an eclipsed conformation of permethylated cyclopentadienyl ligands. This contrasts with the staggered orientation in decamethylferrocene [18,19], and is apparently accommodated by the increased separation of the cyclopentadienyl rings in decamethylruthenocene when compared to the iron analogue, and the polarization stabilization of the ruthenium ion in the field of the two five-membered rings [14].

Osmocene has been prepared in high yield from [{$OsCl_2$(COD)}$_x$] and [$Bu^n_3Sn(C_5H_5)$] [14,17], while decamethylosmocene has been obtained directly from pentamethylcyclopentadiene and either $Na_2[OsCl_6]$ or $H_2[OsCl_6]$ in boiling alcohol, the former providing the superior synthetic route with yields in excess of 80% [14,17]. The X-ray crystal structure of decamethylosmocene has been determined [14] and found to be isostructural with decamethylruthenocene.

Reaction of $Tl[C_5(CO_2Me)_5]$ with [(η-C_5H_5)$Ru(PPh_3)_2Cl$] in air gives a good yield of the mixed ligand ruthenocene [Ru(η-C_5H_5){η-$C_5(CO_2Me)_5$}] [20]. The X-ray crystal structure of this complex (295 K) shows the two ring systems to be in an essentially eclipsed conformation. For the C_5H_5 ring, Ru–C distances are in the range 2.178–2.186 Å, and for the $C_5(CO_2Me)_5$ ligand in the range 2.157–2.178 Å.

Treatment of [(η-C_5H_5)$Ru(NCMe)_3$]PF_6 with 6-(dimethylamino)pentafulvalenes **1** (R^1 = H, Me, NMe_2; R^2 = H; R^1, R^2 = CH_2CH_2; R^3 = H, CO_2Et, Bu^t, $CONMe_2$) gives the isolable ruthenocenyl iminium or amidium salts **2** [21]. These salts react with ethanol and aqueous 2N NaOH to give the corresponding aldehydes, ketones or carboximides **3** (Scheme 1). This sequence provides a novel route to unsymmetrically substituted ruthenocenes carrying one or two substituents on the same ring, including to 1,3-disubstituted derivatives [21].

The unusual carbocation **4** (Fig. 2) has been prepared by the reaction of carbonyl(*p*-fluorophenyl)ruthenocene (itself prepared from ruthenocene-



Scheme 1.

carboxaldehyde and p-FC$_6$H$_4$Br) with trifluoroacetic acid. An estimation of the charge delocalization in **4** compared with that in the corresponding ferrocenyl analogue has been made on the basis of ^{19}F NMR studies [22].

A range of ruthenocene cyclophosphazene derivatives has recently been obtained from the reactions of halophosphazenes with lithioruthenocene or dilithioruthenocene (Scheme 2) [23]. The diverse products of these reactions have been characterized by a combination of ^{31}P, ^{1}H, ^{13}C and ^{19}F NMR spectroscopy, and mass spectrometry. The X-ray crystal structures of **5** and **6** have been determined confirming these particular structural assignments [23].

The novel thermal ring opening polymerization of mononuclear ruthenocene cyclophosphazenes (e.g. **5**) has been reported [24]. The structures of the polymers have been determined by a combination of NMR and IR spectroscopy and elemental analysis; the molecular weights were estimated by gel permeation chromatography. The experimental evidence is supportive of the ring opening polymerization process involving a single, specific cleavage of the cyclotriphosphazene rings [24].

The synthesis and physical properties of what are probably the first covalently linked viologen metallocenes has been reported (Fig. 3) [25]. These derivatives are interesting from the point of view of the potential use of viologen complexes in the photochemical generation of dihydrogen from water [26,27]. These metallocene complexes have some interesting visible

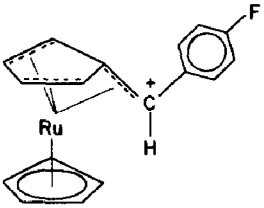


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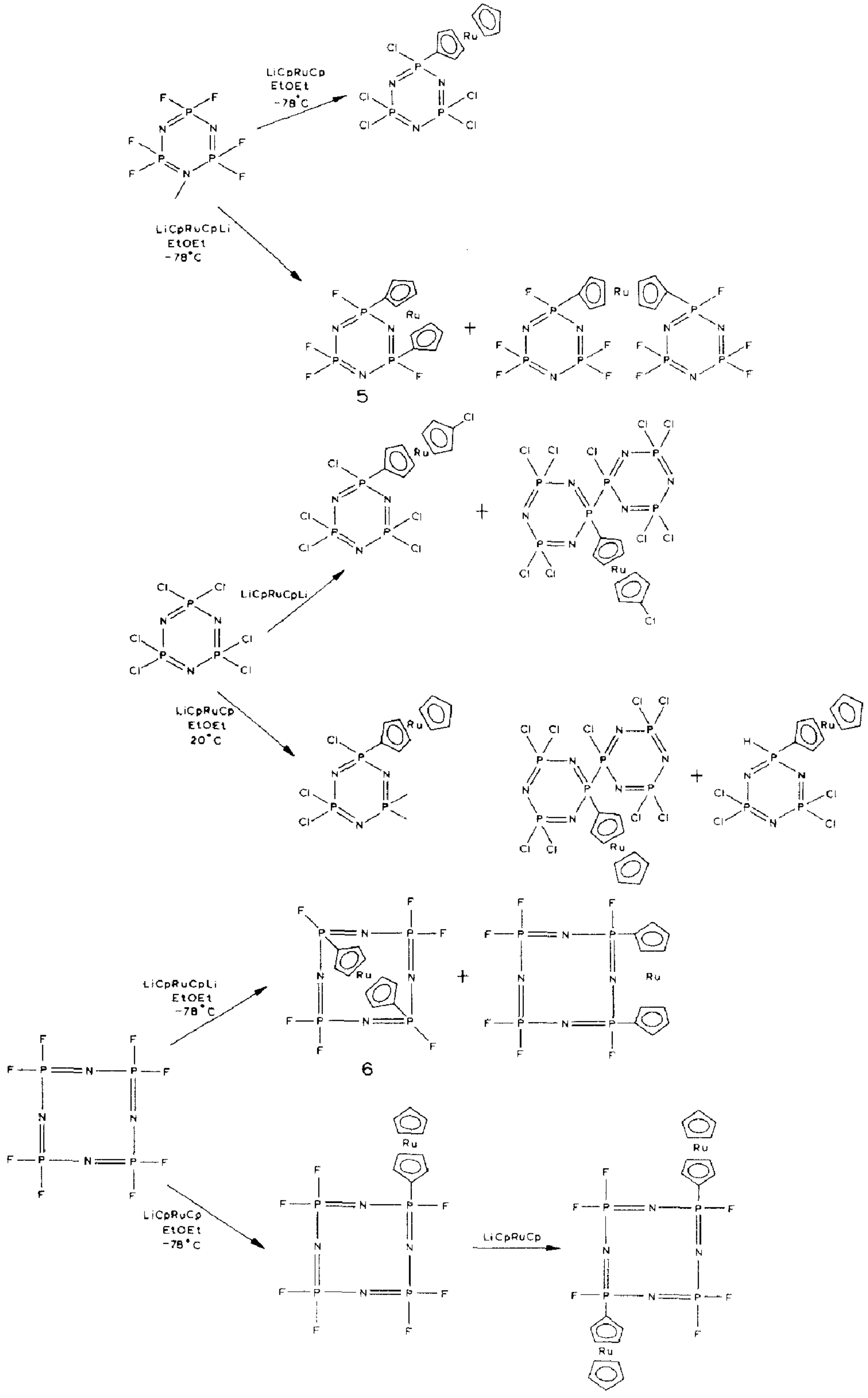
Fig. 2.


LiCpRuCp
EtOEt
-78°C
LiCpRuCpLi
EtOEt
-78°C
5
LiCpRuCpLi
LiCpRuCp
EtOEt
20°C
LiCpRuCpLi
EtOEt
-78°C
6
LiCpRuCp
EtOEt
-78°C
LiCpRuCp

Scheme 2.

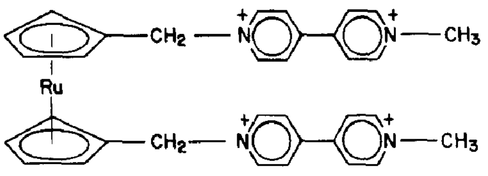


Fig. 3.

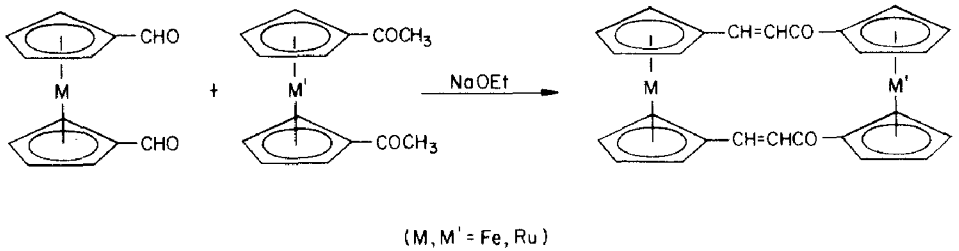
light-absorbing properties although the ruthenocene complexes seem less promising than the ferrocenyl analogues [25]. Work on the attachment of electroactive groups to the surfaces of electrodes for photovoltaic purposes has been extended from the use of ferrocene derivatives [28,29] to include the derivatization of *n*-type silicon electrodes using trichlorosilylruthenocene and 1,1′-dicarboxyruthenocene [30]. The derivatization of these electrodes was studied by cyclic voltametry with disappointing results; neither of the systems showed a photo-response which persisted beyond several hundred cycles [30].

The applications of labelled ruthenocenes, and to a much lesser extent labelled osmocenes, in diagnostic nuclear medicine have been detailed [31,32]. It is beyond the scope of this survey to discuss in detail recent developments in this field, and the reader is referred to a number of recent leading publications [33–39] and patents [40–42] for more information.

Several recent publications on ruthenocene and some of its derivatives, and on osmocene, have focused on the physical properties of these compounds. Measurements of proton spin–lattice relaxation times and differential thermal analysis have located a second- or higher-order phase transition for ruthenocene at 392 K [43]. As part of a detailed study of ^{99}Ru and ^{101}Ru NMR spectroscopy, ruthenocene has been reported to display a chemical shift of δ 1270 (^{99}Ru NMR, 4.614 MHz, 346 K, CH_2Cl_2) [44]. Incoherent quasi-elastic neutron scattering has been applied to the study of the re-orientational motions of the cyclopentadienyl rings in ruthenocene [45]. The results at room temperature show that ring re-orientation is slow and further, that this behaviour resembles that of ferrocene at low temperatures ($<$ 164 K) namely a five-fold jump re-orientation of the cyclopentadienyl ring [45]. The evaporation and sublimation of both ruthenocene and osmocene have been studied over a wide range of temperatures. The heats of sublimation, evaporation and fusion were determined [46]. The charge separation in a number of metallocenes has been studied by a theoretical analysis of IR band intensities using the first approximation of the effective charge model [47]. A mass spectral study of $[Ru(\eta\text{-}C_5H_5)\text{-}(\eta\text{-}C_5H_4R^1)]$ ($R^1 = CH_3$, Ph) and $[Ru(\eta\text{-}C_5H_4COCH_3)_2]$ has been reported [48].

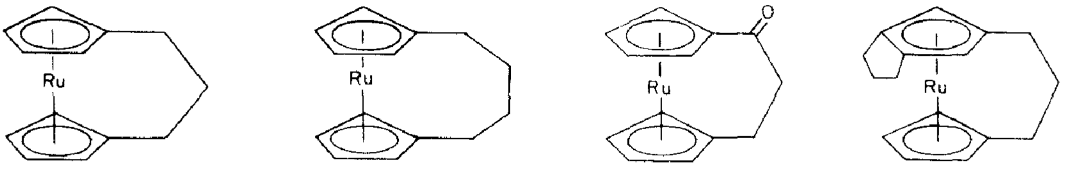
Several bridged ruthenocene derivatives containing the two cyclopentadienyl rings joined by 3-, 4- or 5-carbon bridges (ruthenocenophanes) have been synthesized [49]. The X-ray crystal structures of several such molecules (7–**10**) (Fig. 4) have been reported [50,51]. In all cases the cyclopentadienyl rings take on an eclipsed conformation; dihedral angles between the rings are 14.8, 1.2, 14.6 (and 15.0 for a second independent molecule) and 15.6° (for 7–**10** respectively).

The sodium ethoxide promoted reactions of 1,1′-ruthenocenedicarbaldehyde with 1,1′-diacetylruthenocene or 1,1′-diacetylferrocene, and 1,1′-ferrocenedicarbaldehyde with 1,1′-diacetylruthenocene gives, in good yield, the dibridged bimetallocenes [3,3](1,1′)ruthenocenophane-2,14-diene-1,16-dione, [3.3](1,1′)-ferrocenoruthenocenophane-13,25-diene-1,12-dione and [3.3]-(1,1′)ferrocenoruthenocenophane-2,14-diene-1,16-dione respectively (Scheme 3) [52]. In a similar manner the KOH-catalyzed condensation of 1,1′-ruthenocenedicarbaldehyde with acetone or 1,1′-bis(2-acetylvinyl)ferrocene and 1,1′-diacetylruthenocene with 1,1′-bis(2-formylvinyl)ferrocene gives [5.5](1,1′)ruthenocenophane-2,14,17,29-tetraene-1,16-dione, [5.5](1,1′)ferrocenoruthenocenophane-2,14,17,29-tetraene-1,16-dione and [5.5](1,1′)ferrocenoruthenocenophane-2,4,16,18-tetraene-1,20-dione (Scheme 4) [52].



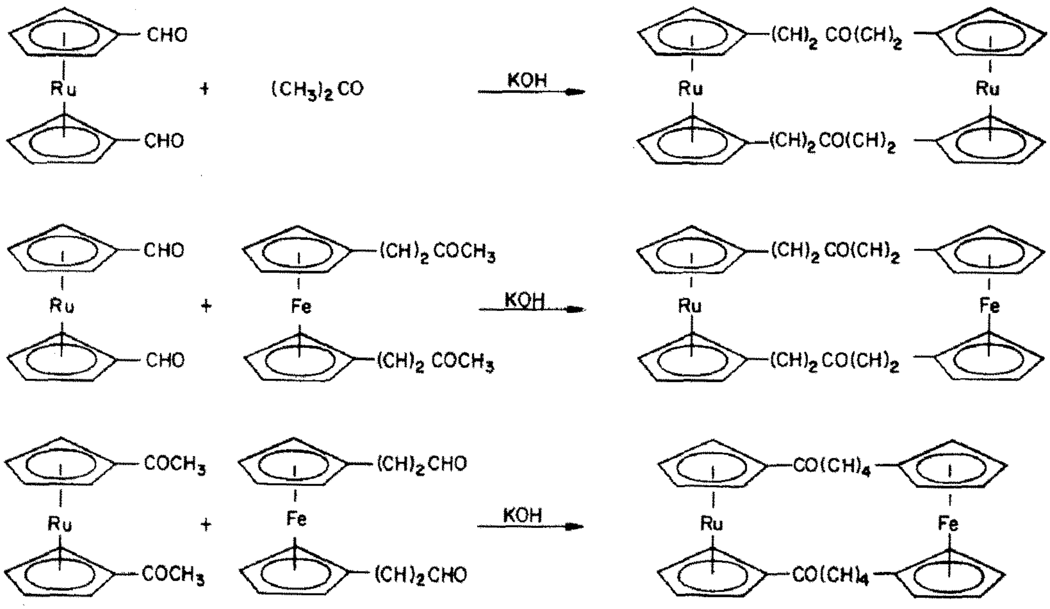
Scheme 3.

Dibridged ruthenocenes containing 3- and 4-carbon bridges [53] have been synthesized from the mono-bridged species (Scheme 5). On the basis of spectroscopic investigations there is some evidence for the expected greater molecular rigidity of these systems compared with the singly bridged ruthenocenophanes and also with the corresponding di-bridged ferrocenophanes.

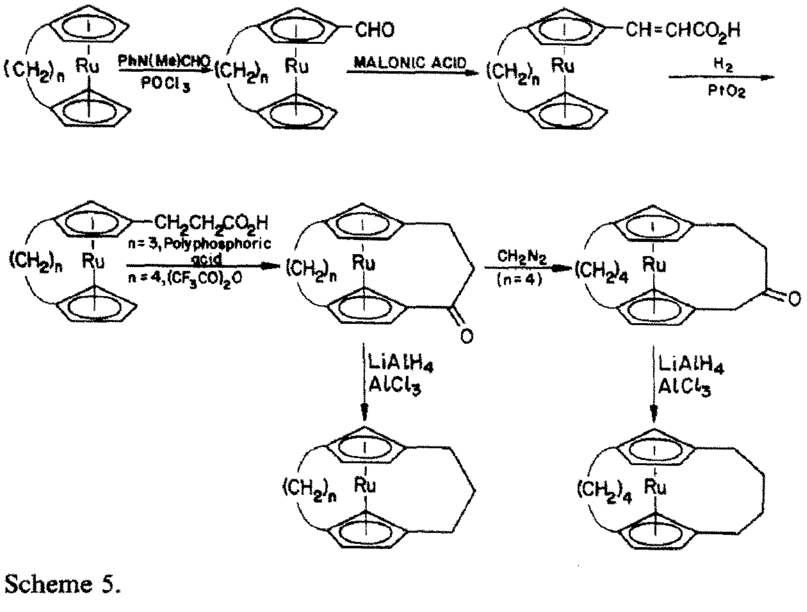


7 8 9 10

Fig. 4.

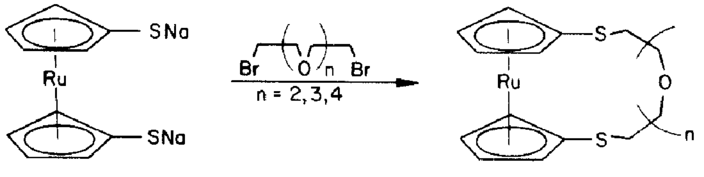


Scheme 4.



Scheme 5.

A novel range of bridged ruthenocene complexes containing unusual or heteroatom bridges has recently been reported. Reaction of 1,1′-dilithioruthenocene with elemental sulfur gave 1,2,3-trithia[*n*]ruthenocenophane which on reduction with $LiAlH_4$ gave ruthenocene-1,1′-dithiolate. Disodium ruthenocene-1,1′-dithiolate, **11**, reacted with the dihalide $BrCH_2(CH_2OCH_2)_4CH_2Br$, to give 1,16-dithia-4,7,10,13-tetraoxa [16]ruthenocenophane. In a similar manner 1,13-dithia-4,7,10-trioxa[13]ruthenocenophane and 1,10-dithia-4,7-dioxa[10]ruthenocenophane were also obtained (Scheme 6) [54,55]. The reactions of 1,1′-bis(3-choropropyl-1-thia)rutheno-



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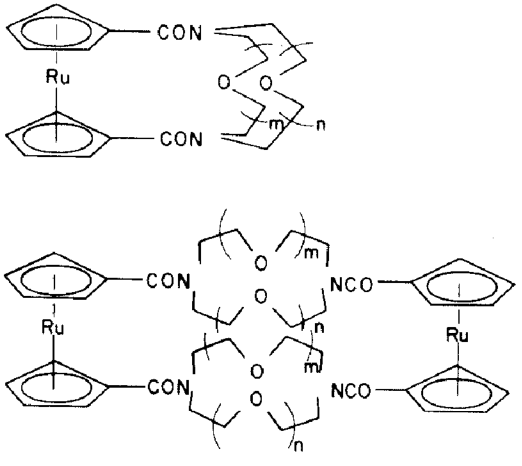
n=2,3,4

Scheme 6.



m , n = 1, 2 or 3

Fig. 5.

cene with disodium dithiolates have given a variety of polythia[*n*]ruthenocenophanes [56]. The ability of these macrocycles to extract alkali, alkaline earth, and transition metal cations has been investigated [54]. Novel ruthenocene-containing cryptands (Fig. 5) have been synthesized by routes originally devised for the analogous ferrocene cryptands [57,58] and have been characterized by ^{13}C NMR spectroscopy using the polarization transfer techniques INEPT and DEPT *, and by 2D-NMR procedures [59]. The separation of diastereomeric polyoxa[*n*]thiaruthenocenophanes by partition thin-layer chromatography and high performance thin-layer chromatography has been described [60].

The synthesis of ruthenocene derivatives containing two metallocene

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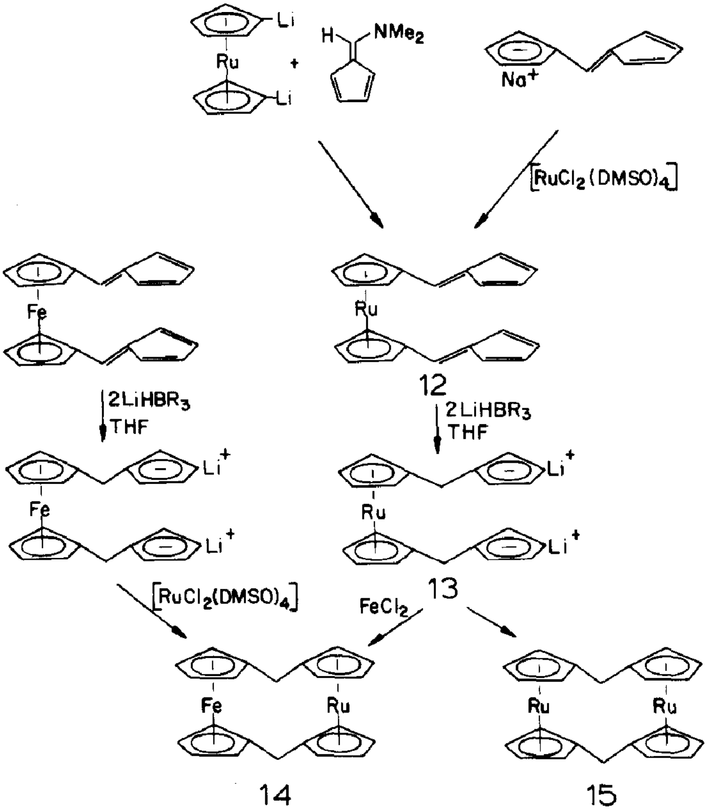
* INEPT = Insensitive Nuclear Enhancement by Polarization Transfer. DEPT = Distortionless Enhancement by Polarization Transfer.

centres has been the subject of recent attention [61]. The reaction of dilithioruthenocene with 6-(dimethylamino)fulvalene or of the fulvenyl cyclopentadienyl anion with $[RuCl_2(DMSO)_4]$ gives the ruthenocene derivative **12** (Scheme 7) [62]. Proton abstraction using a hydride source produces the 1,1′-bis(cyclopentadienylmethyl)ruthenocene dianion **13** which may be converted either to the mixed metal metallocenophane **14** using $FeCl_2$ or by reaction with $[RuCl_2(DMSO)_4]$ to the bis-ruthenium analogue **15** [62].



Scheme 7.

The interesting oxidation chemistry of **14** and **15** has been studied [63] and compared with that of [1.1] ferrocenophane, ferrocene and ruthenocene. The hetero-binuclear iron–ruthenium system **14** undergoes a ferrocene centred, reversible, one-electron oxidation (ferrocene undergoes a single, reversible one-electron oxidation [64,65] whereas [1.1]ferrocenophane undergoes two, reversible, one-electron oxidations [66]), and a ruthenium centred, irreversible, two-electron oxidation (analogous to ruthenocene itself [67]). In contrast though the two ruthenocenes in [1.1]ruthenocenophane **15** appear to interact strongly, the compound showing a quasi-reversible two-electron oxidation at an unusually low potential. The electronic structure of this di-cation awaits investigation but is proposed to be a mixed valence species each containing one ruthenocene and one ruthenocene dictation [63].

^{57}Fe NMR chemical shifts and ^{57}Fe, ^{13}C coupling constants in a series of α-ferrocenyl carbocations, including the binuclear $[(\eta\text{-}C_5H_5)Fe(\eta\text{-}C_5H_4CHC_5H_4)Ru(\eta\text{-}C_5H_5)]BF_4$, have been investigated and interpreted in terms of re-hybridization of the iron nonbonding *d* orbitals (a shielding effect) and the electron withdrawing effect of the substituent on the cyclic ligand (a deshielding effect) [68,69].

The X-ray crystal structure of biruthenocene has been determined [70] showing the molecule to have the biferrocenyl transoid structure [71] with the fulvalene system and both cyclopentadienyl rings planar and parallel (Fig. 6). The extent of rotation of the individual cyclopentadienyl rings in the crystal is suggested to be dependent on intermolecular interactions. In line with this, the intermolecular strain energies in crystals of biruthenocene and ruthenocene have been calculated as a function of the relative orientation of rings in individual molecules and compared with the iron analogue [72].

A recent report has detailed the synthesis of polymeric ruthenocene and osmocene species using the vinyl metallocenes as monomers [73,74]. The homopolymers of vinylruthenocene were found to be brittle and of little technological use, although co-polymers incorporating this unit did show useful physical characteristics. Little has been done on the corresponding osmium materials, although it can be anticipated that the recently reported high yield synthesis of osmocene [14,17] should make this chemistry more accessible.

Ferrocene readily undergoes oxidation reactions and it is thus surprising, considering that the higher oxidation states in the 4*d* and 5*d* metals are favoured compared with the 3*d* metals, that relatively little work has been reported on the oxidation of ruthenocene and osmocene derivatives.

Whereas ferrocene is cleanly oxidized to the ferrocenium ion by halogens, both osmocene and ruthenocene form complexes of the general type $[M(\eta\text{-}C_5H_5)_2X]^+$ containing the formally 7-coordinate metal in the +IV oxida-

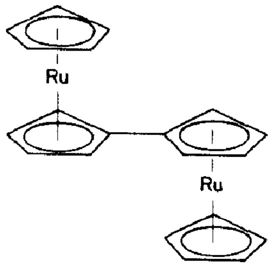


Fig. 6.

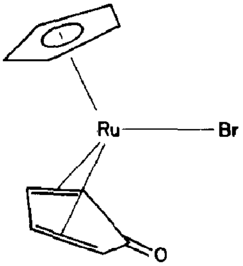


Fig. 7.

tion state [75]. Surprisingly little is known of the chemistry of these high oxidation state species. The major products of the aqueous decomposition of the species $[Ru(\eta\text{-}C_5H_5)_2X]^+$ (X = Cl, Br) are in both cases ruthenocene and the cyclopentadienone ruthenium(II) complexes $[Ru(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4O)X]$ [75]. The X-ray crystal structure of the latter (X = Br) has been determined confirming the assignment (Fig. 7).

It has recently been shown that, contrary to earlier reports [76–78] and in agreement with inferences drawn from electrochemical [79,80] and crystallographic [81] studies, the first stable product of the photochemical reaction of ruthenocene and de-aerated CCl_4 is $[Ru(\eta\text{-}C_5H_5)_2Cl]^+$ and not the ruthenocenium ion [82]. By conventional and laser flash photolysis, a precursor, suggested to be the elusive ruthenocenium species $[Ru(\eta\text{-}C_5H_5)_2Cl]$, has, however, been observed. This intermediate rapidly disproportionates to ruthenocene and $[Ru(\eta\text{-}C_5H_5)_2Cl]^+$

$$[Ru(\eta\text{-}C_5H_5)_2]\cdot CCl_4 \xrightarrow{h\nu} CT^{\#} \rightarrow [Ru(\eta\text{-}C_5H_5)_2Cl] + \cdot CCl_3$$

$$2[Ru(\eta\text{-}C_5H_5)_2Cl] \rightarrow [Ru(\eta\text{-}C_5H_5)_2] + Cl^- + [Ru(\eta\text{-}C_5H_5)_2Cl]^+$$

lending support to this assignment. Preliminary results on the gas-phase self-exchange electron transfer reaction

$$[Ru(\eta\text{-}C_5H_5)_2] + [Ru^*(\eta\text{-}C_5H_5)_2]^+ \rightleftharpoons [Ru(\eta\text{-}C_5H_5)_2]^+ + [Ru^*(\eta\text{-}C_5H_5)_2]$$

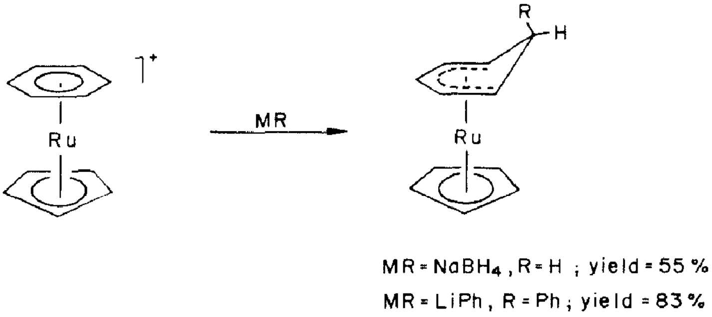
have been reported [83]. In marked contrast to ruthenocene, decamethylruthenocene is readily and cleanly oxidized to the ruthenocenium species using both electrochemical and chemical means [14,15,17]. The cation $[Ru(\eta\text{-}C_5Me_5)_2]^+$ has been the subject of an ESR study (CH_2Cl_2, 77 K) [15], although to date no structural information is available. The decamethylruthenocenium ion $[Ru(\eta\text{-}C_5Me_5)_2]^+$ undergoes facile, Lewis base promoted, deprotonation/oxidation reactions to yield, together with quantities of decamethylruthenocene, the tetramethylfulvalene cation $[(\eta\text{-}C_5$

[#] CT represents the reactive charge-transfer state.

Me$_5$)Ru(η^4-C$_5$Me$_4$-*exo*-CH$_2$)]$^+$. The latter may also be generated from [Ru(η-C$_5$Me$_5$)$_2$] and Ph$_3$C$^+$BF$_4^-$, and reacts with nucleophiles to give the neutral metallocenes [Ru(η-C$_5$Me$_5$)(η-C$_5$Me$_4$CH$_2$X)] (X = Pr$_2^i$N, 2,6-Pr$_2^i$-C$_6$H$_3$O, HO) [84]. The ruthenium- and osmium(IV) species [M(η-C$_5$Me$_5$)$_2$X]$^+$ (X = Br, I) have been obtained from the respective metallocene and the halogens [14,17]. Further, strong acids reversibly protonate the electron-rich metal centres. With CF$_3$CO$_2$H the cationic hydride complexes [M(η-C$_5$Me$_5$)$_2$H]$^+$ have been inferred from high field ^{1}H NMR resonances appearing at δ −8.30 (M = Ru) and δ − 15.67 (M = Os) [14,17].

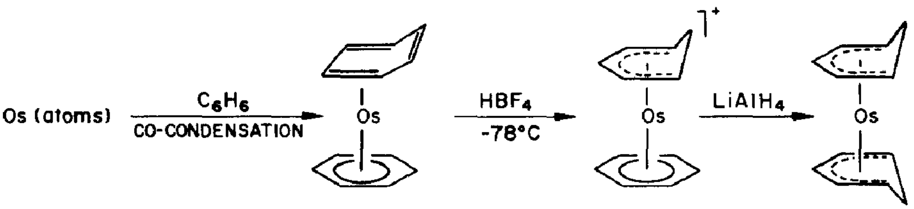
While there exists an extensive, well-documented structural and synthetic chemistry of ruthenocenes (and also to a certain extent of osmocenes), relatively little has, to date, been reported on ruthenium and osmium complexes containing the η^5-dienyl fragment either as part of larger cyclic, and of acyclic hydrocarbon ligand systems (the so-called "open metallocenes").

As expected, [(η-C$_5$H$_5$)Ru(η^6-arene)]$^+$ cations undergo nucleophilic attack on the arene ligand to give cyclopentadienylcyclohexadienylruthenium(II) complexes [85]. Thus, treatment of [(η-C$_5$H$_5$)Ru(η^6-C$_6$H$_6$)]BF$_4$ with NaBH$_4$ or phenyllithium gives the cyclohexadienyl complexes [Ru(η-C$_5$H$_5$)(η^5-C$_6$H$_7$)] and *exo*-[Ru(η-C$_5$H$_5$)(η^5-C$_6$H$_6$Ph)] respectively (Scheme 8) [86]. The most characteristic reaction of the former is the abstraction of hydride ion by *N*-bromosuccinimide to regenerate the starting complex. The complex *exo*-[Ru(η-C$_5$H$_5$)(η^5-C$_6$H$_6$Ph)] on the other hand, gives under similar conditions, a mixture of [(η-C$_5$H$_5$)Ru(η^6-C$_6$H$_5$Ph)]$^+$ and [(η-C$_5$H$_5$)Ru(η^6-C$_6$H$_6$)]$^+$ [86].



Scheme 8.

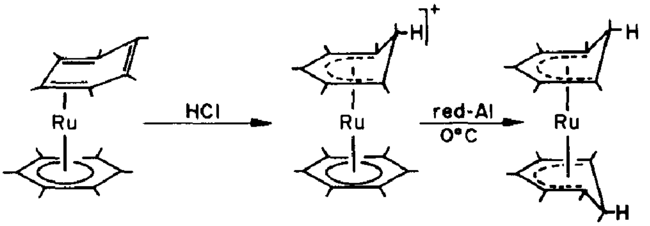
Co-condensation of osmium atoms with an excess of benzene gives the orange crystalline compound [Os(η^6-C$_6$H$_6$)(η^4-C$_6$H$_6$)], **16**, (Scheme 9) [87]. Protonation of **16** gives the cationic penta-*hapto* cyclohexadienyl compound [Os(η^6-C$_6$H$_6$)(η^5-C$_6$H$_7$)]BF$_4$, while hydride addition to the latter leads further to the neutral metallocene analogue [Os(η^5-C$_6$H$_7$)$_2$].



16

Scheme 9.

In a similar manner η^4,η^6-bis(arene)ruthenium(0) compounds have been treated first with HCl giving the η^5-cyclohexadienyl cations, then with sodium bis(2-methoxyethoxy)aluminium hydride at 0 °C to give the cyclohexadienyl analogues of ruthenocene (Scheme 10) [88]. The preparation of bis(η^5-cycloheptadienyl)-ruthenium (zinc reduction of $RuCl_3 \cdot xH_2O$ in ethanol in the presence of cyclohepta-1,3-diene) has been published [89].



Scheme 10.

The synthesis of the true "open metallocenes" bis(2,4-dimethylpentadienyl)ruthenium, **17**, and bis(2,3,4-trimethylpentadienyl)ruthenium, **18**, has been reported [90]. The reaction of ruthenium trichloride with zinc dust and the pentadienes in ethanol gives moderate yields of the products as reasonably air-stable, yellow, crystalline solids. In the room temperature ^1H NMR spectrum of **17**, four resonances are observed, while at low temperature, seven resonances emerge attributable to two (mirror imaged) rotational isomers which are frozen out in the unsymmetrical *gauche*-eclipsed conformation ($\Delta G^{\neq} = 9.73$ kcal mol^{-1}) (Fig. 8). In the case of **18**, similar behaviour is observed consistent with a similar unsymmetric, *gauche*-eclipsed ground state ($\Delta G^{\neq} = 10.16$ kcal mol^{-1}). The X-ray crystal structure of **18** has been determined [90], confirming that this complex does indeed adopt a

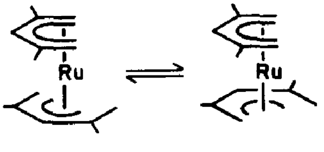
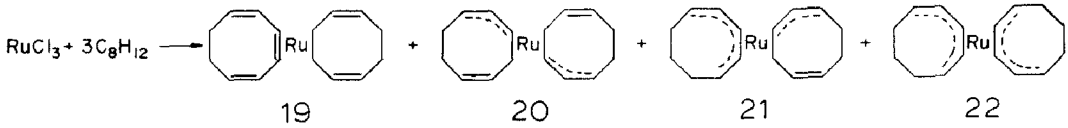


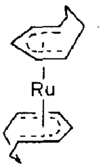
Fig. 8.

gauche-eclipsed conformation rather than the, at first sight, perhaps more favourable *anti* conformation.

The reaction of ruthenium trichloride, zinc powder and cycloocta-1,5-diene in ethanol has been reported as a route to the ruthenium(0)-cyclopolyolefin complex [Ru(η^6-cyclooctatriene)(η^4-cyclooctadiene)] [9, 89,91]. However, this reaction is more complex than at first sight involving at least the four isomers **19**–**22** (Scheme 11) [92]. As might have been expected, **19**–**21** are kinetic products of the reaction and were thus found to isomerize thermally to the thermodynamic product **22**. The high stability of **22** is attributed to both the extensive delocalization of π-electrons within the planar "open ruthenocene" η^5-ligand, and to minimal inter-ring steric repulsions. In this regard, the most stable conformation of **22** is shown in Fig. 9.



Scheme 11.



22

Fig. 9.

C. HALF-SANDWICH COMPOUNDS

A not unexpected feature of the chemistry of ruthenocene and osmocene is the somewhat limited reactivity of these compounds, encompassing essentially substitutive chemistry of the cyclopentadienyl ligands and certain well-defined reactions of the metal core e.g. oxidation, protonation, adduct formation with Lewis acids [93–95]. In contrast, half-sandwich complexes of ruthenium and osmium, containing only a single cyclopentadienyl ligand, would be expected to display considerably enhanced reactivity still partly controlled by the cyclopentadienyl ligand, but largely dictated by the remaining ligands in the coordination sphere of the metal. In fact, the spectrum of reactivity and chemistry shown by half-sandwich complexes of ruthenium and osmium is remarkable, especially considering the limited number of synthetic precursors which have been utilized to date.

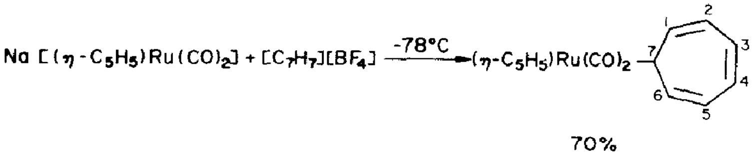
(i) Complexes of the type $[(\eta\text{-}C_5R_5)M(CO)_2X]$ (M = Ru, Os)

The preparation and fundamental reactivity patterns of the neutral half-sandwich complexes $[(\eta\text{-}C_5H_5)Ru(CO)_2X]$ (X = H, halide, alkyl etc.) have been surveyed [7]. Other synthetic procedures [96] involve the direct reaction of $[(\eta\text{-}C_5H_5)_2Ru_2(CO)_4]$ with CX_4 (X = Cl, Br) giving $[(\eta\text{-}C_5H_5)Ru(CO)_2X]$ in good yields, or alternatively, the reaction of $[(\eta\text{-}C_5H_5)Ru(CO)_2H]$ with CX_4 (X = Cl, Br). The iodo derivative $[(\eta\text{-}C_5H_5)Ru(CO)_2I]$ is prepared from $[(\eta\text{-}C_5H_5)Ru(CO)_2H]$ and MeI [96]. The X-ray crystal structures of $[(\eta\text{-}C_5H_5)Ru(CO)_2Br]$ and $[(\eta\text{-}C_5Me_4Et)Ru(CO)_2Br]$ have recently been determined [97]; the former revealed an ordered, delocalized cyclopentadienyl ring positioned so that one carbon atom closely eclipses the bromo ligand, whereas the latter was found to have a staggered conformation with the ring carbon bearing the ethyl substituent *trans* to the bromo ligand [97]. The ultraviolet photoelectron spectrum of $[(\eta\text{-}C_5H_5)Ru(CO)_2Cl]$ together with those of *exo* and *endo* $[(\eta\text{-}C_5H_5)Ru(\eta^3\text{-allyl})(CO)]$ (allyl = C_3H_5, 2-Me-C_3H_4) have been reported [98]. Reaction of $[Ru_3(CO)_{12}]$ with *R*-(−)-menthylcyclopentadiene or *S*-(+)-neomenthylcyclopentadiene in *i*-octane (120 °C, 5 d) gave good yields of $[(\eta\text{-}C_5H_4R^*)_2Ru_2(CO)_4]$ (R* = menthyl, neomenthyl) [99]. Using established procedures [100–102] the mononuclear complexes $[(\eta\text{-}C_5H_4R^*)Ru(CO)_2X]$ (R* = menthyl, X = Cl, Br; R* = neomenthyl, X = Cl, Br, I) have been synthesized.

Treatment of THF solutions of $[(\eta\text{-}C_5H_5)_2Ru_2(CO)_4]$ with $M[HBEt_3]$ (M = Li, Na, K) followed by the addition of methyl iodide or benzyl chloride has given 30–40% yields of the alkyl ruthenium complexes $[(\eta\text{-}C_5H_5)Ru(CO)_2R]$ (R = Me, $CH_2C_6H_5$) [103,104]. The best yields are obtained with the potassium salt. Decided advantages of this synthetic procedure (which incidentally should be generally applicable) as opposed to the more traditional sodium amalgam route include improved yields of product and simplified work-up procedures. UV irradiation of $[(\eta\text{-}C_5H_5)Ru(CO)_2Me]$ in the presence of PPh_3 gives $[(\eta\text{-}C_5H_5)Ru(CO)(PPh_3)Me]$ in good yield, a compound also obtained by the carbonylation of $[(\eta\text{-}C_5H_5)Ru(PPh_3)_2Me]$ [104].

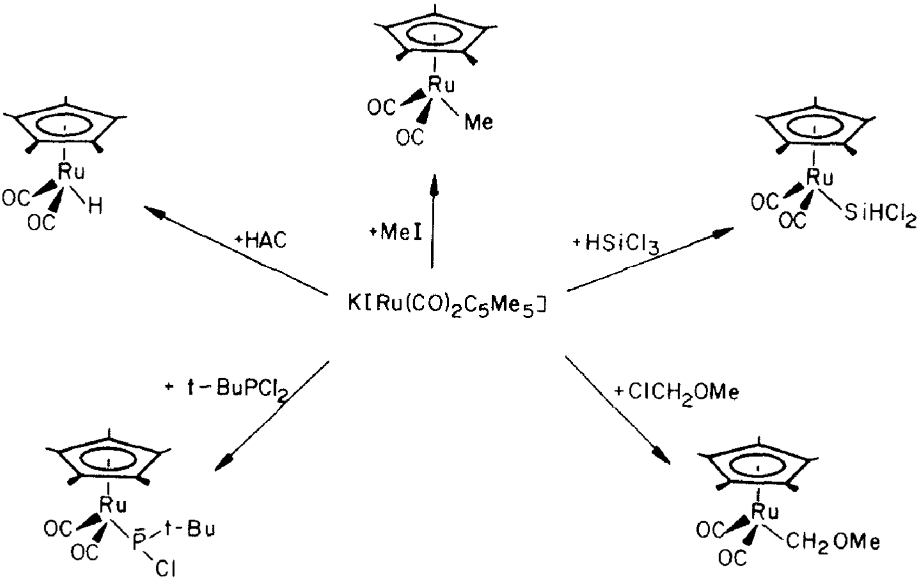
Traces of the haloalkyl complex $[(\eta\text{-}C_5H_5)Ru(CO)_2(CH_2Cl)]$ are obtained, together with $[(\eta\text{-}C_5H_5)Ru(CO)_2(CH_2OMe)]$, as the products of treating $Na[(\eta\text{-}C_5H_5)Ru(CO)_2]$ with chloromethylmethyl ether [105]. Moderate yields (15%) of $[(\eta\text{-}C_5H_5)Ru(CO)_2(CH_2Cl)]$ are, however, obtained by the treatment of a hexane solution of $[(\eta\text{-}C_5H_5)Ru(CO)_2(CH_2OMe)]$ with dry HCl [105]. The attempted carbonyl substitution of $[(\eta\text{-}C_5H_5)Ru(CO)_2(CH_2Cl)]$ with PPh_3 in methanol (reflux, 5 d) gave only the alcoholysis product $[(\eta\text{-}C_5H_5)Ru(CO)_2(CH_2OMe)]$ [106].

The recently synthesized $[Re(CO)_5(7\text{-}\eta^1\text{-}C_7H_7)]$, the first η^1-cycloheptatrienyl complex of a transition metal, is fluxional by a 1,2-migration of the metal [107]. The ruthenium complex $[(\eta\text{-}C_5H_5)Ru(CO)_2(7\text{-}\eta^1\text{-}C_7H_7)]$ (Scheme 12) displays two concurrent fluxional pathways, 1,2- and 1,4-migration. The former is the dominant pathway occurring at a rate five or six times faster than 1,4-migration. No evidence was found for a 1,3-migration [108].



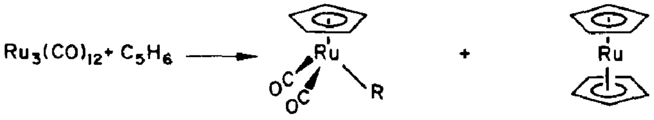
Scheme 12.

The smooth reduction of $[(\eta\text{-}C_5Me_5)_2Ru_2(CO)_4]$ occurs with Na–K alloy giving the anion $K[(\eta\text{-}C_5Me_5)Ru(CO)_2]$ isolable as a light-brown, pyrophoric powder. Treatment of the anion with HCl, MeI, $MeOCH_2Cl$, $HSiCl_3$ and PBu^tCl_2 gives the complexes $[(\eta\text{-}C_5Me_5)Ru(CO)_2X]$ (X = H, Me, CH_2OMe, $SiHCl_2$, PBu^tCl) (Scheme 13). Treatment of $[(\eta\text{-}C_5Me_5)Ru(CO)_2(CH_2OMe)]$ with HCl gives $[(\eta\text{-}C_5Me_5)Ru(CO)_2(CH_2Cl)]$ [109].



Scheme 13.

The preparation of $[(\eta\text{-}C_5H_5)_2Ru_2(CO)_4]$ from $[Ru_3(CO)_{12}]$ and cyclopentadiene was reported by Humphries and Knox [110] to proceed in boiling heptane via the intermediate hydride complex $[(\eta\text{-}C_5H_5)Ru(CO)_2H]$. A similar reaction carried out in boiling methylcyclohexane [111] revealed a second, in this case major, product [(η-C_5H_5)Ru$(CO)_2$($COC_{10}H_{13}$)], **23**, (20–60% yield) together with small amounts of [(η-C_5H_5)Ru$(CO)_2$($C_{10}H_{13}$)], **24**, (1–2%) and ruthenocene (Scheme 14). The X-ray crystal structure of **23** has been determined revealing that the tricyclic organic unit assumes an *endo* configuration and the acyl function is *exo* linked at the C(13) position (Fig. 10). Assuming that the carbonylation of **24** to **23** occurs with retention of configuration at the C(13) site, **24** can only be derived from a stereo- and regiospecific *exo* addition of the ruthenium hydride bond in [(η-C_5H_5)Ru$(CO)_2$H] to the C(5) position of *endo*-dicyclopentadiene (Scheme 15).



23, R = $COC_{10}H_{13}$, 20-60%
24, R = $C_{10}H_{13}$, 1 - 2 %

Scheme 14.

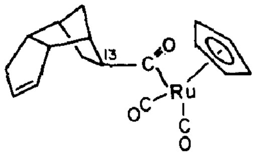
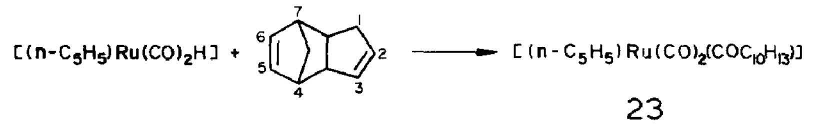


Fig. 10.



Scheme 15.

The oxidative cleavage reactions of the alkyl complex [(η-C_5H_5)Ru$(CO)_2$Me] and of the compounds [(η-C_5H_5)Ru(PPh_3)(L)R] (L = CO, PPh_3; R = Me, $CH_2C_6H_5$) with halogens, hydrogen chloride, mercury(II) halides and copper(II) halides have been investigated and compared with the reactivity of the corresponding iron systems [103,104]. The compound [(η-C_5H_5)Ru$(CO)_2$Me] is more difficult to oxidize than its iron counterpart and also has a higher oxidation potential than the compounds [(η-C_5H_5)Ru(PPh_3)(L)R] (L = CO, PPh_3; R = Me, $CH_2C_6H_5$). A summary of results is presented in Table 1.

TABLE 1

Cleavage reactions of $[(\eta\text{-}C_5H_5)Ru(CO)_2Me]$ with a variety of oxidants [a]

Oxidant	Solvent	Products (% yields)	
$HgCl_2$	acetone-d_6	$[(\eta\text{-}C_5H_5)Ru(CO)_2Cl]$ (100)	MeHgCl (100)
$HgBr_2$	acetone-d_6	$[(\eta\text{-}C_5H_5)Ru(CO)_2Br]$ (100)	MeHgBr (100)
$HgCl_2$	dichloromethane-d_2	no reaction after 4 h	–
Br_2	chloroform-d_1	$[(\eta\text{-}C_5H_5)Ru(CO)_2Br]$ (70)	MeBr (100)
I_2	chloroform-d_1	$[(\eta\text{-}C_5H_5)Ru(CO)_2I]$ (100)	MeI (100)
$CuBr_2$ (Cu:Ru 2:1)	acetone-d_6	$[(\eta\text{-}C_5H_5)Ru(CO)_2Br]$ (100)	MeBr (100)
$CuBr_2$ (Cu:Ru > 4:1)	dichloromethane-d_2	no reaction after 1 h	–
$CuCl_2 \cdot 2H_2O$ (Cu:Ru > 4:1)	acetone-d_6	no reaction after 5 h	–

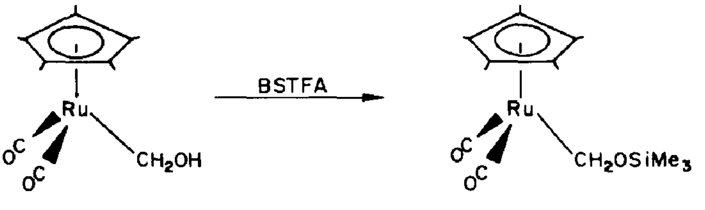
[a] Data reported in ref. 104.

The ruthenium methyl complex $[(\eta\text{-}C_5H_5)Ru(CO)_2Me]$ not unexpectedly inserts CO (60°C, 1000 p.s.i.g.) giving the acyl species $[(\eta\text{-}C_5H_5)Ru(CO)_2\{C(O)Me\}]$ in moderate yield [112].

The photolysis reactions of $[(\eta\text{-}C_5H_5)Ru(CO)_2R]$ ($R = Me$, Et, $n\text{-}C_5H_{11}$) have been shown to involve dissociative loss of CO as the primary pathway of photoreaction [113–115]. In a detailed study, the photolysis reactions of $[(\eta\text{-}C_5H_5)Ru(CO)_2R]$ (**25**, R = Me; **26**, R = Et) have been investigated by a combination of solution (243 K) and matrix isolation (12 K) techniques [115]. The mechanisms of the photoreactions of these complexes in alkanes in the absence and presence of potential ligands have been proposed to involve dissociative loss of CO as the primary process subsequent to near-UV excitation. Photolysis of **25** alone in pentane at -30°C yields the dimer $[(\eta\text{-}C_5H_5)_2Ru_2(CO)_4]$ together with CH_4, C_2H_6 and traces of CO. Matrix isolation studies, in particular the observation of bands assignable to $[(\eta\text{-}C_5H_5)Ru(^{12}CO)Me]$ and $[(\eta\text{-}C_5H_5)Ru(^{13}CO)Me]$ in ^{13}CO-doped CH_4 matrices, provides evidence for the coordinatively unsaturated species $[(\eta\text{-}C_5H_5)Ru(CO)Me]$. The expected reactivity of the sixteen-electron species has been demonstrated by trapping with N_2 and C_2H_4 giving $[(\eta\text{-}C_5H_5)Ru(CO)(N_2)Me]$ and $[(\eta\text{-}C_5H_5)Ru(CO)(C_2H_4)Me]$ respectively at 12 K. The latter has also been synthesized at -30°C in pentane by the irradiation of **25** in the presence of C_2H_4, providing in this way some evidence for the intermediacy of $[(\eta\text{-}C_5H_5)Ru(CO)Me]$ in the formation of $[(\eta\text{-}C_5H_5)_2Ru_2(CO)_4]$ dimers under similar conditions. The UV irradiation of **26** in pentane at -30°C proceeds more slowly than that of the methyl complex, giving via the primary photoproduct $[(\eta\text{-}C_5H_5)Ru(CO)_2H]$, the dinuclear complex $[(\eta\text{-}C_5H_5)_2Ru_2(CO)_2(\mu\text{-}H)_2]$ which contains a formal ruthenium–ruthenium double bond by analogy with $[(\eta\text{-}C_5Me_5)_2M_2(CO)_2(\mu\text{-}H)_2]$ (M = Ru [116], Os [117,118]). Photolysis of $[(\eta\text{-}$

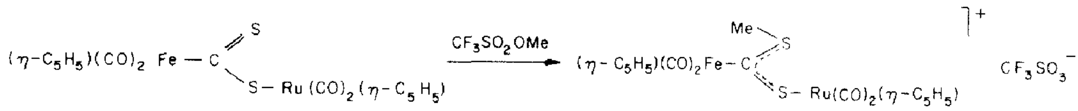
$C_5H_5)Ru(CO)_2Et]$ in CH_4 matrices gives the β-elimination product $[(\eta$-$C_5H_5)Ru(CO)_2H]$ together with $[(\eta$-$C_5H_5)Ru(CO)(C_2H_4)H]$, while in N_2 doped matrices $[(\eta$-$C_5H_5)Ru(CO)(N_2)H]$ is formed. An interesting feature of the photochemistry of **26** is revealed in CO matrices where there is some evidence for ring-slippage products of the type $[(\eta^3$-$C_5H_5)Ru(CO)_3Et]$ and $[(\eta^3$-$C_5H_5)Ru(CO)_3H]$ [115].

The synthesis and characterization of the hydroxymethyl complexes $[(\eta$-$C_5H_5)Ru(CO)_2(CH_2OH)]$, **27**, [119] and $[(\eta$-$C_5Me_5)Ru(CO)_2(CH_2OH)]$, **28**, [120] (analogues of the osmium complex $[(\eta$-$C_5Me_5)Os(CO)_2(CH_2OH)]$ [121]) have recently been reported. In each case, reduction of the tricarbonyl cations $[(\eta$-$C_5R_5)Ru(CO)_3]^+$ ($R = H$, Me) with excess $NaBH_3CN$ in methanol gives the products in moderate yield. (The complex $[(\eta$-$C_5Me_5)Ru(CO)_2(CH_2OH)]$ has also been obtained in lower yields utilizing a range of other reducing systems including $NaBH_4/THF/H_2O$ and NaH_2AlEt [120].) In the case of $[(\eta$-$C_5Me_5)Ru(CO)_2(CH_2OH)]$ other products of the reaction included $[(\eta$-$C_5Me_5)Ru(CO)_2H]$ and $[(\eta$-$C_5Me_5)Ru(CO)_2(CH_2OCH_3)]$ [120]; the latter compound is the major isolated product if only one equivalent of $NaBH_3CN$ is used. Complex **27** is stable in solution below 60 ° C, while **28** can be heated at 85 ° C for several hours with no significant decomposition. However, at 127 ° C (toluene-d_8), **28** undergoes a first-order decomposition ($k = 2.9 \times 10^{-3}$ s^{-1}, $\Delta G^{\neq}_{400} = 28.3$ kcal mol^{-1}). Both **27** and **28** do not undergo carbon monoxide insertion even under extreme conditions (4000–5000 p.s.i., 80 ° C) and are functionalized by trimethylsilylating agents (Scheme 16). Complex **27** reacts instantaneously with Bu^tOK in THF to eliminate formaldehyde, and with acetyl chloride and pyridine or acetic anhydride to give the ester derivative $[(\eta$-$C_5H_5)Ru(CO)_2\{CH_2OC(O)CH_3\}]$. The methoxymethyl complex $[(\eta$-$C_5H_5)Ru(CO)_2(CH_2OMe)]$ is formed slowly from **27** and methanol [119].



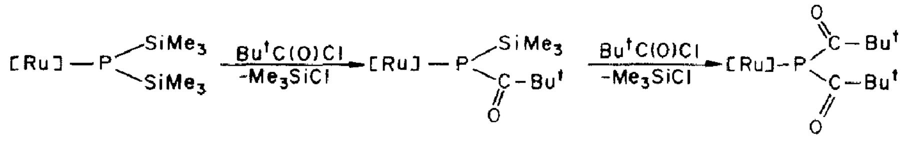
Scheme 16.

Displacement of the halide in $[(\eta$-$C_5H_5)Ru(CO)_2I]$ by $[(\eta$-$C_5H_5)Fe(CO)_2(CS_2)]^-$ affords the ferrio(dithiocarboxylate) complex $[(\eta$-$C_5H_5)Ru(CO)_2SC(S)Fe(CO)_2(\eta$-$C_5H_5)]$, **29**, [122]. The thione–sulfur function readily reacts with electrophiles; thus **29** is readily alkylated by methyl trifluoromethane sulfonate in CH_2Cl_2 to give the stable dithiocarbene triflate salt **30** (Scheme 17).



Scheme 17.

The reaction of $[(\eta\text{-}C_5Me_5)Ru(CO)_2\{P(SiMe_3)_2\}]$ with two equivalents of pivaloyl chloride in cyclopentane (20 °C, 1 h) gives, after work-up, orange-yellow crystals of the diacyl-phosphido complex $[(\eta\text{-}C_5Me_5)Ru(CO)_2P\{C(O)Bu^t\}_2]$, **31**, [123]. An X-ray crystal structure determination reveals the presence of a pair of enantiomeric molecules of the complex in the asymmetric unit. The two pivaloyl substituents are accommodated as right and left oriented "propellors". A probable mechanism for the formation of **31** is depicted in Scheme 18.



31

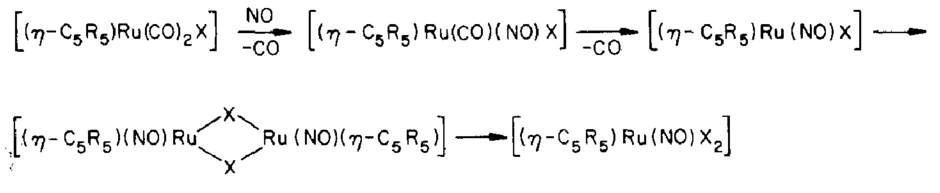
([Ru] = $(\eta\text{-}C_5Me_5)Ru(CO)_2$)

Scheme 18.

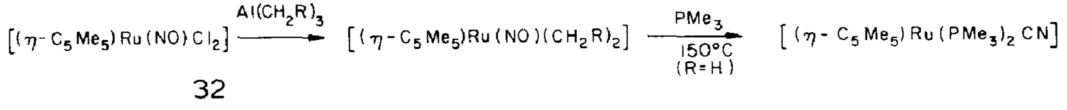
One of the distinctive features of the chemistry of $[(\eta\text{-}C_5H_5)Ru(CO)_2X]$ type complexes is the reluctance to undergo carbonyl substitution reactions. The substitution of one or both carbonyl groups by isonitriles is facilitated by the use of carbonyl substitution catalysts, in this case $[(\eta\text{-}C_5R_5)_2Fe_2(CO)_4]$ (R = H, Me) [124]. Complexes of the type $[(\eta\text{-}C_5H_5)Ru(CNR)(CO)X]$, $[(\eta\text{-}C_5H_5)Ru(CNR)_2X]$ and $[(\eta\text{-}C_5H_5)Ru(CNR)_3]X$ ($R = Bu^t$, $CH_2C_6H_5$, 2,6-$Me_2C_6H_3$; X = Cl, I) have been characterized [124]. It is to be noted that the physical properties of some of these products differ significantly from that of $[(\eta\text{-}C_5H_5)Ru(CNBu^t)_2Cl]$, recently reported by Bruce and Wallis [125], casting some doubt on the identity of the compound described in this report.

Perhaps one of the most significant advances in the chemistry of half-sandwich complexes of ruthenium in recent years has been the discovery of synthetic routes to surprisingly stable ruthenium(IV) complexes containing the cyclopentadienyl moiety. The oxidative addition of allylic halides to $[(\eta\text{-}C_5H_5)Ru(CO)_2X]$ and $[(\eta\text{-}C_5Me_5)Ru(CO)_2X]$ (X = Br, Cl) in *n*-decane (typically 140 °C, 3–10 h) gives good yields of the ruthenium(IV)-allyl complexes $[(\eta\text{-}C_5R_5)Ru(\eta^3\text{-allyl})X_2]$ [126]. Similar products have been obtained from the treatment of $[\{(\eta\text{-}C_5Me_5)RuCl_2\}_x]$ with allyl halides [127] and the unusual oxidative additions of allyl and vinyl halides with the reactive complexes $[(\eta\text{-}C_5R_5)Ru(\eta\text{-}C_8H_{12})X]$ (R = H, alkyl; C_8H_{12} = cycloocta-1,5-diene; X = halide) [128]. Reaction of the compounds $[(\eta\text{-}C_5R_5)Ru(\eta^3\text{-allyl})X_2]$ (R = H, Me; X = Cl, Br) with carbon monoxide (140 °C in diglyme) regenerates the ruthenium(II) complexes $[(\eta\text{-}C_5R_5)Ru(CO)_2X]$ and (in less than quantitative yields) the allyl halides [126]. Carbonylation of the allyl moiety was not observed to occur. Treatment of $[(\eta\text{-}C_5R_5)Ru(\eta^3\text{-allyl})X_2]$ with methyl lithium (giving $[(\eta\text{-}C_5R_5)Ru(\eta^3\text{-allyl})(CH_3)(X)]$) followed by thermal decomposition in the presence of donor ligands leads to a range of $[(\eta\text{-}C_5R_5)RuL_2X]$ type complexes including, in the presence of CO, $[(\eta\text{-}C_5R_5)Ru(CO)_2X]$ [129].

The compounds $[(\eta\text{-}C_5R_5)Ru(CO)_2X]$ (R = H, Me; X = Cl, Br, I) react readily with NO under UV irradiation to give the ruthenium(IV) nitrosyl complexes $[(\eta\text{-}C_5R_5)Ru(NO)X_2]$ (yields 30–45%) [130]. These complexes have an analogue in iron chemistry $[(\eta\text{-}C_5H_5)Fe(NO)I_2]$, obtained by the oxidative cleavage of $[(\eta\text{-}C_5H_5)_2Fe_2(NO)_2]$ with iodine [131]. A possible mechanism which would account for the formation of the compounds $[(\eta\text{-}C_5R_5)Ru(NO)X_2]$ is shown in Scheme 19. It is interesting to note that one proposed intermediate $[(\eta\text{-}C_5R_5)_2Ru_2(NO)_2Cl_2]$ has recently been obtained by the treatment of $[(\eta\text{-}C_5R_5)Ru(\eta\text{-}C_8H_{12})Cl]$ with NO [132]. Reaction of this compound with excess iodine gives essentially quantitative yields of the ruthenium(IV) species $[(\eta\text{-}C_5R_5)Ru(NO)I_2]$ [132]. Treatment of $[(\eta\text{-}C_5Me_5)Ru(CO)_2Cl]$ with NOCl in dichloromethane provides a further synthetic route to $[(\eta\text{-}C_5Me_5)Ru(NO)Cl_2]$, **32**, [133]. Dialkylation of **32** is readily achieved with trialkylaluminium compounds $Al(CH_2R)_3$ (R = H, Me) giving the complexes $[(\eta\text{-}C_5Me_5)Ru(NO)(CH_2R)_2]$ (Scheme 20) in good

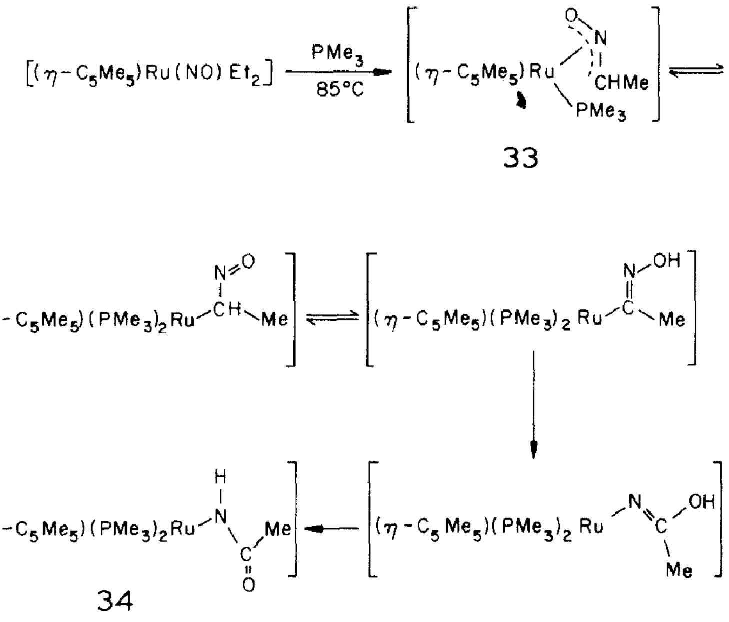


Scheme 19.



Scheme 20.

yield. In contrast to [(η-C_5Me_5)Fe(NO)Me_2] [134], these derivatives show unusual thermal stability. Nevertheless, heating [(η-C_5Me_5)Ru(NO)Me_2] in benzene (150 °C, 20 h) with trimethylphosphine gives the complex [(η-C_5Me_5)Ru(PMe_3)$_2$CN], also obtainable from [(η-C_5Me_5)Ru(PMe_3)$_2$Cl] and KCN in methanol. Heating [(η-C_5Me_5)Ru(NO)Et_2] at 85 °C in benzene with PMe_3 gives the ruthenium oximate complex [(η-C_5Me_5)Ru(PMe_3)$_2$(η-ONCHCH_3)], **33** (Scheme 21). Further heating of **33** gives the isomeric *N*-ruthenium amide complex **34**. Confirmation of this assignment was obtained by the independent synthesis of **34** from [(η-C_5Me_5)Ru(PMe_3)$_2$Cl] and $CH_3CONHLi$. A proposed mechanism to account for these reactions is given in Scheme 21. The novel 16-electron complexes [(η-C_5H_5)M(NO)R_2]

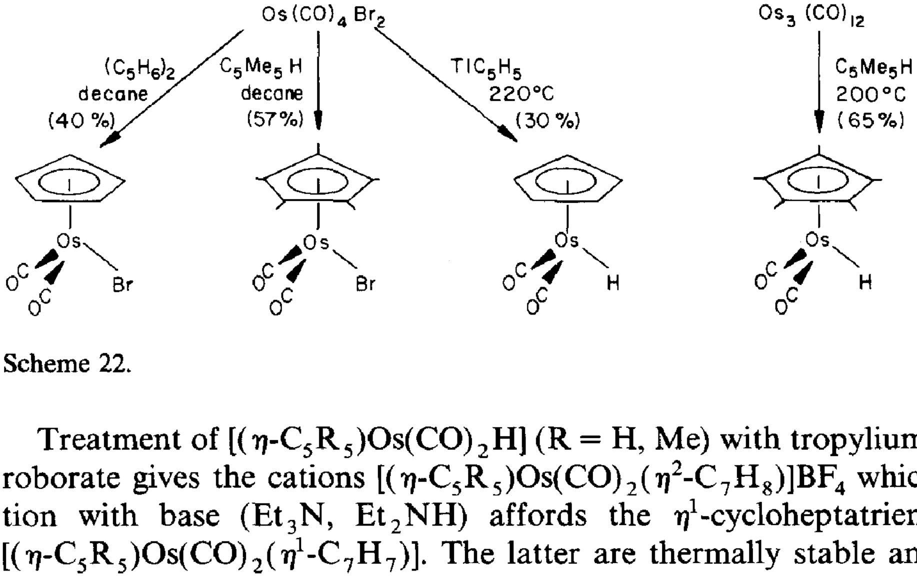


Scheme 21.

(M = Mo, W) have been modelled by the use of Fenske–Hall MO calculations performed on the 18-electron [(η-C_5H_5)Ru(NO)Me_2] [135].

In contrast to the well-documented lack of substitutive reactivity which is associated with the halide complexes [(η-C_5R_5)Ru(CO)$_2$X], the compound [(η-C_5H_5)Ru(CO)$_2$H] has recently been reported to undergo, in boiling heptane, substitution of both the carbonyl ligands with diphosphines to give complexes of the type [(η-C_5H_5)RuL_2H] [L_2 = dppe, dppb, (*R*)-$Ph_2PCH_2CH(Me)PPh_2$] in good yield [136]. The authors ascribe this unexpected result to the labilizing effect of the hydrido ligand, contrasting markedly with the stability towards substitution of the phosphine ligands in the complex [(η-C_5H_5)Ru(PPh_3)$_2$H] [137]. In the absence of any mechanistic data it is difficult, however, to formulate any prognosis as to whether this finding will have general implications for the chemistry of the somewhat neglected $[(\eta\text{-}C_5R_5)Ru(CO)_2H]$ class of complexes, and further developments are awaited.

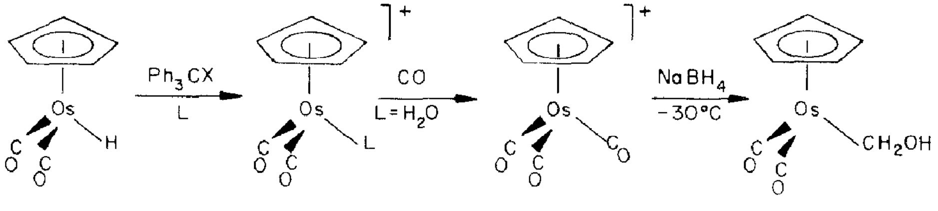
While numerous derivatives of the $\{(\eta\text{-}C_5R_5)Ru(CO)_2\}$ group are now known, relatively little information has to date been forthcoming on the corresponding osmium derivatives. Bromination of $[(\eta\text{-}C_5H_5)_2Os_2(CO)_4]$ has been reported to yield $[(\eta\text{-}C_5H_5)Os(CO)_2Br]$ [138], while $[(\eta\text{-}C_5H_5)Os(CO)_2H]$ has been obtained from $[H_2Os_3(CO)_{10}]$ and cyclopentadiene (yield ca. 11%) [139] and from $[(\eta\text{-}C_5H_5)Os(CO)_3]PF_6$ in liquid ammonia (yield 3.1%) [140]. (The latter cation was obtained from $[(\eta\text{-}C_5H_5)Os(CO)_2Cl]$ by treatment with $AlCl_3$ in benzene under a CO atmosphere [141].) Excellent synthetic routes to the complexes $[(\eta\text{-}C_5H_5)Os(PPh_3)_2Br]$ and $[(\eta\text{-}C_5H_5)Os(CO)(PPh_3)Br]$ have been reported [142,143]. Only recently, however, have convenient preparations of $[(\eta\text{-}C_5H_5)Os(CO)_2Br]$, $[(\eta\text{-}C_5Me_5)Os(CO)_2Br]$, $[(\eta\text{-}C_5H_5)Os(CO)_2H]$ and $[(\eta\text{-}C_5Me_5)Os(CO)_2H]$ (Scheme 22) been published [117]. Treatment of $[(\eta\text{-}C_5R_5)Os(CO)_2H]$ (R = H, Me) with I_2 in hexane gives the iodide derivatives $[(\eta\text{-}C_5R_5)Os(CO)_2I]$. The hydride complexes can be regenerated by reaction of the latter with $NaBH_4$ in THF while treatment with lithium reagents LiR′ (R′ = Me, $SnMe_3$, $SnPh_3$) gives the derivatives $[(\eta\text{-}C_5R_5)Os(CO)_2R']$.



Scheme 22.

Treatment of $[(\eta\text{-}C_5R_5)Os(CO)_2H]$ (R = H, Me) with tropylium tetrafluoroborate gives the cations $[(\eta\text{-}C_5R_5)Os(CO)_2(\eta^2\text{-}C_7H_8)]BF_4$ which on reaction with base (Et_3N, Et_2NH) affords the η^1-cycloheptatrienyl species $[(\eta\text{-}C_5R_5)Os(CO)_2(\eta^1\text{-}C_7H_7)]$. The latter are thermally stable and no fluxional behaviour was detected at ambient temperature [117].

The compounds $[(\eta\text{-}C_5R_5)Os(CO)_2H]$ react smoothly with trityl cation (as the BF_4^- and PF_6^- salts) in the presence of donor ligands L (L = CH_3CN, THF, H_2O) to give the cations $[(\eta\text{-}C_5R_5)Os(CO)_2(L)]X$ (X = BF_4, PF_6). The aqua cations $[(\eta\text{-}C_5R_5)Os(CO)_2(H_2O)]BF_4$ have themselves proved useful precursors to the high yield synthesis of the tricarbonyl cations [(η-C_5R_5)Os$(CO)_3$]BF_4 (210 atm. CO, 40°C). Reduction of [(η-C_5Me_5)Os$(CO)_3$]BF_4 with $NaBH_4$ in THF/H_2O at −30°C affords a high yield of the hydroxymethyl compound [(η-C_5Me_5)Os$(CO)_2$(CH_2OH)], **35**, (Scheme 23) [121]. Irradiation of **35** in THF-d_8 or cyclohexane-d_{12} gave [(η-C_5Me_5)Os$(CO)_2$H] and CO and H_2 as the gaseous products. Similar results were obtained under strictly thermal conditions, [(η-C_5Me_5)Os$(CO)_2$H] being formed in high yield (> 95%) as the only carbonyl-containing product (observed first-order rate plot, $k = 9.0 \times 10^{-5}$ sec^{-1}, $\Delta G^{\neq}_{447} = 34.8$ kcal mol^{-1}). Photolysis of [(η-C_5Me_5)Os$(CO)_2$(CD_2OD)] (prepared in the same manner as **35** except using $NaBD_4$ in THF-d_8) in protio-THF gave only [(η-C_5Me_5)Os$(CO)_2$D], while irradiation of [(η-C_5Me_5)Os$(CO)_2$$CD_2OH$] gave 94% [(η-$C_5Me_5$)Os$(CO)_2$D] and 6% [(η-$C_5Me_5$)Os$(CO)_2$H]. (The gaseous products were HD, H_2, D_2 and CO.) A plausible mechanism for these reactions which is consistent with the results is shown in Scheme 24.



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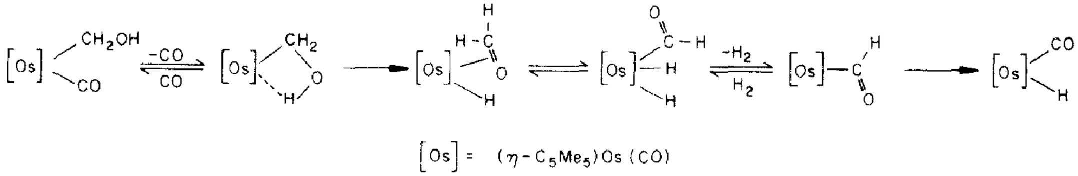
Scheme 23.



Scheme 24.

(ii) Complexes of the type [(η-C_5R_5)ML_2X] (M = Ru, Os: L = Group 5 donor ligand)

The ready availability of the synthetic precursor [(η-C_5H_5)Ru$(PPh_3)_2$Cl] (prepared directly from $RuCl_3 \cdot xH_2O$, PPh_3 and cyclopentadiene in boiling ethanol [7,144]), and its congeners (prepared by ligand replacement at ruthenium e.g. [(η-C_5H_5)Ru{P$(OMe)_3$}$_2$Cl] [145]) has ensured that considerable attention has been focused on these complexes as synthetic precursors in half-sandwich chemistry [146]. A feature of the chemistry of [(η-

$C_5H_5)Ru(PPh_3)_2Cl]$ is the ready substitution of the triphenylphosphine ligands (one is lost very easily, probably as a consequence of the steric bulk of the ligands), and the facile ionization of the chloro ligand. Indeed, rate and equilibrium constants for the acetonitrile solvolysis of the halide ligand in this compound, and a range of congeners $[(\eta\text{-}C_5H_5)RuL_2X]$ (L = phosphine, phosphonite, phosphite; L_2 = bidentate phosphine ligand; X = Cl, Br), have been determined [147].

The neutral ruthenium hydride $[(\eta\text{-}C_5H_5)Ru(PMe_3)_2H]$ forms an adduct with trimethylaluminium

$$[(\eta\text{-}C_5H_5)Ru(PMe_3)_2H] + 1/2Al_2Me_6 \\ \rightarrow [(\eta\text{-}C_5H_5)Ru(PMe_3)_2(\mu\text{-}H)(AlMe_3)]$$

which appears, on the basis of ^1H NMR data, to have a Ru–H–Al bridge [148].

A wide range of amine, phosphine, phosphite, arsine, and stibine substituted complexes $[(\eta\text{-}C_5H_5)RuL_2X]$ (L = N, P, As, Sb donor ligands; X = halide) is available by the treatment of the labile cyclooctadiene complex $[(\eta\text{-}C_5H_5)Ru(\eta\text{-}C_8H_{12})X]$ (C_8H_{12} = cycloocta-1,5-diene) with the appropriate ligand in acetone. Yields of these products are typically greater than 90% [12,13].

Replacement of the chloride in $[(\eta\text{-}C_5H_5)Ru(PPh_3)_2Cl]$ by other anionic groups occurs with little difficulty. The cyano complexes $[(\eta\text{-}C_5H_5)Ru(PPh_3)_2CN]$ and $[(\eta\text{-}C_5H_5)Ru(dppe)CN]$ have been prepared by exchange reactions on the corresponding chlorides with methanolic potassium cyanide [149]. A wide range of compounds containing hydrocarbon functionality (e.g. alkyl, aryl groups) have been synthesized [146]. Reaction of $[(\eta\text{-}C_5H_5)Ru(PPh_3)_2Cl]$ with primary alkyl magnesium halides (R = Et, Pr, Bu^n, Bu^i) leads to the corresponding alkyl ruthenium complexes [150]. Alkenyl ruthenium(II) complexes $[(\eta\text{-}C_5H_5)Ru(PPh_3)_2R]$ (R = $CH{=}CH_2$, $CH_2CH_2CH{=}CH_2$, $CH_2CH_2CH_2C(CH_3){=}CH_2$) have been synthesized from the chloride and the corresponding organomagnesium halides [151]. The large-scale synthesis of $[(\eta\text{-}C_5H_5)Ru(PPh_3)_2(C_2Ph)]$ has been reported [144], as well as the syntheses of mono- and dinuclear derivatives obtained from hexa-1,5-diyne [152], and the phosphine-substituted derivatives $[(\eta\text{-}C_5H_5)Ru(PPh_3)(PMe_3)(C_2R)]$ (R = Me, Bu^t) obtained by the treatment of the corresponding triphenylphosphine compounds with PMe_3 [152]. The crystal structure of $[(\eta\text{-}C_5H_5)Ru(PPh_3)_2(C_2Ph)]$ has been determined [153].

The complex $[(\eta\text{-}C_5H_5)Os(PPh_3)_2Br]$ can be prepared by the sequential reactions of osmium tetraoxide with HBr, PPh_3 and cyclopentadiene [143,154], while the complex $[(\eta\text{-}C_5H_5)Os(PPh_3)_2Cl]$ has been synthesized by the reaction of the corresponding hydride and chloroform [155]. The

X-ray crystal structure of $[(\eta\text{-}C_5H_5)Os(PPh_3)_2Cl]$ has been determined and compared with the ruthenium analogue [155].

The indenyl complex $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)_2Cl]$, **36**, has recently been prepared by the reaction of $[RuCl_2(PPh_3)_3]$ with indene and potassium hydroxide in ethanol [156]. The analogues $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)_2X]$ (X = H, CH_3, I, $SnCl_3$, C_2Ph) have been synthesized by the treatment of **36** with NaOMe, MeMgI, HI, $SnCl_2$ and PhC≡CH/KOH respectively. Both triphenylphosphine groups in **36** are readily displaced by dppe in toluene giving $[(\eta^5\text{-}C_9H_7)Ru(dppe)Cl]$ [156].

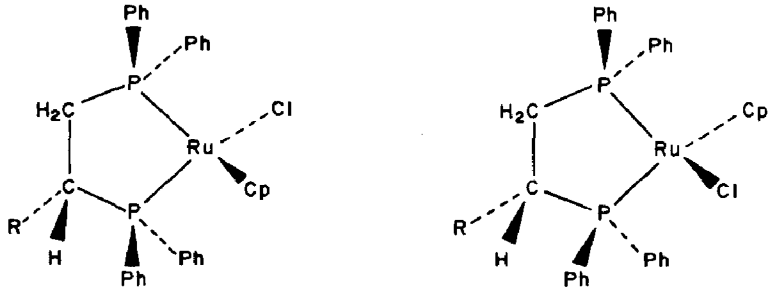
Reports on the chemistry of pentamethylcyclopentadienyl ruthenium complexes are still relatively rare. Bercaw and co-workers [16] have attempted to synthesize $[(\eta\text{-}C_5Me_5)Ru(PPh_3)_2Cl]$ and the corresponding PMe_3 compound by the direct route from $RuCl_3 \cdot xH_2O$, phosphine and C_5Me_5H ($[RuCl_2(PPh_3)_3]$ and $[RuCl_2(PMe_3)_4]$ were the only isolated products). The complex $[(\eta\text{-}C_5Me_5)Ru(PMe_3)_2Cl]$ has, however, been prepared by the reaction of $[(\eta\text{-}C_5Me_5)Ru(NBD)Cl]$ (NBD = bicyclo[2.2.1]hepta-2,5-diene) (obtained in low yield by the reaction of $[\{(NBD)RuCl_2\}_x]$ with LiC_5Me_5) with excess PMe_3. A second route involves the reaction of the paramagnetic ruthenium(III) species $[\{(\eta\text{-}C_5Me_5)RuCl_2\}_x]$ with excess PMe_3 in dichloromethane giving $[(\eta\text{-}C_5Me_5)Ru(PMe_3)_2Cl]$ together with $[RuCl_2(PMe_3)_4]$ (ratio 1 : 2.5). The recent report [157] on the facile synthesis of $[(\eta\text{-}C_5Me_5)Ru(diolefin)Cl]$ (diolefin = norbornadiene, cycloocta-1,5-diene) (obtained directly from $[\{(\eta\text{-}C_5Me_5)RuCl_2\}_x]$ and diolefin in boiling ethanol [157]) should, however, make this a more convenient route to $[(\eta\text{-}C_5Me_5)Ru(PR_3)_2Cl]$-type complexes. Bercaw and co-workers [16] have also prepared the primary alkyl derivatives $[(\eta\text{-}C_5Me_5)Ru(PMe_3)_2R]$ (R = Me, Et, CH_2CMe_3, CH_2SiMe_3) by the action of the appropriate Grignard reagents on the chloride. Attempts to prepare secondary or tertiary alkyls (Pr^i, Bu^t), however, gave the hydride complex $[(\eta\text{-}C_5Me_5)Ru(PMe_3)_2H]$ as the only isolated product.

Further aspects of the chemistry of $[(\eta\text{-}C_5Me_5)Ru(PMe_3)_2Cl]$ resemble that of $[(\eta\text{-}C_5H_5)Ru(PPh_3)_2Cl]$. The carbonyl cation $[(\eta\text{-}C_5Me_5)Ru(PMe_3)_2(CO)]PF_6$ is obtained from the chloride in boiling methanol under an atmosphere of CO in the presence of KPF_6. The basicity of the complex $[(\eta\text{-}C_5Me_5)Ru(PMe_3)_2Cl]$ allows the isolation of cationic hydride complexes via protonation; in boiling THF, protonation occurs simply using NH_4PF_6, generating the ruthenium(IV)-hydride complex $[(\eta\text{-}C_5Me_5)Ru(PMe_3)_2(Cl)H]PF_6$ [16].

Treatment of $[(\eta\text{-}C_5H_5)Ru(PMe_3)_2Cl]$ or $[(\eta\text{-}C_5H_5)Os(PR_3)_2Br]$ (R = Me, Ph) with HBF_4 or HPF_6 has given the d^4 hydride-cations $[(\eta\text{-}C_5H_5)Ru(PMe_3)_2(Cl)H]^+$, $[(\eta\text{-}C_5H_5)Os(PPh_3)_2(Br)H]^+$ and $[(\eta\text{-}C_5H_5)Os(PMe_3)_2(Br)H]^+$. The ^1H NMR spectra show hydride resonances at δ −9.7, −12.5

and -14.9 respectively for these products confirming the direct metal–hydrogen bond [158]. The complex $[(\eta\text{-}C_5H_5)Ru(PMe_3)_2Cl]$ (in contrast to $[(\eta\text{-}C_5H_5)Ru(PPh_3)_2Cl]$) reacts with chlorine in the presence of NH_4PF_6 to give $[(\eta\text{-}C_5H_5)Ru(PMe_3)_2Cl_2]PF_6$. The product of the reaction of $[(\eta\text{-}C_5H_5)Ru(PMe_3)_2Cl]$ with $NOPF_6$ is the complex $[(\eta\text{-}C_5H_5)Ru(NO)(PMe_3)_2](PF_6)_2$. The corresponding PPh_3 complex was unstable and could not be isolated, while the corresponding osmium complexes $[(\eta\text{-}C_5H_5)Os(NO)(PR_3)_2](PF_6)_2$ (R = Me, Ph) were also of limited stability. The X-ray crystal structure of $[(\eta\text{-}C_5H_5)Os(NO)(PMe_3)_2](PF_6)_2$ has, however, been determined [158]. These studies add to the growing body of knowledge which suggests that there are no a priori reasons why there should not be an extensive chemistry of ruthenium- and osmium(IV) organometallic complexes.

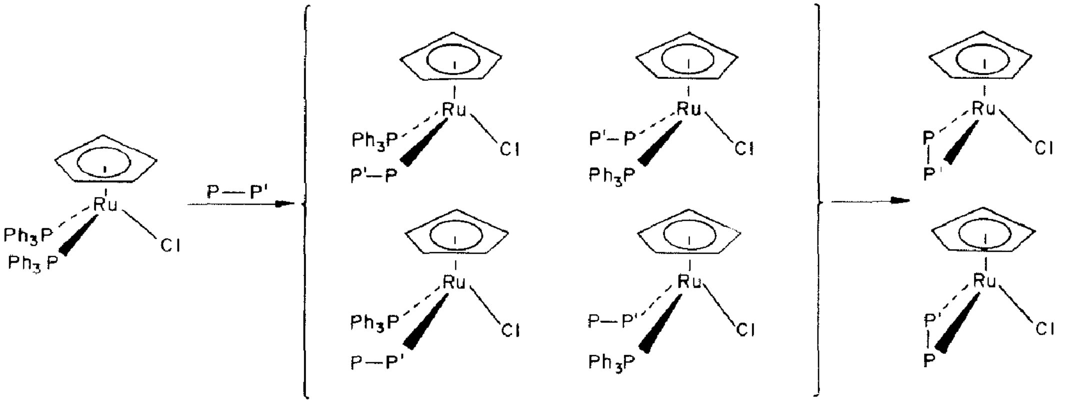
The complexes $[(\eta\text{-}C_5H_5)Ru(diphos)X]$ (X = halide), in which diphos represents a chiral bidentate phosphine ligand, have recently been obtained by the displacement of PPh_3 from $[(\eta\text{-}C_5H_5)Ru(PPh_3)_2Cl]$ by (+)-(*R*)-1,2-bis(diphenylphosphino)propane [(*R*)-dppp], (−)-(*S*)-1-cyclohexyl-1,2-bis(diphenylphosphino)ethane [(*S*)-cdppe], (−)-(R)-1-phenyl-1,2-bis(diphenylphosphino)ethane [(*R*)-dppe] and (−)-(2*S*, 3*S*)-2,3-bis(diphenylphosphino)butane [159]. In the case of the first three ligands, two diastereomers are expected to form (Fig. 11) with different configurations at the ruthenium atom. Over short periods of time (48 h) the ratios of the two diastereomers do not change, but over longer periods (e.g. 26 d) there is some evidence for slow epimerization at the ruthenium atom. The PPh_3 displacement reactions do not go to completion even after 26 days, and the decrease in the reaction rate with conversion suggests that the replacement of triphenylphosphine takes place via a dissociation of the PPh_3 ligand. This stepwise replacement of the two triphenylphosphine ligands is supported by ^{31}P NMR evidence;



$(Cp = \eta\text{-}C_5H_5;\ R = Me, C_6H_{11}, C_6H_5)$

Fig. 11.

resonances assignable to monodentate ligands are observed, except in the case of (−)-(2*S*, 3*S*)-2,3-bis(diphenylphosphino)butane where only the signals due to free ligand and complexed chelate ligand appear. For the three unsymmetrical chelates a stepwise displacement would result in four different intermediates (Scheme 25) [159].



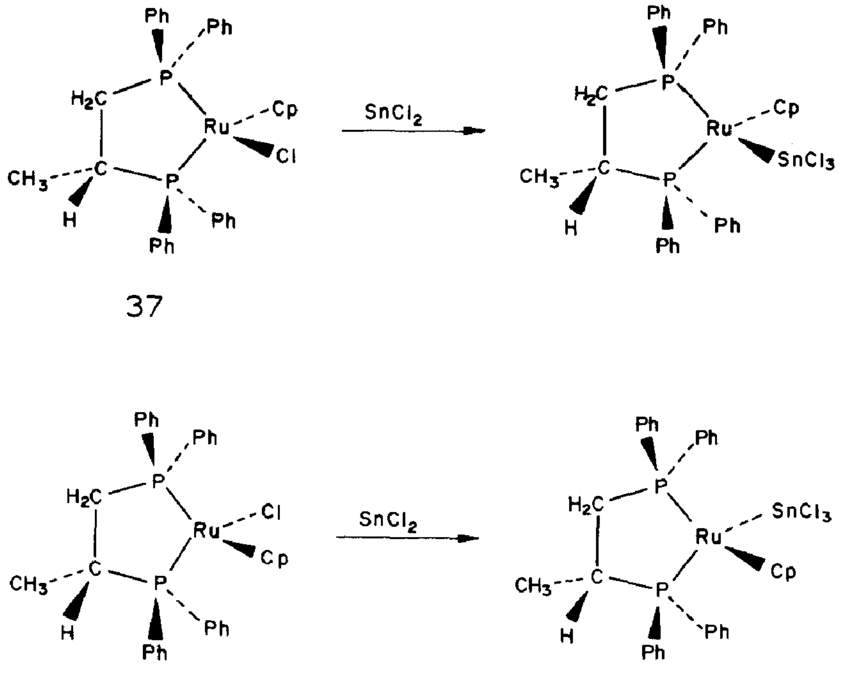
(P—P'=optically active diphos ligand)

Scheme 25.

The diastereomeric products formed in the reactions of (+)-(*R*)-1,2-bis(diphenylphosphino)propane, (−)-(*S*)-1-cyclohexyl-1,2-bis(diphenylphosphino)ethane and (−)-(*R*)-1-phenyl-1,2-bis(diphenylphosphino)ethane with [(η-C_5H_5)Ru(PPh_3)$_2$Cl] have been separated by fractional crystallization. The X-ray crystal structure of the diastereomer [(*S*)-(η-C_5H_5)Ru{(*R*)-$Ph_2PCH(Me)CH_2PPh_2$}Cl] has been determined [160].

The stereochemistry of ligand substitution reactions in chiral complexes of the type [(η-C_5H_5)Ru(diphos)Cl] has been investigated [161–164]. The reaction of the diastereomers [(*S*)-(η-C_5H_5)Ru{(*R*)-$Ph_2PCH(Me)CH_2$ PPh_2}Cl] and [(*R*)-(η-C_5H_5)Ru{(*R*)-$Ph_2PCH(Me)CH_2PPh_2$}Cl] with $SnCl_2$ (Scheme 26) has been found to proceed with retention of the geometry at the ruthenium atom, confirmed by the X-ray crystal structure determination of [(*R*)-(η-C_5H_5)Ru{(*R*)-$Ph_2PCH(Me)CH_2PPh_2$}$SnCl_3$] [163]. Although no mechanistic detail on this reaction is yet available, it is clear from the results that dissociation of a phosphorus atom cannot be involved in the formation of the trichlorostannate complex.

The diastereomers [(*S*)-(η-C_5H_5)Ru{(*R*)-$Ph_2PCH(Me)CH_2PPh_2$}Cl], **37**, and [(*R*)-(η-C_5H_5)Ru{(*R*)-$Ph_2PCH(Me)CH_2PPh_2$}Cl], **38**, are alkylated by methyl and ethylmagnesium bromide to give [(*R*)(η-C_5H_5)Ru{(*R*)-Ph_2 $PCH(Me)CH_2PPh_2$}R] and [(*S*)-(η-C_5H_5)Ru{(*R*)-$Ph_2PCH(Me)CH_2$ PPh_2}R] (R = Me, Et) with stereospecific retention of configuration at the



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38

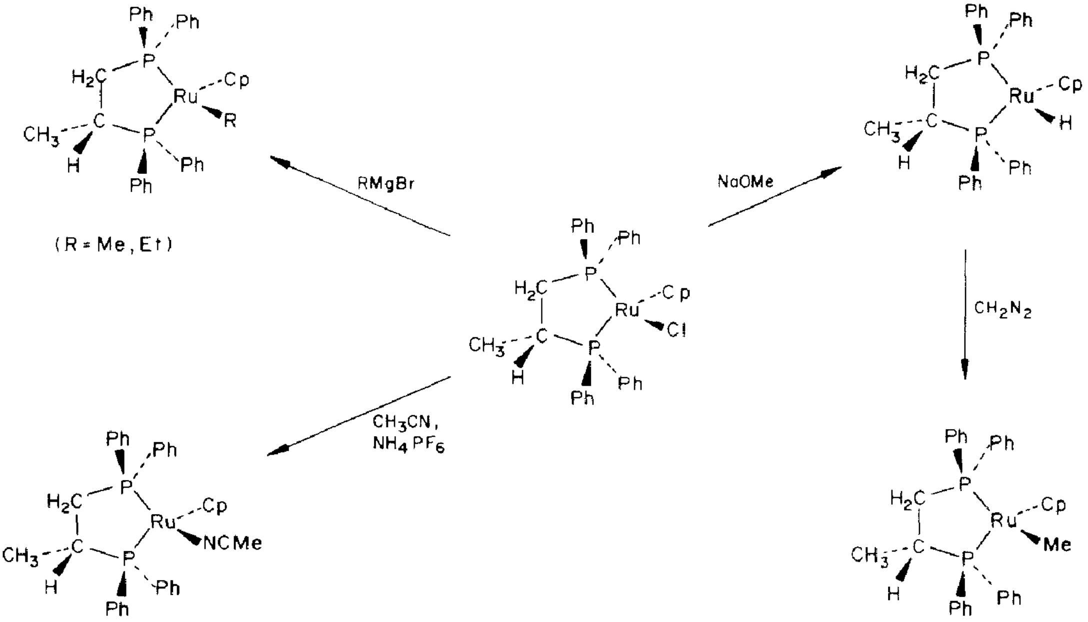
Scheme 26.

ruthenium atom (the X-ray crystal structure of [(*S*)-(η-C_5H_5)Ru{(*R*)-$Ph_2PCH(Me)CH_2PPh_2$}Me] has been determined) [161,162,164].

Hydride formation is the only reaction observed to occur upon treatment of **37** and **38** with Bu^{s}MgBr; on the basis of NOE experiments this occurs with retention of configuration. Similar observations are made when **37** and **38** are treated with NaOMe. The hydride complexes react with CH_2N_2 in the presence of $Pd(OAc)_2$ as catalyst to give methyl compounds, also with retention of configuration. Some other stereospecific transformations are shown in Scheme 27. Reduction of the methoxycarbene complexes [(η-C_5H_5)Ru{$Ph_2PCH(R)CH(R')PPh_2$}{C(OMe)CH_2Ph}] (where R, R′ = H or Me) with $LiAlH_4$ in THF at −80 °C gives, instead of η^1-α-methoxyalkyl systems [165–167], the 2-phenylethyl complexes [(η-C_5H_5)Ru{$Ph_2PCH(R)CH(R')PPh_2$}(CH_2CH_2Ph)] [168]. The reaction takes place with retention of configuration at the ruthenium atom.

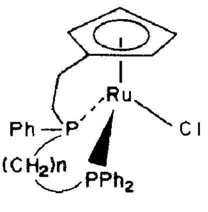
The unusual complexes **39** and **40** have been synthesized from [$RuCl_2(PPh_3)_3$] and the cyclopentadiene–phosphine ligands $Ph_2P(CH_2)_nP(Ph)(CH_2)_2C_5H_5$ ($n = 3$, 4) (Fig. 12) [169], and used as homogeneous hydrogenation catalysts.

Bidentate tertiary phosphine ligands (e.g. dppe, dppm) characteristically displace both triphenylphosphine ligands in [(η-C_5H_5)Ru$(PPh_3)_2$Cl] giving complexes of the type [(η-C_5H_5)Ru(diphos)Cl]. In boiling methanol in the



Scheme 27.

presence of NH_4PF_6, however, complexes of the type $[(\eta\text{-}C_5H_5)Ru(PPh_3)(diphos)]PF_6$ are obtained, reportedly via the intermediacy of $[(\eta\text{-}C_5H_5)Ru(PPh_3)(\eta^1\text{-}diphos)Cl]$ [154,159]. In a modification of these experimental conditions, $[(\eta\text{-}C_5H_5)Ru(PPh_3)_2Cl]$ reacts with an equimolar amount of bis(diphenylphosphino)methane in boiling benzene to give a good yield of $[(\eta\text{-}C_5H_5)Ru(PPh_3)(\eta^1\text{-}dppm)Cl]$, **41**, fully characterized by X-ray crystallography [170]. Heating of **41** in polar solvents (e.g. acetonitrile) results in rapid expulsion of chloride ion giving the salt $[(\eta\text{-}C_5H_5)Ru(PPh_3)(dppm)]Cl$ in which the dppm ligand is coordinated in the bidentate mode. Attempts to methylate the free PPh_2 group in **41** with $[Me_3O]BF_4$ failed; on the other hand, heating with MeI gave, with concomitant halide exchange, $[(\eta\text{-}C_5H_5)Ru(PPh_3)(Ph_2PCH_2PMePh_2)I]I$. Treatment of **41** with further amounts of dppm in benzene gives $[(\eta\text{-}C_5H_5)Ru(dppm)_2]Cl$, proposed to

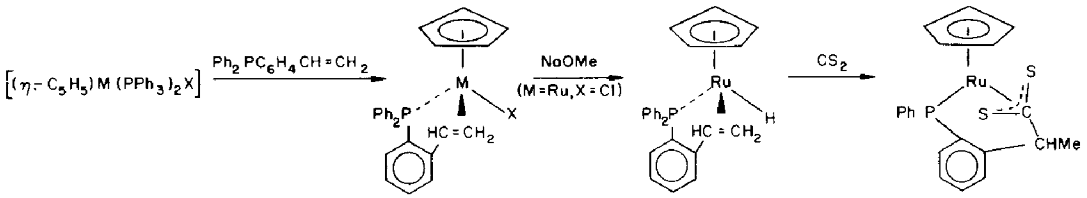


(39, n = 3; 40, n = 4)

Fig. 12.

contain one bidentate and one monodentate dppm ligand [170].

Reactions between $[(\eta\text{-}C_5H_5)M(PPh_3)_2X]$ (M = Ru, X = Cl; M = Os, X = Br) and $2\text{-}CH_2{=}CHC_6H_4PPh_2$ afford the products $[(\eta\text{-}C_5H_5)M(\eta\text{-}CH_2{=}CHC_6H_4PPh_2)X]$ (Scheme 28) [171]. The osmium complex exists in solution as two isomeric forms as shown by ^1H NMR spectroscopy. The X-ray crystal structure of the major isomer has been determined, the most important feature of this structure being the almost co-planar orientation of the C=C double bond with respect to the Os–Br vector, with the terminal carbon atom *cis* to Br. It is assumed that the minor isomer has the alternative, sterically more crowded, conformation with the β-carbon atom *cis* to Br. The complex $[(\eta\text{-}C_5H_5)Ru(\eta\text{-}CH_2{=}CHC_6H_4PPh_2)Cl]$ reacts with sodium methoxide in methanol to give the corresponding hydride complex **42** which also exists in two isomeric forms (presumably analogous to the osmium complexes) in solution. Chlorination with $CDCl_3$ regenerated the chloride complex. Reaction of **42** with CS_2 occurs readily to give the complex $[(\eta\text{-}C_5H_5)Ru(S_2CCHMeC_6H_4PPh_2)Cl]$, **43** (Scheme 28), together with a minor isomer proposed to be $[(\eta\text{-}C_5H_5)Ru\{S_2C(CH_2)_2C_6H_4PPh_2\}Cl]$. The X-ray crystal structure of **43** has been determined, confirming the unusual $\eta^3\text{-}S_2C$ mode of coordination of the dithio acid group (Ru–S 2.418, 2.426, Ru–C 2.175 Å).



42 **43**

Scheme 28.

The lack of success, to date, in preparing complexes of the type $[(\eta\text{-}C_5H_5)Ru(PPh_3)_2(L)]^+$ (L = olefin, allene, alkyne) has been attributed to the difficulty of fitting even the smallest C_2 unit in the η^2-mode in the vacant coordination site left by the departing Cl ligand [172]. However, reactions between $[(\eta\text{-}C_5H_5)Ru(PMe_3)_2Cl]$ and unsaturated hydrocarbons in methanol in the presence of NH_4PF_6 have given $[(\eta\text{-}C_5H_5)Ru(PMe_3)_2(L)]PF_6$ (L = ethylene, fumaronitrile, buta-1,3-diene, allene, 1,1′-dimethylallene, diphenylacetylene, 1,4-diphenylbut-1,3-diyne, ethylphenylpropiolate, dimethylacetylenedicarboxylate, hexafluorobut-2-yne) [172,173]. The X-ray crystal structures of $[(\eta\text{-}C_5H_5)Ru(PMe_3)_2(\eta^2\text{-buta-1,3-diene})]PF_6$ and $[(\eta\text{-}C_5H_5)Ru(PMe_3)_2(\eta^2\text{-allene})]PF_6$ have been determined [172].

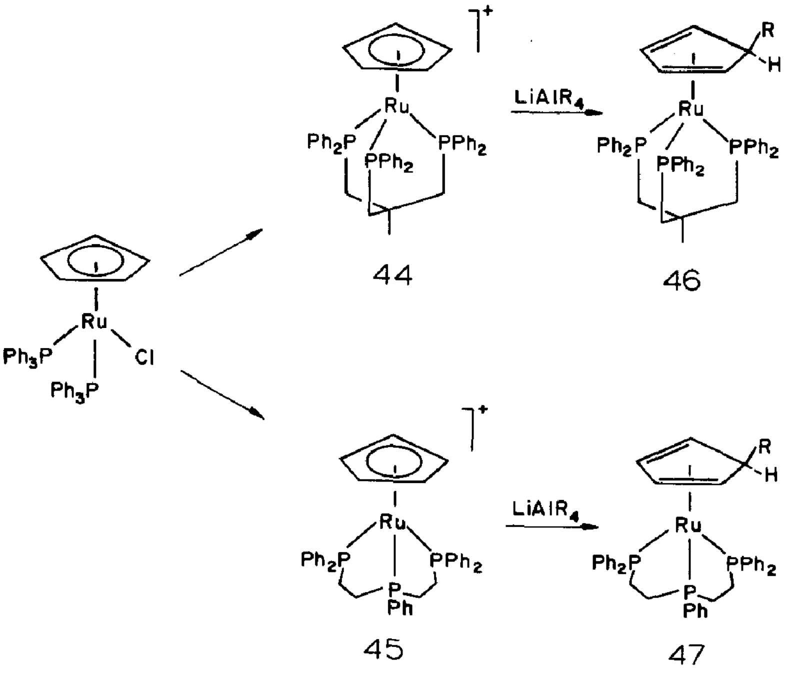
Complexes of the general formula $[(\eta\text{-}C_5H_5)Ru(diamine)(PPh_3)]ClO_4$ [diamine = ethylenediamine, propylenediamine, 2,2′-bipyridine, 1,10-phenanthroline, biimidazole, bibenzimidazole, 2-(2′-pyridylbenzimidazole)] have been synthesized by the reaction of [(η-C_5H_5)Ru(PPh_3)$_2$Cl] with the diamine in methanol in the presence of $NaClO_4$ [174]. The diolefins, 2,5-norbornadiene and tetrafluorobenzobarrelene, react with [(η-C_5H_5)Ru (PPh_3)$_2$Cl] in a similar manner giving the complexes [(η-C_5H_5)Ru(diolefin)(PPh_3)]ClO_4 in good yields. The X-ray crystal structure of [(η-C_5H_5)Ru(norbornadiene)(PPh_3)]ClO_4 has been determined [174]. Heating of [(η-C_5H_5)Ru(PPh_3)$_2$Cl] in methanol in the presence of oxygen and $NaClO_4$ leads to oxidation of the phosphine ligands giving the complex [(η-C_5H_5)Ru{(η^6-C_6H_5)P(O)Ph_2}]ClO_4. An X-ray crystal structure determination has confirmed the sandwich structure of this molecule [174].

In work closely related to this, the indenyl complex [(η^5-C_9H_7)Ru (PPh_3)$_2$Cl] reacts with ligands L(L = CH_3CN, 2-ClC_6H_4CN, CH_2=CHCN, 1,2-(CN)$_2C_6H_4$, C_2H_4(CN)$_2$, N_2H_4, Bu^{t}NC, CO, C_2H_4) and ligands L_2 (L_2 = norbornadiene, tetrafluorobenzobarrelene, ethylenediamine, propylenediamine, biimidazole, 2,2′-bipyridine, 1,10-phenanthroline) in the presence of $NaClO_4$ in methanol, to give cationic complexes [(η^5-C_9H_7)Ru(PPh_3)$_2$L]ClO_4 and [(η^5-C_9H_7)Ru(PPh_3)L_2]ClO_4 [156]. With phenylacetylene under similar conditions, the vinylidene complex [(η^5-C_9H_7)Ru(PPh_3)$_2$(=C=CHPh)]ClO_4 is formed, again closely parallelling the chemistry of the analogous cyclopentadienyl system [175,176]. The X-ray crystal structure of [(η^5-C_9H_7)Ru(PPh_3)$_2$(CO)]ClO_4 has been determined; the indenyl ligand is unsymmetrically coordinated, three Ru–C bond lengths (2.239, 2.246, 2.265 Å) being significantly shorter than those involving the ring-shared carbon atoms (2.356, 2.352 Å) [156].

The ruthenium cations **44** and **45** have been prepared by the treatment of [(η-C_5H_5)Ru(PPh_3)$_2$Cl] with the tridentate phosphine ligands in boiling decalin (Scheme 29). Reduction of **44** and **45** with lithium aluminium hydride or deuteride in THF involves direct attack of hydride *exo* to the cyclopentadienyl ligand giving the cyclopentadiene complexes **46** and **47** (Scheme 29) [177]. The assignment of the stereochemistry in these systems has been made on the basis of long range $^1H-^{31}P$ spin–spin coupling constants [177,178], ^1H NMR and IR spectroscopy [177].

The electron-rich cyano complexes [(η-C_5H_5)RuL_2CN] (L = PPh_3, L_2 = dppe) readily undergo alkylation at the cyanide functionality with electrophiles giving in moderate yields the isonitrile cations [(η-C_5H_5)RuL_2(CNR)]$^+$ (Scheme 30) [149]. Presumably the simpler derivatives are better obtained by the reactions of [(η-C_5H_5)Ru(PPh_3)$_2$Cl] with isonitrile in methanol, but this does provide the only synthetic route to isonitrile cations containing unusually substituted isonitrile ligands.

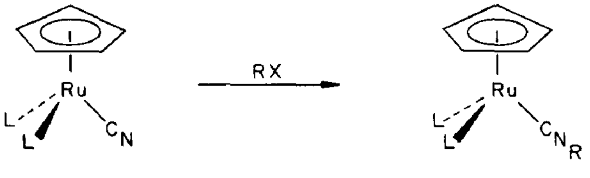
Treatment of the cyano complexes [(η-C_5H_5)RuL_2CN] (L = PPh_3, L_2 =



(R=H,D)

Scheme 29.

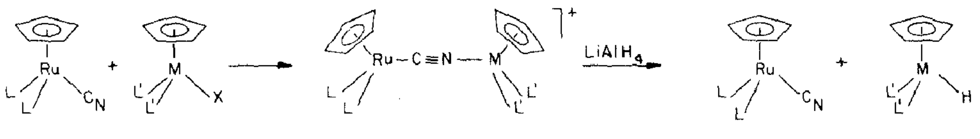
dppe) with [(η-C_5H_5)RuL_2Cl] or [(η-C_5H_5)Fe(dppe)Br] in the presence of NH_4PF_6 in boiling methanol gives the di-ruthenium and mixed iron–ruthenium cyano-bridged cations shown in Scheme 31 [179]. The X-ray crystal structure of [(η-C_5H_5)Ru(dppe)(μ-CN)Ru$(PPh_3)_2$(η-C_5H_5)]PF_6 has been determined (Fig. 13) showing the Ru–CN–Ru linkage to be essentially linear. Bond length data for this linkage support the charge distribution Ru–C≡N–Ru$^+$ with the charge being localized on the nitrogen-bearing metal. Hydride reduction of the cyano-bridged cations regenerates the cyano starting materials and gives from the other half of the complex, metal



(L = PPh_3, L_2= dppe)

(R = Me, CH_2Ph, $CH_2CH=CH_2$, C_2H_5OH)

Scheme 30.



(M = Fe, X = Br, L = PPh$_3$ or L$_2$ = dppe, L'$_2$ = dppe; M = Ru, X = Cl, L, L' = dppe or L$_2$L'$_2$ = dppe)

Scheme 31.

hydride species [(η-C_5H_5)ML_2H] (M = Fe, Ru, L_2 = dppe; M = Ru, L = PPh_3) (Scheme 31). In one case (M = Ru, L = PPh_3), a third product, the trihydride ruthenium(IV) complex [(η-C_5H_5)-Ru(PPh_3)H_3] was also obtained; this compound is more readily synthesized by the treatment of [(η-C_5H_5)Ru(PPh_3)$_2$Cl] with $LiAlH_4$ [179,180]. The trideuteride is prepared from [(η-C_5H_5)Ru(PPh_3)$_2$Cl] and $LiAlD_4$ [179].

In the temperature range 50–80 °C the complexes [(η-C_5H_5)Ru(PPh_3)$_2$R] (R = Et, Pr, Bu^n, Bu^i) lose a triphenylphosphine ligand, and via a β-elimination process, form the η-alkene-hydride ruthenium complexes [(η-C_5H_5)Ru(PPh_3)(η-CH_2=CR^1R^2)H] (R^1, R^2 = H, Me; R^1 = H, R^2 = Et) (Scheme 32). Above 100 °C alkane elimination occurs giving the orthometal-

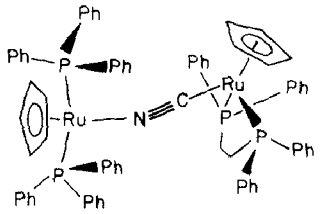
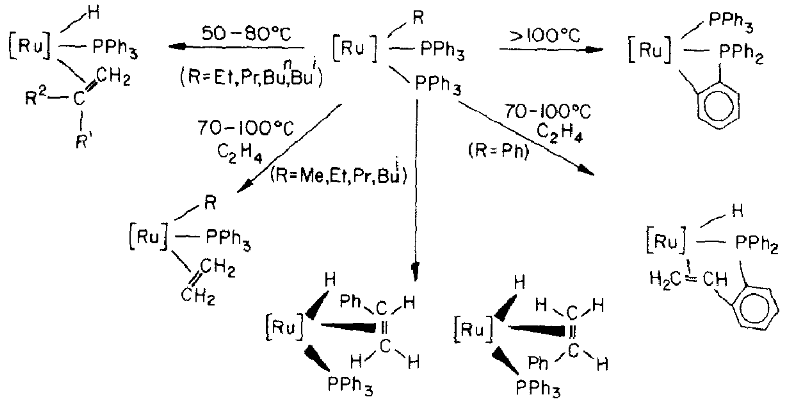


Fig. 13.



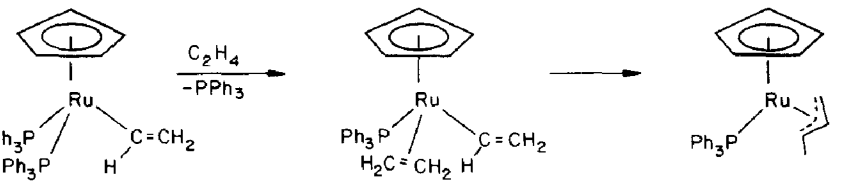
48

49

([Ru] = (η-C_5H_5)Ru)

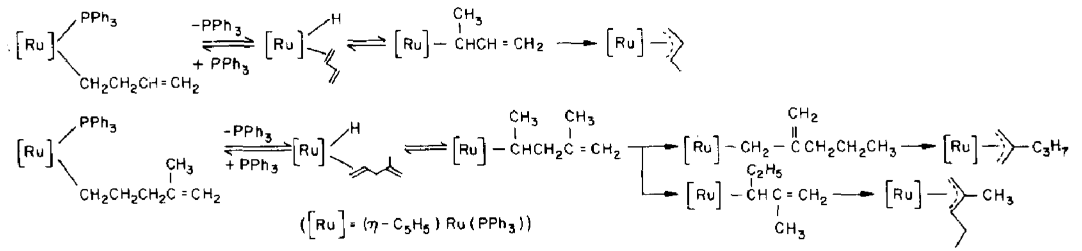
Scheme 32.

lated complex $[(\eta\text{-}C_5H_5)\overline{Ru(PPh_3)(Ph_2PC_6H_4)}]$. Under a pressure of ethylene though, at 70–100 °C, the coordinatively unsaturated intermediate $[(\eta\text{-}C_5H_5)Ru(PPh_3)R]$ (R = Me, Et, Pr [181], Bu^i [150]) can be trapped by complexation with ethylene as $[(\eta\text{-}C_5H_5)Ru(PPh_3)(CH_2{=}CH_2)R]$. The σ-phenyl ruthenium complex $[(\eta\text{-}C_5H_5)Ru(PPh_3)_2Ph]$ reacts under similar conditions by ethylene insertion into the ruthenium–phenyl bond. Subsequent β-elimination gives the diastereomeric η^2-styrene hydride ruthenium compounds shown in Scheme 32. At a low ethylene pressure, orthometallation followed by rapid ethylene insertion into the resulting ruthenium–phenyl bond and β-elimination gives the diastereomeric compounds **48** and **49** shown in Scheme 32. The alkenyl complex $[(\eta\text{-}C_5H_5)Ru(PPh_3)_2(CH{=}CH_2)]$ eliminates a phosphine ligand above 100 °C and reacts with ethylene via an insertion process to give the η^3-allyl complex $[(\eta\text{-}C_5H_5)Ru(PPh_3)(\eta^3\text{-}CH_2CHCHCH_3)]$ (Scheme 33) [151]. The 3- and 4- alkenyl complexes



Scheme 33.

$[(\eta\text{-}C_5H_5)Ru(PPh_3)_2R]$ [R = $CH_2CH_2CH{=}CH_2$, $CH_2CH_2CH_2C(CH_3){=}CH_2$] isomerize at 80–100 °C (after dissociation of one PPh_3) via an η^2-alkadiene-hydride ruthenium intermediate to form the η^3-allyl complexes shown in Scheme 34 [151].

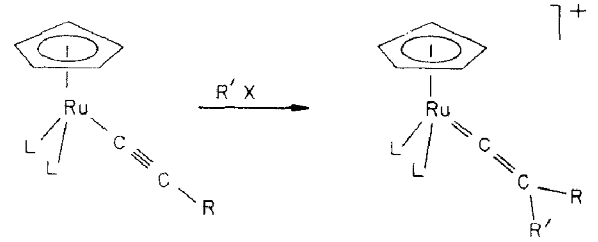


Scheme 34.

The chiral hydride–ethylene complex $[(\eta\text{-}C_5H_5)Ru(PPh_3)(CH_2{=}CH_2)H]$ is fluxional [182], two different processes accounting for this behaviour. The first, olefin rotation, takes place exclusively about the metal–olefin coordination axis. The second, identified by high temperature magnetization transfer experiments, is the exchange of the hydrido ligand with olefinic hydrogens. The phosphorus couplings are retained during this process indicating that it proceeds in an intramolecular manner. This represents a direct observation of the reversible intramolecular β-hydrogen elimination reaction with $[(\eta\text{-}C_5H_5)Ru(PPh_3)(CH_2CH_3)]$ as the transition state [182].

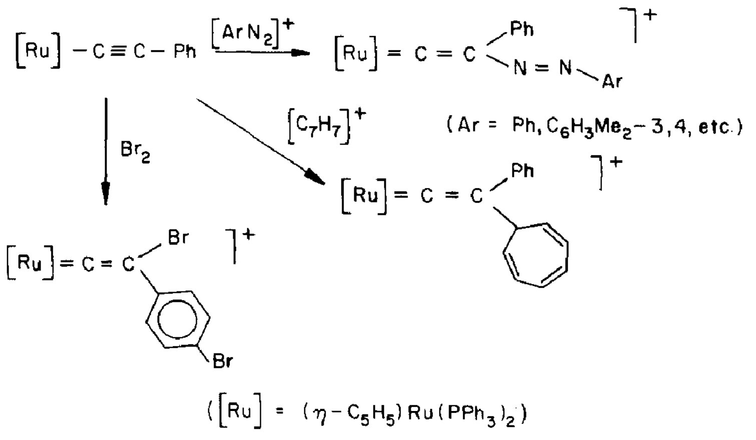
The complex $[(\eta\text{-}C_5H_5)Ru(PMe_3)_2Cl]$ reacts rapidly with acetylene, propyne, and phenylacetylene in methanol in the presence of NH_4PF_6 to give the vinylidene species $[(\eta\text{-}C_5H_5)Ru(PMe_3)_2(C{=}CHR)]PF_6$ (R = H, Me, Ph) [183]. Deprotonation of $[(\eta\text{-}C_5H_5)Ru(PMe_3)_2(C{=}CHMe)]PF_6$ gives the acetylide complex $[(\eta\text{-}C_5H_5)Ru(PMe_3)_2(C{\equiv}CMe)]$, more conveniently prepared by phosphine exchange in $[(\eta\text{-}C_5H_5)Ru(PPh_3)_2(C{\equiv}CMe)]$ with PMe_3. Other related acetylide complexes $[(\eta\text{-}C_5H_5)Ru(PMe_3)_n(PPh_3)_{2-n}(C{\equiv}CPh)]$ ($n = 1$, 2) have been obtained by the treatment of $[(\eta\text{-}C_5H_5)Ru(PPh_3)_2(C{\equiv}CPh)]$ with PMe_3. Alkylation of $[(\eta\text{-}C_5H_5)Ru(PMe_3)_2(C{\equiv}CPh)]$ with trimethyloxoniumhexafluorophosphate affords the disubstituted vinylidene complex $[(\eta\text{-}C_5H_5)Ru(PMe_3)_2(C{=}CMePh)]PF_6$ in moderate yield. The X-ray crystal structure of $[(\eta\text{-}C_5H_5)Ru(PMe_3)_2(C{=}CHMe)]PF_6$ has been determined [183]. The Ru–C–C system is linear with bond lengths Ru–C_α 1.845, C_α–C_β 1.313 and C_β–C_γ 1.485 Å.

Nucleophilic attack at the β-carbon of the acetylide ligand in $[(\eta\text{-}C_5H_5)RuL_2(C{\equiv}CR)]$ (L = PPh_3, L_2 = dppe; R = Me, Et, Bu^n, Ph) with a range of electrophiles (MeI, EtI, $PhCH_2Br$) has given the disubstituted vinylidene cations $[(\eta\text{-}C_5H_5)RuL_2(C{=}CRR')]^+$ in excellent yield [184]. Intramolecular alkylation may also be achieved to give cyclic vinylidene complexes (Scheme 35). Addition of arenediazonium or tropylium salts to $[(\eta\text{-}C_5H_5)RuL_2(C_2Ph)]$ (L = PPh_3, L_2 = dppe) has given the cationic aryldiazovinylidene and cycloheptatrienyl vinylidene complexes respectively (Scheme 36) [185]. Treatment of $[(\eta\text{-}C_5H_5)Ru(PPh_3)_2(C{\equiv}CPh)]$ with liquid bromine has given another unusual vinylidene complex $[(\eta\text{-}C_5H_5)Ru(PPh_3)_2\{C{=}CBr(C_6H_4Br\text{-}4)\}]Br_3$ [186], although in this case the reaction is complicated by bromination of the phenyl substituent on the vinylidene unit (Scheme 36). A remarkable feature of this reaction is the resistance of the Ru–C bond in the acetylide complex to oxidative cleavage by the halogen. The X-ray crystal structures of all three of these unusual ruthenium vinyli-



(L = PPh_3, L_2 = dppe; R = Me, Et, Bu^n, Ph; R′ = Me, Et, CH_2Ph)

Scheme 35.

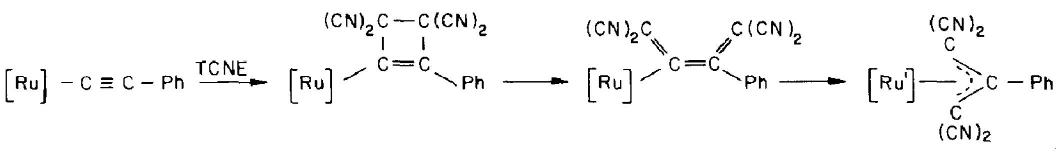


$([Ru] = (\eta\text{-}C_5H_5)Ru(PPh_3)_2)$

Scheme 36.

dene complexes have been reported [185,186].

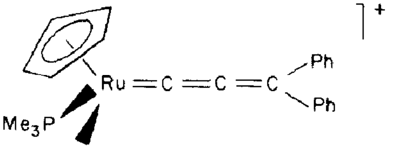
The reactions between the acetylide complexes $[(\eta\text{-}C_5H_5)Ru(L)(L')(C_2R)]$ ($R = Me$, Ph; $L = PPh_3$; $L' = PPh_3$, CO, $P(OPh)_3$; $LL' =$ dppe) and tetracyanoethylene proceed via paramagnetic intermediates and a combination of cycloaddition and other processes, to a range of cyclobutenyl, "butadienyl" and allyl complexes (Scheme 37) [187]. The X-ray crystal structure of $[(\eta\text{-}C_5H_5)Ru(dppe)\{C[=C(CN)_2]C(Ph)=C(CN)_2\}]$ has been determined [187].



$([Ru] = (\eta\text{-}C_5H_5)RuLL'$; $L = PPh_3$, $L' = CO, P(OMe)_3$, $LL' =$ dppe; $[Ru'] = (\eta\text{-}C_5H_5)Ru(PPh_3))$

Scheme 37.

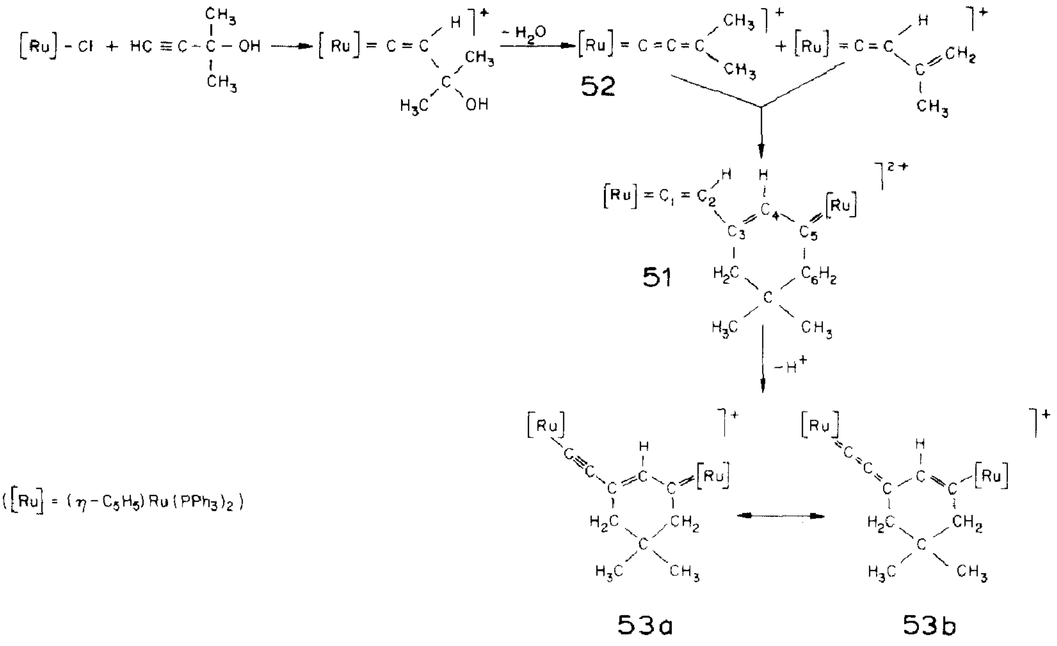
The reaction of $[(\eta\text{-}C_5H_5)Ru(PMe_3)_2Cl]$ with the acetylenic alcohol $Ph_2C(OH)C{\equiv}CH$ and NH_4PF_6 in ethanol (25°C, 27 h) gives, in high yield, the diphenylallenylidene complex $[(\eta\text{-}C_5H_5)Ru(PMe_3)_2(C_3Ph_2)]$, **50**, (Fig. 14) [188]. The X-ray crystal structure of **50** has been determined confirming the formulation. The ruthenium–C_α bond length (1.884 Å) is considerably shorter than a typical Ru–C single bond length (ca. 2.1 Å) and slightly shorter than most ruthenium to carbonyl bonds (1.92–1.93 Å). The C_α–C_β bond length (1.255 Å) is nearly as short as a carbon–carbon triple bond (1.20–1.21 Å), while the C_β–C_γ bond length (1.329 Å) is typical of an allene $C(sp)$–$C(sp^2)$ double bond. These structural parameters support substantial



50

Fig. 14.

contributions from two different mesomeric forms $[(\eta\text{-}C_5H_5)Ru(PMe_3)_2({=}C{=}C{=}CPh_2)]^+ \leftrightarrow [(\eta\text{-}C_5H_5)Ru(PMe_3)_2(-C{\equiv}C-CPh_2)]^+$ with the cationic charge stabilized by both the metal centre and the diphenylcarbenium species [188]. When $[(\eta\text{-}C_5H_5)Ru(PPh_3)_2Cl]$ is treated with $Me_2C(OH)C{\equiv}CH$ in methanol in the presence of NH_4PF_6, the reaction takes a different course [189]. X-ray crystallography has revealed that the red-purple, crystalline product with stoichiometry $[(\eta\text{-}C_5H_5)_2Ru_2(PPh_3)_4(\mu\text{-}C_{10}H_{12})](PF_6)_2$, **51**, is a dimer of the expected dimethylallenylidene complex **52** (Scheme 38). Two



Scheme 38.

$\{(\eta\text{-}C_5H_5)Ru(PPh_3)_2\}$ units are found bonded to a bridging $C_{10}H_{12}$ ligand which can be formulated as bonding as a vinylidene [Ru(1)–C(1)–C(2)–C(3)] to one ruthenium atom and as an alkylidene [Ru(2)–C(5)] to the other (see Table 2). Solutions of **51** become blue-violet on exposure to atmospheric moisture or triethylamine. The resulting product **53** is suggested, on the basis of spectroscopic evidence, to arise from deprotonation of the vinylidene

TABLE 2

Selected bond length data for **49** [a]

Bond	Distance (Å)
Ru(1)–C(1)	1.83(2)
C(1)–C(2)	1.29(2)
C(2)–C(3)	1.45(2)
Ru(2)–C(5)	2.30(2)

[a] Data reported in ref. 189.

β-proton in **51** to give $[(\eta\text{-}C_5H_5)_2Ru_2(PPh_3)_4(\mu\text{-}C_{10}H_{11})]PF_6$ which can best be regarded as a resonance hybrid of an alkynyl–alkylidene complex (**53a**, Scheme 38) and an allenylidene–vinyl complex (**53b**, Scheme 38). Addition of a strong acid (e.g. CF_3COOH) regenerates **51**.

(iii) Complexes of the type [(η-C₅R₅)M(CO)(L)X] (M = Ru, Os; L = Group 5 donor ligand)

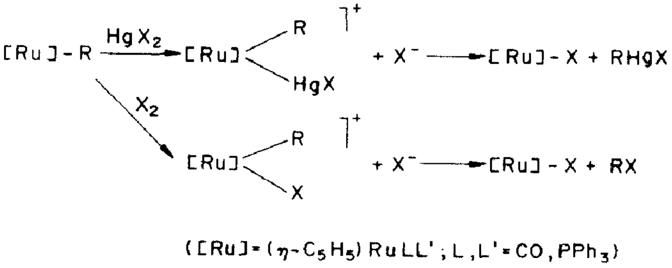
A feature of the chemistry of $[(\eta\text{-}C_5H_5)Ru(PPh_3)_2Cl]$ is the tendency to lose one of the bulky phosphine ligands to give derivatives of the type $[(\eta\text{-}C_5H_5)Ru(L)(PPh_3)Cl]$ (L = donor ligand e.g. PMe_3). A potentially useful starting material which may possess different properties to both $[(\eta\text{-}C_5H_5)Ru(PPh_3)_2Cl]$ and $[(\eta\text{-}C_5H_5)Ru(CO)_2Cl]$, is $[(\eta\text{-}C_5H_5)Ru(CO)(PPh_3)Cl]$, first synthesized by Stone and co-workers from $[(\eta\text{-}C_5H_5)Ru(PPh_3)_2Cl]$ via either a carbonylation procedure (150 atm.) or by reaction with the relatively expensive $[Fe_2(CO)_9]$ [142,190]. These routes have proved difficult to reproduce, and Davies and co-workers have recently published an improved, novel synthesis of this compound [191]. Heating toluene or xylene solutions of $[(\eta\text{-}C_5H_5)Ru(PPh_3)_2Cl]$ with sulfur in the presence of CO (1–3 atm.) has given near quantitative yields of $[(\eta\text{-}C_5H_5)Ru(CO)(PPh_3)Cl]$, the other product being $Ph_3P{=}S$. To date, little further use has been made of this potentially very useful reaction and it can be anticipated that a range of reactions of $[(\eta\text{-}C_5H_5)Ru(PPh_3)_2Cl]$ (essentially dissociative in terms of PPh_3) can be substantially altered or facilitated in the presence of elemental sulfur.

The compound $[(\eta\text{-}C_5H_5)Ru(CO)(PPh_3)Cl]$ has not been the subject of extensive investigations to date; it is significant, however, that it readily forms cationic complexes of the type $[(\eta\text{-}C_5H_5)Ru(CO)(PPh_3)(L)]^+$ [L = CO, PMe_3, $P(OPh)_3$], the last two complexes representing the first examples of the chiral species $[(\eta\text{-}C_5H_5)Ru(L^1)(L^2)(L^3)]^+$ [191]. The use of $[(\eta\text{-}C_5Me_5)_2Fe_2(CO)_4]$ or $[(\eta\text{-}C_5Me_5)_2Ru_2(CO)_4]$ to catalyze the carbonyl substitution reactions of $[(\eta\text{-}C_5H_5)Ru(CO)_2I]$ has been reported to produce a range of neutral and cationic ruthenium(II) complexes [(η-C_5H_5)Ru(CO)(L)I] [L = PPh_3, $PMePh_2$, PMe_2Ph, $P(OPh)_3$, $P(OMe)_3$, $P(OEt)_3$, $P(OPr^i)_3$, η^1-dppm] and [(η-C_5H_5)Ru(CO)L_2]I (L = $PMePh_2$, PMe_2Ph; L_2 = dppm, dppe, dppp, dppb) respectively [192]. Improved methods for the synthesis of the alkyl derivatives [(η-C_5H_5)Ru(CO)(PPh_3)R] (R = Me, $CH_2C_6H_5$) have been reported [104]; the former is obtained by the photochemical substitution of [(η-C_5H_5)Ru$(CO)_2$Me] by PPh_3, the latter by bubbling CO through a toluene solution of [(η-C_5H_5)Ru$(PPh_3)_2$($CH_2C_6H_5$)].

Oxidative cleavage reactions of a range of compounds of the type [(η-C_5H_5)Ru(L)(L′)R] (L, L′ = CO, PPh_3; R = Me, $CH_2C_6H_5$) with halogens, hydrogen chloride, mercury(II) halides and copper(II) halides have been reported [104]. Reactions with mercury(II) halides proceeded cleanly

$$[(\eta\text{-}C_5H_5)Ru(L)(L')R] + HgX_2 \rightarrow [(\eta\text{-}C_5H_5)Ru(L)(L')X] + RHgX$$

and are proposed to occur via an oxidative mechanism (Scheme 39) similar to that previously postulated for the corresponding iron system. The results of the halogen cleavage reactions (Scheme 39) suggest a stoichiometry and



Scheme 39.

probably a mechanism similar to the iron system, although particularly in the case of bromine, complicating side reactions occur. Treatment of [(η-C_5H_5)Ru(CO)(PPh_3)(CH_2Ph)] with HCl

$$[(\eta\text{-}C_5H_5)Ru(CO)(PPh_3)(CH_2PH)] + HCl \rightarrow [(\eta\text{-}C_5H_5)Ru(CO)(PPh_3)Cl] + C_6H_5CH_3$$

is proposed to occur via the ruthenium(IV)–hydride complex [(η-C_5H_5)Ru(CO)(PPh_3)(CH_2Ph)H]$^+$Cl$^-$, followed by reductive elimination of toluene. The copper(II) cleavage reactions were found to be more complex in nature, the data being consistent with one-electron oxidation processes to form the 17-electron intermediate [(η-C_5H_5)Ru(L)(L′)R]$^+$

$$[(\eta\text{-}C_5H_5)Ru(L)(L')R] + CuX_2 \rightarrow [(\eta\text{-}C_5H_5)Ru(L)(L')R]^+ + X^- + CuX$$

Nucleophilic attack by X^- on the α-carbon atom of the alkyl function would yield RX, and the radical $[(\eta\text{-}C_5H_5)Ru(L)(L')]^{\cdot}$ could then abstract a halogen atom from a second CuX_2 to complete the reaction [104].

The synthesis of the unusual metallocarboxylic acid $[(\eta\text{-}C_5H_5)Ru(CO)(PPh_3)(CO_2H)]$ by the treatment of $[(\eta\text{-}C_5H_5)Ru(CO)_2(PPh_3)]BF_4$ with Et_4NOH at 0 °C has been reported [193]. This reaction parallels an improved synthesis of the previously reported iron analogue. The thermolysis of $[(\eta\text{-}C_5H_5)Ru(CO)(PPh_3)(CO_2H)]$ in acetone (2 h, 50 °C) gave $[(\eta\text{-}C_5H_5)Ru(CO)(PPh_3)H]$ exclusively, with no evidence of dinuclear products (observed as products in the corresponding iron reaction) [193].

Several alkoxy(alkyl) carbene complexes $[(\eta\text{-}C_5H_5)Ru(CO)(PPh_3)\{C(OR)CH_2R'\}]$ ($R = Me, Et, Pr^i$; $R' = Ph$) have been synthesized and deprotonated to give the corresponding vinyl ether derivatives, as observed similarly with $[(\eta\text{-}C_5H_5)RuL_2\{C(OR)CH_2R'\}]$ ($L = PPh_3$; $L_2 =$ dppm) [194]. The X-ray crystal structure of $[(\eta\text{-}C_5H_5)Ru(CO)(PPh_3)\{C(OPr^i) = CHPh\}]$ has been determined; the vinyl ether ligand was found to have the *E* configuration i.e. with the ruthenium atom *trans* to the phenyl group (Fig. 15). As part of a study of the base promoted rearrangements of cyclopentadienyl acyl- and carboxyalkyl-iron and ruthenium complexes, the treatment of $[(\eta\text{-}C_5H_5)Ru(CO)(PPh_3)\{C(O)Bu^n\}]$ with *n*-butyllithium at −78 °C followed by methyl iodide gives the methyl complex $[(\eta\text{-}C_5H_5)Ru(CO)(PPh_3)Me]$ as the sole product [195]. This contrasts with the corresponding iron reaction which was found to give the cyclopentadienyl ring substituted products $[(\eta\text{-}C_5H_4CO_2R)Fe(CO)(PPh_3)Me]$ instead.

The menthyl- and neomenthylcyclopentadienyl ruthenium complexes $[(\eta\text{-}C_5H_4R^*)Ru(CO)(L)X]$ [R^* = menthyl, neomenthyl; $L = PBu^n_3$, PPh_3, PPh_2Me, $P(OPh)_3$; X = Cl, Br, I] have an optically active ruthenium centre and are configurationally stable in solution for extended periods. The X-ray crystal structures of $[(S)\text{-}CD(-)_{310}(\eta\text{-}C_5H_4R^*)Ru(CO)(PPh_3)Cl]$ (R^* = menthyl) and $[(R)\text{-}CD(-)_{325}(\eta\text{-}C_5H_4R^*)Ru(CO)(PPh_3)I]$ (R^* = neomenthyl) have established the absolute configuration of these complexes [99,196,197]. The reaction of $[(\eta\text{-}C_5H_4R^*)Ru(CO)(PPh_3)Cl]$ (**54**, R^* = neomenthyl) with $AgBF_4$ in acetonitrile leads to the cationic complex

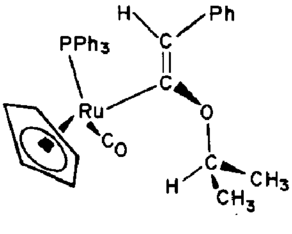


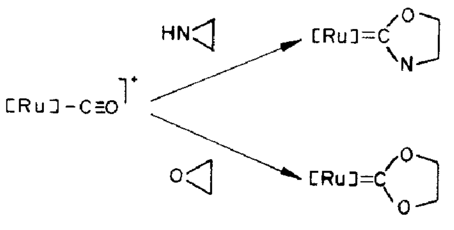
Fig. 15.

$[(\eta\text{-}C_5H_4R^*)Ru(CO)(PPh_3)(NCCH_3)]BF_4$, **55**, which on heating in deuterated acetonitrile undergoes exchange to give $[(\eta\text{-}C_5H_4R^*)Ru(CO)(PPh_3)(NCCD_3)]BF_4$, **56**. Further, reaction of **56** with NaI yields $[(\eta\text{-}C_5H_4R^*)Ru(CO)(PPh_3)I]$, **57**. All the transformations **54** → **55** → **56** → **57** take place with retention of configuration; the X-ray crystal structure of (R)-$[(\eta\text{-}C_5H_4R^*)Ru(CO)(PPh_3)(NCCH_3)]PF_6$, (**55**, R^* = neomenthyl) has been determined [198].

(iv) Complexes of the type $[(\eta\text{-}C_5R_5)ML_3]^+$ (M = Ru, Os; L = CO, MeCN etc; L_3 = arene, triene)

Methods for the preparation of the cation $[(\eta\text{-}C_5H_5)Ru(CO)_3]^+$ have been well documented [199]. A further procedure, treatment of $[(\eta\text{-}C_5H_5)_2Ru_2(CO)_4]$ with SO_2Cl_2 in benzene [200] has been reported. In a related fashion, cleavage of $[(\eta\text{-}C_5H_5)_2Ru_2(CO)_4]$ with $4\text{-}MeC_6H_4SO_3H$ in acetonitrile has given the cation $[(\eta\text{-}C_5H_5)Ru(CO)_2(NCMe)]^+$ in good yield [201].

The reaction of the cation $[(\eta\text{-}C_5H_5)Ru(CO)_3]^+$ with aziridine and oxirane [202] has given the heterocyclic carbene complexes shown in Scheme 40. The reaction of the metal hydride cluster $[\{(Ph_3P)CuH\}_6]$ with $[(\eta\text{-}C_5Me_5)Ru(CO)_3]BF_4$ gives a 1 : 1 mixture of $[(\eta\text{-}C_5Me_5)Ru(CO)_2H]$ and the formyl complex $[(\eta\text{-}C_5Me_5)Ru(CO)_2(CHO)]$ [203]: the latter decomposes via a radical pathway. When the preparation is carried out in the presence of 9,10-dihydroanthracene, a known hydrogen atom donor, the formyl complex is obtained in quantitative yield. The more stable product $[(\eta\text{-}C_5Me_5)Ru(CO)(PMe_2Ph)(CHO)]$ is obtained from $[(\eta\text{-}C_5Me_5)Ru(CO)_2(PMe_2Ph)]^+$ using either $[\{(Ph_3P)CuH\}_6]$ or $NaBH_4$ in THF/H_2O. At 40°C $[(\eta\text{-}C_5Me_5)Ru(CO)(PMe_2Ph)(CHO)]$ decomposes within one hour initially to a 1 : 1 mixture of $[(\eta\text{-}C_5Me_5)Ru(CO)_2H]$ and $[(\eta\text{-}C_5Me_5)Ru(CO)(PMe_2Ph)H]$, after which the former slowly converts entirely to the latter complex. In the presence of 9,10-dihydroanthracene, however, $[(\eta\text{-}C_5Me_5)Ru(CO)(PMe_2Ph)$

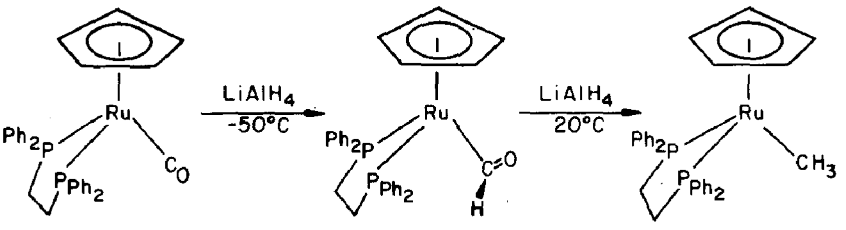


([Ru] = $(\eta\text{-}C_5H_5)RuLL'$; L,L' = CO, PPh_3)

Scheme 40.

(CHO)] took 14 days to decompose to the mixture of the hydride complexes. These results are in accord with the decomposition of the formyl complexes occurring by radical chain processes, presumably involving cleavage of the carbon-to-hydrogen bond of the formyl group in the rate determining step followed by decomposition of the resulting acyl radical to a more stable ruthenium based radical, the chain carrier in this process [203].

Reduction of the cation $[(\eta\text{-}C_5H_5)Ru(dppe)(CO)]^+$ at −50°C with $LiAlH_4$ gives the unstable formyl complex $[(\eta\text{-}C_5H_5)Ru(dppe)(CHO)]$ as the sole product [204]. As the reaction temperature is raised to 20°C, the methyl compound $[(\eta\text{-}C_5H_5)Ru(dppe)Me]$ is formed (Scheme 41). These results contrast with those found for the corresponding iron system [205], and for $[(\eta\text{-}C_5H_5)Ru(PPh_3)_2(CO)]^+$ which, depending on the reaction conditions, will give three products, $[(\eta\text{-}C_5H_5)Ru(PPh_3)_2H]$, $[(\eta\text{-}C_5H_5)Ru(PPh_3)_2Me]$ and $[(\eta^4\text{-}C_5H_6)Ru(PPh_3)_2(CO)]$ on treatment with $LiAlH_4$, without apparently forming a formyl intermediate [204].



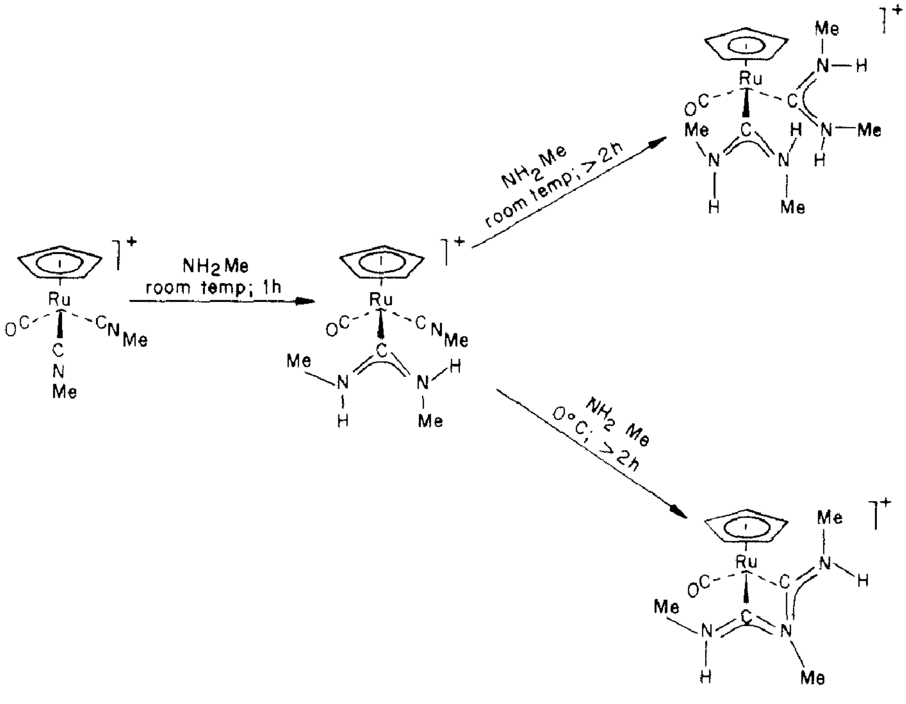
Scheme 41.

The cationic complex $[(\eta\text{-}C_5Me_5)Ru(CO)_3]BF_4$ reacts with the lithium phosphides $Li[P(SiMe_3)_2]\cdot 2THF$, $Li[PBu^t(SiMe_3)]$ and $Li[PPh(SiMe_3)]$ in ether at −78°C to give the ruthenium phosphinocarbonyl complexes $[(\eta\text{-}C_5Me_5)Ru(CO)_2\{COPR(SiMe_3)\}]$ ($R = SiMe_3$, Bu^t, Ph) [206]. Only when $R = Bu^t$ could the product of the reaction be isolated as a solid. In the other cases, product decomposition occurred during work-up to give the ruthenium phosphido complexes $[(\eta\text{-}C_5Me_5)Ru(CO)_2\{PR(SiMe_3)\}]$, compounds also obtained, together with $[(\eta\text{-}C_5Me_5)Ru(CO)_2\{PBu^t(SiMe_3)\}]$ from the reaction of $Li[PR(SiMe_3)]$ ($R = SiMe_3$, Bu^t, Ph) with $[(\eta\text{-}C_5Me_5)Ru(CO)_2Br]$. The X-ray crystal structure of $[(\eta\text{-}C_5Me_5)Ru(CO)_2\{C(O)PBu^t(SiMe_3)\}]$ has been determined [206] confirming the $\{C(O)PBu^t(SiMe_3)\}$ unit, and establishing its linkage to the metal by a covalent Ru–C bond.

The anion $K[(\eta\text{-}C_5H_5)Ru(CO)(CN)_2]$, **58**, has been synthesized by the treatment of $[(\eta\text{-}C_5H_5)Ru(CO)_2Br]$ with excess KCN in dry methanol [207]. Alkylation of **58** with methyl iodide in boiling acetonitrile gives complete conversion to $[(\eta\text{-}C_5H_5)Ru(CO)(CNMe)_2]I$ within 16 h. Under milder reaction conditions (50°C, 5 h) the neutral compound $[(\eta\text{-}C_5H_5)Ru(CO)(CNMe)CN]$ is obtained. Photolysis of $[(\eta\text{-}C_5H_5)Ru(CO)(CNMe)_2]I$ in dichloromethane with $AgPF_6$ gives $[(\eta\text{-}C_5H_5)Ru(CNMe)_3]PF_6$. Treatment of $[(\eta\text{-}C_5H_5)Ru(CO)(PPh_3)Br]$ with $AgBF_4$ in THF followed by cyanide anion addition and alkylation with MeI has given $[(\eta\text{-}C_5H_5)Ru(CO)(PPh_3)(CNMe)]I$ in 77% yield [207]. Both primary and secondary methyl amines react with the neutral monoisocyanide complex $[(\eta\text{-}C_5H_5)Ru(CO)(CNMe)CN]$ to produce di- and trisubstituted carbene complexes

$$[(\eta\text{-}C_5H_5)Ru(CO)(CNMe)CN] + MeNH_2$$
$$\rightarrow [(\eta\text{-}C_5H_5)Ru(CO)\{C(NHMe)_2\}CN]$$
$$[(\eta\text{-}C_5H_5)Ru(CO)(CNMe)CN] + Me_2NH$$
$$\rightleftharpoons [(\eta\text{-}C_5H_5)Ru(CO)\{C(NHMe)(NMe_2)\}CN]$$

The reaction of $[(\eta\text{-}C_5H_5)Ru(CO)(CNMe)_2]^+$ with excess methylamine gives, depending on the reaction conditions, the three products shown in Scheme 42. With dimethylamine, $[(\eta\text{-}C_5H_5)Ru(CO)(CNMe)_2]^+$ reacted to give the

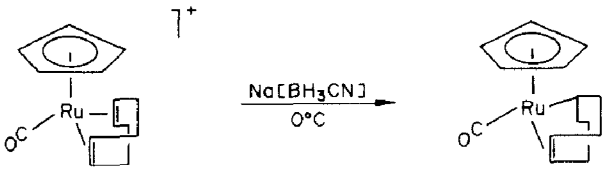


Scheme 42.

cationic trisubstituted diaminocarbene complex $[(\eta\text{-}C_5H_5)Ru(CO)(CNMe)\{C(NHMe)(NMe_2)\}]^+$. Longer reaction times gave a product assigned on the basis of spectroscopic data, the chelate structure $[(\eta\text{-}C_5H_5)Ru(CO)\{C(NHMe)(NMe)C(NMe_2)\}]^+$ and a third product believed to be the deprotonated chelate species $[(\eta\text{-}C_5H_5)Ru(CO)\{C(NMe)(NMe)C(NMe_2)\}]$. The tris-isocyanide cation $[(\eta\text{-}C_5H_5)Ru(CNMe)_3]^+$ reacts with methylamine to give $[(\eta\text{-}C_5H_5)Ru(CNMe)_2\{C(NHMe)_2\}]^+$, while extended reaction times with excess methylamine establishes an equilibrium between this product and a second material believed to be the di-carbene $[(\eta\text{-}C_5H_5)Ru(CNMe)\{C(NHMe)_2\}_2]^+$. All the diaminocarbene complexes feature restricted rotation about the C–N bond; NMR spectroscopy has been used to establish that the methyl carbene substituents, frozen in *cis*- or *trans*- to metal positions, broaden and coalesce on raising the temperature. Rotational free energy barriers have been calculated from these measurements [208].

UV irradiation of a solution of $[(\eta\text{-}C_5H_5)Ru(CO)_2(NCMe)]BF_4$ in acetonitrile affords $[(\eta\text{-}C_5H_5)Ru(CO)(NCMe)_2]BF_4$, **59**. In common with the $[(\eta\text{-}C_5H_5)Ru(NCMe)_3]^+$ cation, the acetonitrile ligands in **59** are substitution labile and reaction of **59** with a range of dienes (buta-1,3-diene, isoprene, 1,4-diphenylbuta-1,3-diene, cyclohexa-1,3-diene) gives single isomers of the complexes $[(\eta\text{-}C_5H_5)Ru(\eta\text{-}1,3\text{-diene})(CO)]BF_4$ in good yields [209]. The X-ray crystal structure of the cyclohexa-1,3-diene cation [209] established that the molecule adopts an *exo* configuration relative to the cyclopentadienyl ring. The C_6 ring shows marked folding. Reaction of **59** with *trans*-penta-1,3-diene afforded the *exo* complex $[(\eta\text{-}C_5H_5)Ru(\eta\text{-}trans\text{-}C_5H_8)(CO)]BF_4$, while reaction with *cis*-penta-1,3-diene gave an isomeric mixture (39 : 28 : 11 : 4) of *exo* and *endo* isomers of both $[(\eta\text{-}C_5H_5)Ru(\eta\text{-}cis\text{-}C_5H_8)(CO)]BF_4$ and $[(\eta\text{-}C_5H_5)Ru(\eta\text{-}trans\text{-}C_5H_8)(CO)]BF_4$. A mechanism involving a hydrogen shift process and a ruthenium(II) ↔ ruthenium(IV) redox process has been proposed to account for these observations. While cycloocta-1,3-diene does not react with **59**, both cycloocta-1,5-diene and cyclooctatetraene react giving the complexes $[(\eta\text{-}C_5H_5)Ru(\eta\text{-}C_8H_{12})(CO)]BF_4$ and $[(\eta\text{-}C_5H_5)Ru(\eta\text{-}C_8H_8)(CO)]BF_4$, respectively. The latter complex loses CO on UV irradiation to give $[(\eta\text{-}C_5H_5)Ru(\eta^6\text{-}C_8H_8)]BF_4$. The diene cations readily react with nucleophiles to give η^3-allyl complexes. Thus treatment of $[(\eta\text{-}C_5H_5)Ru(\eta\text{-}C_4H_6)(CO)]BF_4$ with lithium diphenylcuprate in THF gives $[(\eta\text{-}C_5H_5)Ru(\eta^3\text{-}CH_2CHCHCH_2Ph)(CO)]$ in which the allyl moiety is assigned an *exo* configuration with the benzyl group occupying an *anti* configuration. Other *exo* allyl systems are obtained by the treatment of the isoprene and cyclohexa-1,3-diene cations with $Na[BH_3CN]$. The X-ray crystal structure of $[(\eta\text{-}C_5H_5)Ru(\eta^3\text{-}C_6H_9)(CO)]$ has been determined establishing that the six-membered ring adopts a boat-like conformation. On the basis of ^1H–^1H NMR coupling between the allylic protons and the adjacent alkyl protons, a similar ring conformation is assigned to the solution structure of this complex. Treatment of the cycloocta-1,5-diene cation with $Na[BH_3CN]$ gives $[(\eta\text{-}C_5H_5)Ru(\eta^2,\eta^1\text{-}C_8H_{13})(CO)]$ (Scheme 43), which does not isomerize to the η^3-allyl species [209].

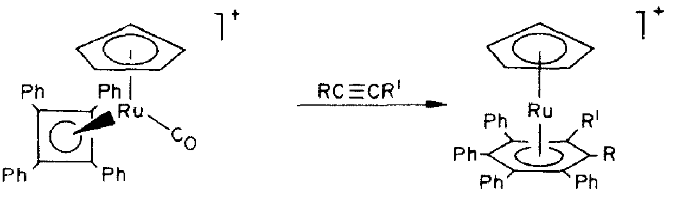
The tris-acetonitrile cation $[(\eta\text{-}C_5H_5)Ru(NCMe)_3]^+$ has, by virtue of the



Scheme 43.

facile displacement of the acetonitrile ligands in the metal coordination sphere, provided a facile synthetic route to unsymmetrically substituted ruthenocenes carrying one or two substituents on the same ring by reaction with 6-(dimethylamino)pentafulvalenes [21].

The addition of $AgBF_4$ to a solution of $[(\eta\text{-}C_5H_5)_2Ru_2(CO)_4]$ and diphenylacetylene in dichloromethane gives a separable mixture of $[(\eta\text{-}C_5H_5)Ru(\eta^4\text{-}C_4Ph_4)CO]BF_4$, **60**, (47% yield), $[(\eta\text{-}C_5H_5)Ru(CO)_2(PhC_2Ph)]BF_4$ and $[(\eta\text{-}C_5H_5)Ru(CO)_3]BF_4$ [210]. UV irradiation of **60** in acetonitrile gives a good yield of $[(\eta\text{-}C_5H_5)Ru(\eta^4\text{-}C_4Ph_4)(NCMe)]BF_4$, **61**. The X-ray crystal structure of **61** has been determined. An interesting feature of this molecule relates to the coordination of the tetraphenylcyclobutadiene and cyclopentadienyl ligands. The coordination of the butadiene ligand is not symmetrical (Ru–C 2.192, 2.208, 2.177, 2.175 Å). Furthermore, the butadiene ring is rectangular in shape (C–C 1.438, 1.457, 1.486, 1.497 Å). This distortion is accounted for in terms of the frontier orbitals of the d^6 $\{(\eta\text{-}C_5H_5)RuL\}^+$ fragment which break the degeneracy of the e_g set of cyclobutadiene orbitals and result in greater occupancy of the a'' (relative to a') cyclobutadiene molecular orbital. A complementary variation within the cyclopentadienyl ligand is attributed to the effect of the $\{Ru(\eta^4\text{-}C_4Ph_4)L\}^{2+}$ fragment on the e_1'' orbitals. Irradiation of **60** in the presence of diphenylacetylene leads to the arene-ruthenium cation $[(\eta\text{-}C_5H_5)Ru(\eta^6\text{-}C_6Ph_6)]^+$ in high yield. In a similar manner irradiation in the presence of PhC_2Me, MeC_2Me or $MeO_2CC_2CO_2Me$ gave a range of similar cations (Scheme 44). Irradiation of **60** in the presence of ethylene gives 1,2,3,4-tetraphenylcyclohexa-1,3-diene and $[(\eta\text{-}C_5H_5)Ru(CH_2{=}CH_2)_3]BF_4$.

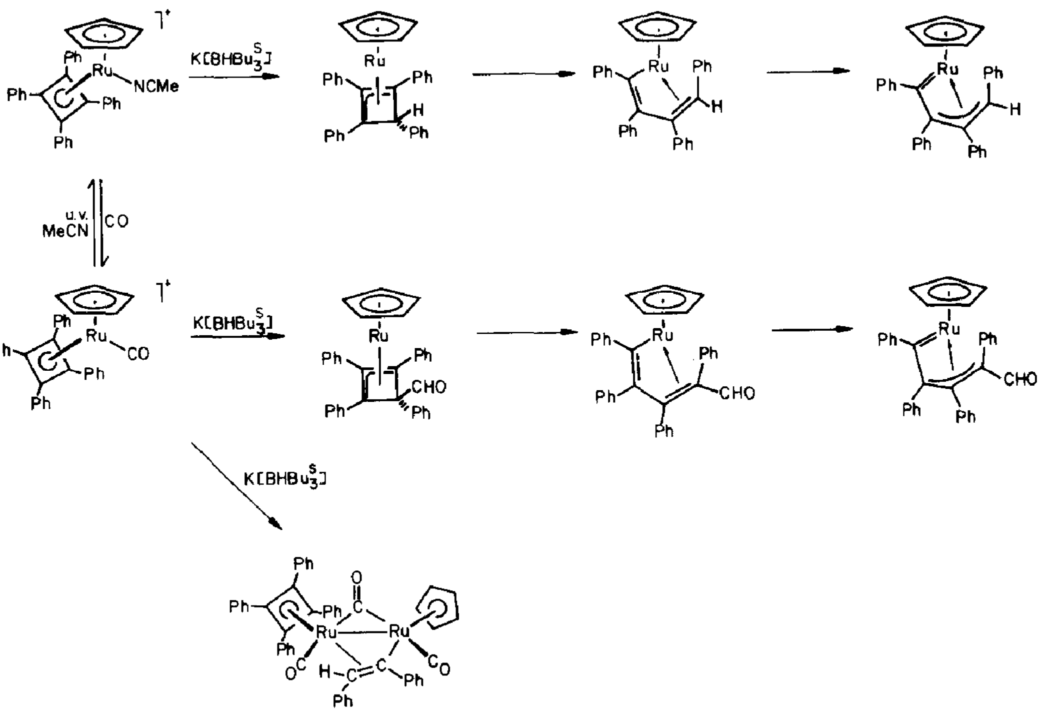


(R,R' = Me, CO_2Me, Ph; R = Me, R' = Ph)

Scheme 44.

Reaction of $[(\eta\text{-}C_5H_5)Ru(\eta^4\text{-}C_4Ph_4)(NCMe)]BF_4$ with $K[BHBu^s_3]$

(−78°C, THF) gave a complex of stoichiometry [(η-C_5H_5)Ru {C(Ph)C(Ph)C(Ph)CHPh}] which has been characterized by X-ray crystallography [211]. The structure establishes that ring opening has occurred (Scheme 45); all four carbon atoms of the C_4 chain are bonded to the {(η-C_5H_5)Ru} fragment, one of them as an alkylidene carbon doubly bonded to ruthenium (Ru–C 1.896 Å). The remaining three carbon atoms have ruthenium–carbon distances of 2.204, 2.152 and 2.154 Å characteristic of an η^3-allyl system. Twisting of the C_4 chain allows the novel η^4-bonding of the butadienyl system to the ruthenium centre. The reaction between [(η-C_5H_5)Ru(η^4-C_4Ph_4)(CO)]BF_4 and K[$BHBu^s_3$] affords two products (Scheme 45), the first, suggested on the basis of spectroscopic data (specifically a characteristic low field $^{13}C\{^1H\}$ NMR signal at δ 255.23 attributable to an alkylidene type carbon and a strong band in the IR spectrum at 1643 cm^{-1} indicative of a formyl group) to take the form shown in Scheme 45. The second product was characterized by X-ray crystallography; in the solid state the molecule consists of two ruthenium atoms bound by a single bond (2.802 Å) and bridged by a carbonyl and a (Z)-1,2-diphenylvinyl ligand (Scheme 45).



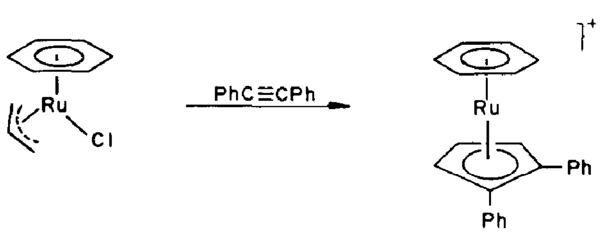
Scheme 45.

Relative to the large number of published reports on the synthesis and reactions of [(η-C_5H_5)Fe(η^6-arene)]$^+$ cations, up to 1982 there were very few papers relating to the corresponding ruthenium and osmium analogues. Briefly, Coffield and Closson patented a synthetic route to $[(\eta\text{-}C_5H_5)M(\eta^6\text{-arene})]^+$ cations (M = Ru, Os) via reaction of $[(\eta\text{-}C_5H_5)M(CO)_3]^+$ cations with the appropriate arene [212], reaction of $[(\eta\text{-}C_5H_5)Ru(PPh_3)_2Cl]$ with $NaBPh_4$ gave the zwitterion $[(\eta\text{-}C_5H_5)Ru(\eta^6\text{-}C_6H_5BPh_3)]$ [213,214], reaction of $[\{(\eta^6\text{-}C_6H_6)RuCl_2\}_2]$ with TlC_5H_5 gave $[(\eta\text{-}C_5H_5)Ru(\eta^6\text{-}C_6H_6)]Cl$ [215], while the well-known Nesmeyanov route ($[M(\eta\text{-}C_5H_5)_2]$, $AlCl_3$, Al, arene) had been used to synthesize several $[(\eta\text{-}C_5H_5)Ru(\eta^6\text{-arene})]^+$ cations [216–218].

Stephenson and co-workers [219] recently reported the high yield synthesis of the cations $[(\eta\text{-}C_5H_5)M(\eta^6\text{-arene})]^+$ (M = Ru, arene = C_6H_6, $p\text{-}MeC_6H_4CHMe_2$, C_6H_5OMe, C_6Me_6; M = Os, arene = C_6H_6, $p\text{-}MeC_6H_4CHMe_2$) by the treatment of the appropriate $[\{(\eta^6\text{-arene})MCl_2\}_2]$ complex with TlC_5H_5 (molar ratio 1 : 2) in acetonitrile. The cations were isolated variously as the PF_6^-, BPh_4^- or Cl^- salts and were characterized by ^1H and ^{13}C NMR spectroscopy. Vol'kenau and co-workers [10] have reported improvements to the original Nesmeyanov route to $[(\eta\text{-}C_5H_5)Ru(\eta^6\text{-arene})]^+$ cations from ruthenocene. The reactions were carried out in an autoclave at higher temperatures, and a small amount of water was also used to promote the reactions [10].

The reaction of $[(\eta\text{-}C_5H_5)Ru(\eta\text{-}C_8H_{12})Cl]$ (C_8H_{12} = cycloocta-1,5-diene) with arenes (e.g. benzene, hexamethylbenzene) in boiling ethanol yields, after anion exchange with NH_4PF_6, the cationic complexes $[(\eta\text{-}C_5H_5)Ru(\eta^6\text{-}C_6R_6)]PF_6$ in high yield. A notable feature of these reactions is that this route readily provides η-arene complexes of both highly, and unusually, substituted aromatic moieties in high yield [12–14]. Cations of the type $[(\eta\text{-}C_5H_5)Ru(\eta^6\text{-arene})]^+$ have also been obtained as the products of the dehydrogenation of 1,4- and 1,3-cyclohexadiene ligands in $[(\eta\text{-}C_5H_5)Ru(\eta\text{-diene})Cl]$ [220].

Treatment of $[(\eta\text{-}C_6H_6)Ru(\eta^3\text{-}C_3H_5)Cl]$ with $AgBF_4$ followed by the addition of diphenylacetylene at room temperature gives, via novel condensation of the allyl ligand and the alkyne, the salts $[(\eta\text{-}C_5H_3Ph_2\text{-}1,2)Ru(\eta^6\text{-}C_6H_6)]BF_4$, **62**, [221], characterized by X-ray crystallography (Scheme 46). In a similar fashion the complexes $[(\eta\text{-}C_5H_2Ph_3\text{-}1,2,4)Ru(\eta^6\text{-}C_6H_6)]PF_6$, $[(\eta\text{-}C_5H_2\text{-}1,2\text{-}Ph_2\text{-}3\text{-}C_6H_4F\text{-}p)Ru(\eta^6\text{-}C_6H_6)]PF_6$, $[(\eta\text{-}C_5H_5\text{-}1,2\text{-}Ph_2\text{-}3\text{-}Me)Ru(\eta^6\text{-}C_6H_6)]PF_6$, $[(\eta\text{-}C_5H_3\text{-}1\text{-}Ph\text{-}2\text{-}Me)Ru(\eta^6\text{-}C_6H_6)]PF_6$, $[(\eta\text{-}C_5H_3\text{-}1\text{-}Et\text{-}2\text{-}Pr)Ru(\eta^6\text{-}C_6H_6)]PF_6$ and $[(\eta\text{-}C_5H_3\text{-}1\text{-}Ph\text{-}2\text{-}Et)Ru(\eta^6\text{-}C_6H_6)]PF_6$ have been synthesized [221] providing a unique and reasonably versatile route to cyclopentadienyl–ruthenium arene cations containing unusually substituted cyclopentadienyl groups. Although the authors suggest several mechanisms, it seems certain that the first step is coordination of the alkyne to a 16-electron coordinatively unsaturated species [221]. The osmium com-



62

Scheme 46.

plex $[(\eta^6\text{-}C_6H_6)Os(\eta^3\text{-}C_3H_5)Cl]$ failed to react with diphenylacetylene in the presence of $AgBF_4$.

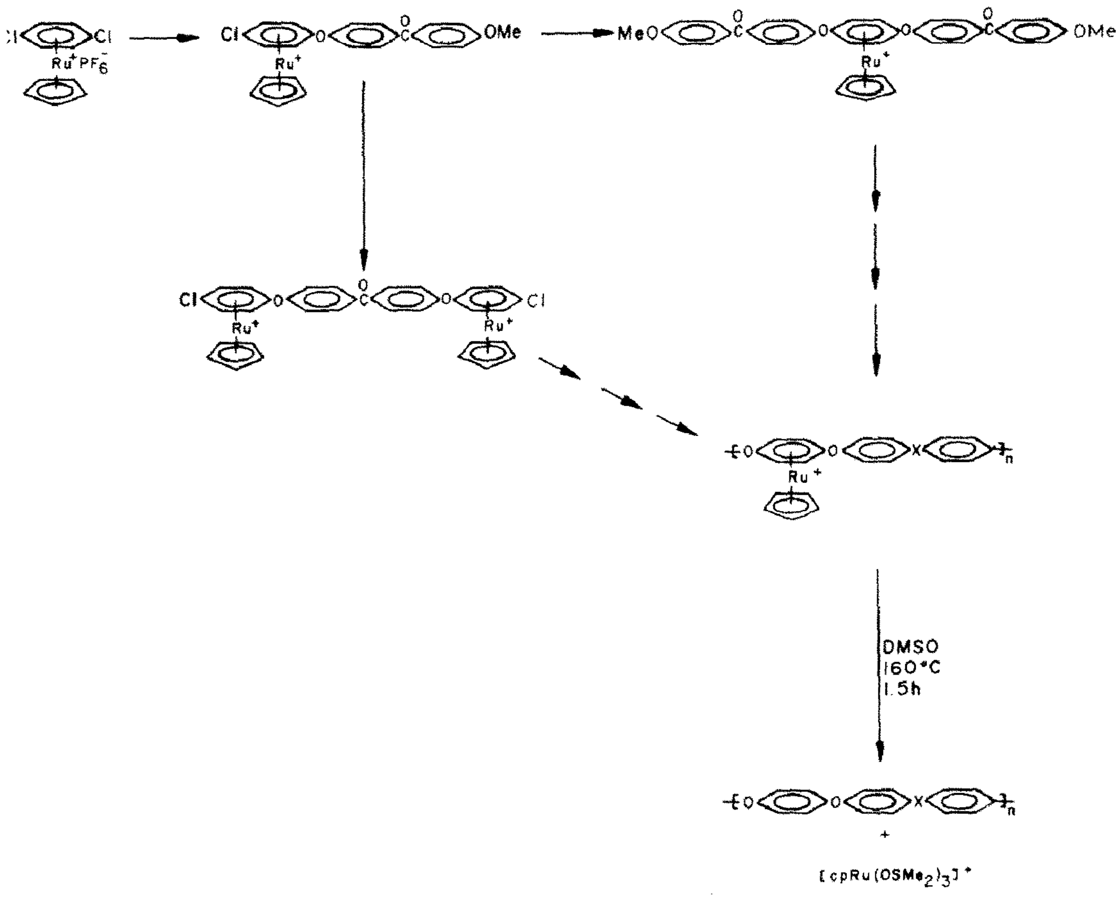
The reactivity of $[(\eta\text{-}C_5H_5)Ru(\eta^6\text{-arene})]^+$ cations has been studied [86]. Phenol-, diphenylsulfide- and cyanobenzenecyclopentadienylruthenium cations were obtained by the substitution of chlorine on the η^6-chlorobenzene complex, while the reaction of $[(\eta\text{-}C_5H_5)Ru(\eta^6\text{-}C_6H_5F)]BF_4$ with methanol in the presence of Na_2CO_3 and with piperidine, gave $[(\eta\text{-}C_5H_5)Ru(\eta^6\text{-}C_6H_5OMe)]BF_4$ and $[(\eta\text{-}C_5H_5)Ru(\eta^6\text{-}C_6H_5NC_5H_{10})]BF_4$ respectively. These routes enable the synthesis of substituted arene complexes not obtainable by other procedures e.g. ligand exchange on ruthenocene [10]. Nucleophilic attack occurs on the arene ligand in $[(\eta\text{-}C_5H_5)Ru(\eta^6\text{-}C_6H_6)]^+$ by the action of $NaBH_4$ or PhLi, giving the cyclohexadienyl complexes $[(\eta\text{-}C_5H_5)Ru(\eta^5\text{-}C_6H_7)]$ and $[(\eta\text{-}C_5H_5)Ru(\eta^5\text{-}C_6H_6Ph)]$ respectively (Scheme 7). Oxidation of $[(\eta\text{-}C_5H_5)Ru(\eta^6\text{-}C_6H_5Me)]BF_4$ and $[(\eta\text{-}C_5H_5)Ru(\eta^6\text{-}C_6H_5SC_6H_5)]BF_4$ with $KMnO_4$ takes place at the arene substituents giving the cations $[(\eta\text{-}C_5H_5)Ru(\eta^6\text{-}C_6H_5CO_2H)]^+$ and $[(\eta\text{-}C_5H_5)Ru(\eta^6\text{-}C_6H_5SO_2C_6H_5)]^+$ [86].

Photolysis of $[(\eta\text{-}C_5H_5)Ru(\eta^6\text{-}C_6H_6)]^+$ in acetonitrile at 313 nm gives, in quantitative yield $[(\eta\text{-}C_5H_5)Ru(NCMe)_3]^+$, **63**, isolated as the hexafluorophosphate salt [222]. The thermal substitution of this complex may be controlled, depending on the reaction conditions i.e. one, two or all three acetonitrile ligands may be selectively replaced. This may be seen with $P(OMe)_3$ substitution reactions: reaction at room temperature gave a quantitative yield of $[(\eta\text{-}C_5H_5)Ru(NCMe)_2\{P(OMe)_3\}]PF_6$, which after several days converted to $[(\eta\text{-}C_5H_5)Ru(NCMe)\{P(OMe)_3\}_2]PF_6$. On heating in dichloroethane the tri-substituted product $[(\eta\text{-}C_5H_5)Ru\{P(OMe)_3\}_3]PF_6$ was formed. In accordance with this, treatment of **63** with hexamethylbenzene, [2.2]-*p*-cyclophane and *p*-dichlorobenzene [222], benzene-d_6, toluene, mesitylene, pentamethylbenzene and di-*tert*-butylbenzene [223], in dichloroethane gave good yields of the corresponding cations $[(\eta\text{-}C_5H_5)Ru(\eta^6\text{-arene})]^+$.

Photolysis of $[(\eta\text{-}C_5H_5)Ru(\eta^6\text{-}C_6H_6)]PF_6$ in CH_2Cl_2 in the absence of ligands gives no net reaction. However, in the presence of $P(OMe)_3$ or

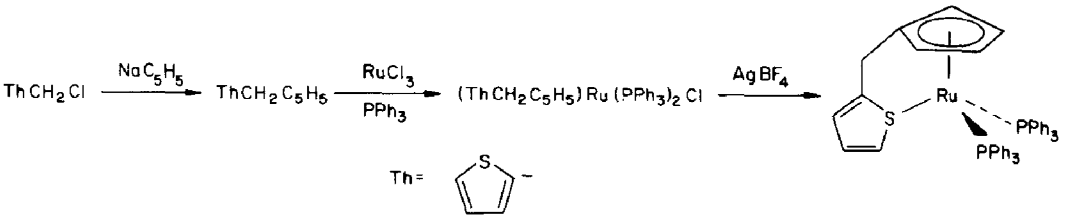
$P(OEt)_3$ in CH_2Cl_2, $[(\eta\text{-}C_5H_5)Ru\{P(OR)_3\}_3]^+$ (R = Me, Et) is obtained. The photochemical removal of the arene ligand from $[(\eta\text{-}C_5H_5)Ru(\eta^6\text{-arene})]^+$ (arene = *p*-dichlorobenzene, benzene, toluene, mesitylene, pentamethylbenzene, hexamethylbenzene and tri-*tert*-butylbenzene) has been studied as a function of arene substituent and temperature [223].

The complex $[(\eta\text{-}C_5H_5)Ru(\eta^6\text{-}C_6H_4Cl_2\text{-}p)]PF_6$ undergoes nucleophilic substitution by phenoxides to give a range of mono- and di-ruthenium complexes containing ring-linked structures (Scheme 47) [224]. These serve as models for the formation of aromatic organoruthenium polymers of the polyether or polyether-ketone class (Scheme 47), the metal-free polymer being obtained by arene displacement in a coordinating solvent e.g. DMSO [224].



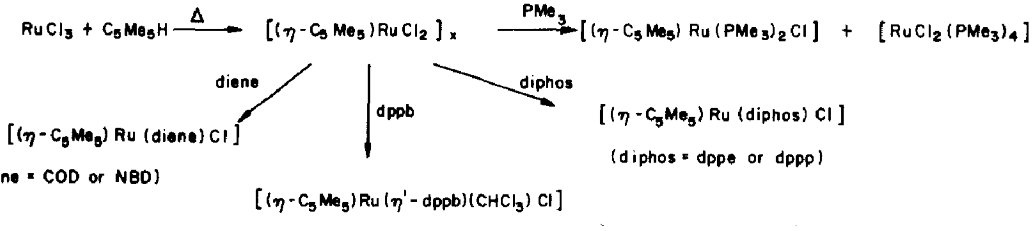
Scheme 47.

The thermolysis of $[(\eta\text{-}C_5H_5)Ru(PPh_3)_2Cl]$ in a number of solvents (e.g. ethylene glycol) has given a range of unusual cyclopentadienyl-ruthenium-arene cations [225]. The unusual complex $[(\eta\text{-}C_5H_5)Ru(\eta^5\text{-}C_4H_4S)]BF_4$, containing the first example of a thiophene ligand π-bound to a second or third row transition metal, has been synthesized by heating [(η-C_5H_5)Ru$(PPh_3)_2$Cl] with thiophene and $AgBF_4$ in boiling methanol [226]. Exchange reactions have given deuteration of the thiophene ligand in the 2,5 positions. Treatment of CD_2Cl_2 solutions of [(η-C_5H_5)Ru$(PPh_3)_2$Cl] with $AgBF_4$ in the presence of thiophene gives the unstable [(η-C_5H_5)Ru$(PPh_3)_2$(η^1-SC_4H_4)]BF_4 which decomposes, on standing, to [(η-C_5H_5)Ru(η^5-C_4H_4S)]$^+$ [227]. A stabilized η^1-thiophene adduct [(η-$C_5H_4CH_2C_4H_3S$)Ru$(PPh_3)_2$]BF_4 has, however, been obtained by the treatment of [(η-$C_5H_4CH_2C_4H_3S$)Ru$(PPh_3)_2$Cl] (prepared from $C_5H_5CH_2C_4H_3S$, $RuCl_3$ and PPh_3) with $AgBF_4$ in CH_2Cl_2 (Scheme 48). The methylene bridge prevents the formation of the η^5-thiophene cationic complex, and while this complex is more stable than [(η-C_5H_5)Ru$(PPh_3)_2$(η^1-SC_4H_4)]BF_4, the sulfur donor is readily displaced by carbon monoxide and by acetonitrile. The X-ray crystal structure of [(η-$C_5H_4CH_2C_4H_3S$)Ru$(PPh_3)_2$]BPh_4 has been determined [227].



Scheme 48.

One of the most remarkable cyclopentadienyl ruthenium complexes to be reported recently is the paramagnetic ruthenium(III) complex [{(η-C_5Me_5)$RuCl_2$}$_x$], **64**, first reported by Bercaw and co-workers [16], but synthesized independently by Suzuki and co-workers [157]. The brown polymeric material is obtained directly from ruthenium trichloride and pentamethylcyclopentadiene in boiling ethanol. Treatment of **64** with donor ligands leads to a variety of neutral and cationic ruthenium(II) complexes (Scheme 49), but apparently no ruthenium(III) species have yet been ob-

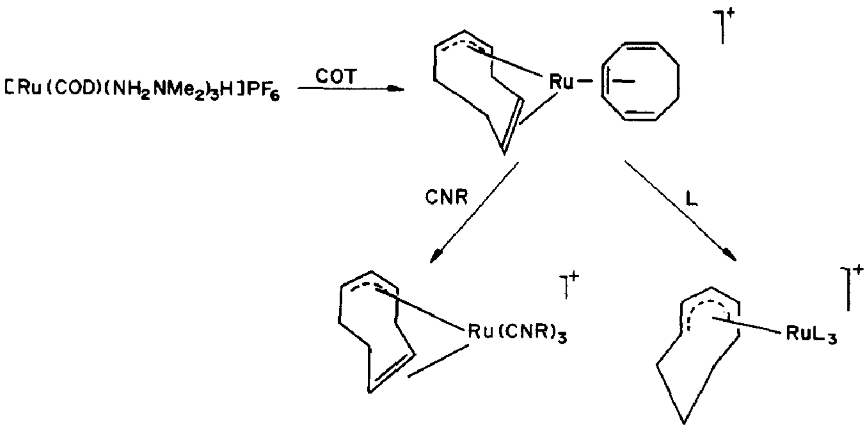


Scheme 49.

tained. (Oxidative additions of allyl halides occur under mild conditions giving the ruthenium(IV)-allyl complexes [(η-C_5Me_5)Ru(η^3-allyl)(Cl)X] [127].) Compounds of particular importance which are obtained from **64** (Scheme 49) include the neutral diolefin compounds [(η-C_5Me_5)Ru(η-diolefin)Cl] (diolefin = cycloocta-1,5-diene, norbornadiene), specific examples of the general class of highly reactive ruthenium(II) complexes [(η-C_5R_5)Ru(η-diolefin)X] (R = H, alkyl; diolefin = typically cycloocta-1,5-diene, X = halide, hydride) [12,129,132]. Some of these compounds have also been obtained by the thermal decomposition of [(η-C_5R_5)Ru(η^3-allyl)(CH_3)X] in the presence of neutral donor ligands e.g. cycloocta-1,5-diene [129].

The complex [(η-C_5H_5)Ru(η-C_8H_{12})Cl] readily undergoes substitution reactions of the cyclooctadiene and/or chloro ligand giving a vast range of neutral and cationic products, of both ruthenium(II) and -(IV) [12,13,128]. Treatment with donor ligands (e.g. phosphines, isocyanides, [12,13] amines [12,13,228]) readily gives compounds of the type [(η-C_5H_5)RuL_2Cl] while reactions with arenes and trienes in boiling ethanol solution gives cations of the type [(η-C_5H_5)Ru(η^6-arene)$]^+$ and [(η-C_5H_5)Ru(η^6-triene)$]^+$ respectively [12–14]. Ruthenium(IV)-allyl complexes of the type [(η-C_5H_5)Ru(η^3-allyl)(Cl)X] are obtained from [(η-C_5H_5)Ru(η-C_8H_{12})Cl] under relatively mild conditions from the oxidative addition of both allylic (e.g. *cis*-3,4-dichlorocyclobutene) and vinylic halides to the ruthenium(II) centre. The X-ray crystal structure of [(η-C_5H_5)Ru(η^3-C_4H_4OMe)Cl_2] has been determined [128]. Treatment of [(η-C_5H_5)Ru(η-C_8H_{12})H] with monodentate ligands (PPh_3, 2,6-$Me_2C_6H_3NC$) results in hydride ligand migration to give the η^3-cyclooctenyl complexes [(η-C_5H_5)RuL(η^3-C_8H_{13})], whereas with chelating diphosphines L_2 (e.g. dmpe, dppm), hydride migration to give the alkenyl complex [(η-C_5H_5)RuL_2(1-η^1-C_8H_{13})] was found to take place. Restricted rotation about the Ru–C bond in [(η-C_5H_5)Ru(dppm)(1-η^1-C_8H_{13})] yields two isomers of this compound, both of which have been structurally characterized by crystallography [229].

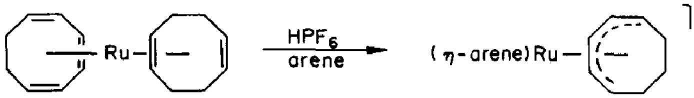
Treatment of acetone or methanol solutions of [(η-C_8H_{12})RuH($NH_2NMe$$)_3$]$PF_6$ (C_8H_{12} = cycloocta-1,5-diene) with excess cyclooctatetraene gives in 30% yield the complex [Ru(η^3,η^2-C_8H_{11})(η^6-cyclooctatriene)]PF_6 (Scheme 50) [230]. The triene ligand is readily displaced by a range of ligands, in the case of phosphine and arsines giving [Ru(η^5-C_8H_{11})(L$)_3$]PF_6, **65**, [L = PMe_2Ph, P(OMe$)_3$, $AsMePh_2$; L_3 = ($Ph_2PCH_2$$)_3$$CCH_3$]. Compounds **65** (L = PMe_2Ph, $AsMePh_2$) are also obtained by heating the hydrido-diene complexes [(η-C_8H_{12})RuH(L$)_3$]PF_6 in dioxane at 100 °C in the presence of excess cycloocta-1,5-diene which is converted to a mixture of cyclooctene, 1,3-, 1,4- and 1,5-cyclooctadiene [230]. When a suspension of [(η-C_8H_{12})RuH($PMe_2Ph$$)_3$]$PF_6$ is treated with an excess of



Scheme 50.

cyclooctatetraene in methanol at 60 ° C, the unusual compound [Ru(2-6-η-bicyclo[5.1.0]octadienyl)(PMe$_2$Ph)$_3$]PF$_6$, **66**, (Fig. 16) is formed in good yield. The X-ray crystal structure of **66** has been determined; the cyclopropyl ring lies in a position *exo* to the metal atom with perhaps the most remarkable feature being the elongated bond (1.63 Å) common to the three- and seven-membered rings. ^1J(CH) coupling constants have been explored as a definitive method for assigning the cyclopropyl ring in such systems [231].

Protonation of [Ru(η^6-cycloocta-1,3,5-triene)(η^4-cycloocta-1,5-diene)], **67**, with HPF$_6$ in aromatic solvents affords [Ru(η^6-arene)(η^5-cyclooctadienyl)]PF$_6$ (arene = C_6H_6, 1,4-$Me_2C_6H_4$, C_6H_5Cl) cations in near quantitative yields (Scheme 51) [232,233]. In the presence of donor ligands other than arenes e.g. phosphines, a similar reaction takes place giving [Ru(η^5-C_8H_{11})(L)$_3$]$^+$ cations. A possible pathway for the reaction could



Scheme 51.

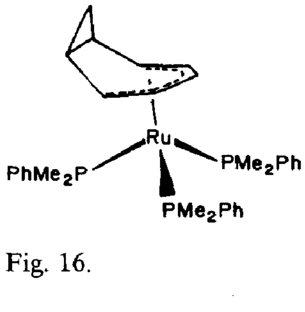
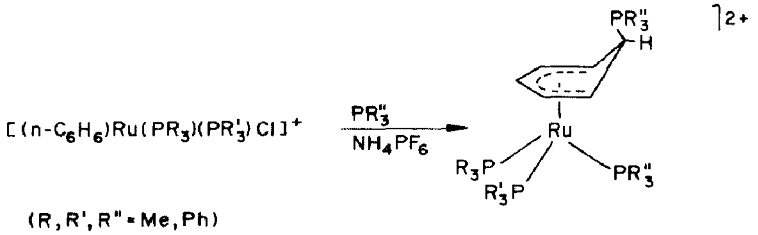


Fig. 16.

involve the addition of a proton to **67** followed by hydride migration to the cyclooctatriene ligand to form the cyclooctadienyl group, and isomerization of the cycloocta-1,5-diene to cycloocta-1,3-diene. The latter would probably be sufficiently labile to be replaced by arenes or other donor groups [233].

The complexes $[(\eta^6\text{-}C_6H_6)RuCl(PR_3)(PR'_3)]PF_6$ and $[(\eta^6\text{-}C_6H_6)RuCl_2(PR_3)]$ react with phosphines PR''_3 in the presence of NH_4PF_6 to give the (6-phosphonio-η^5-cyclohexadienyl)ruthenium(II) compounds $[(6\text{-}R''_3P\text{-}\eta^5\text{-}C_6H_6)Ru(PR_3)(PR'_3)(PR''_3)](PF_6)_2$ in good yield (Scheme 52) [234]. In a similar manner, reaction of $[(\eta^6\text{-}C_6H_6)Ru(NCMe)_3](PF_6)_2$ with PMe_3 gives $[(6\text{-}Me_3P\text{-}\eta^5\text{-}C_6H_6)Ru(PMe_3)_2(NCMe)](PF_6)_2$. On the basis of spectroscopic data the phosphino groups are located in the *exo*-position. Below −30 °C rotation about the metal–cyclohexadienyl bond is frozen out and rigid conformers are detected [234].



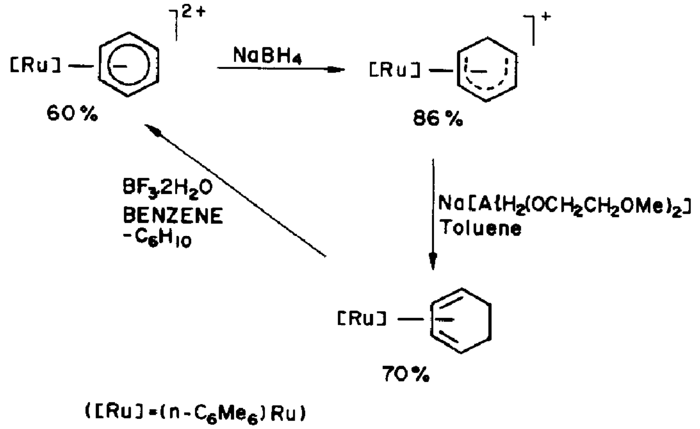
Scheme 52.

The complex $[(\eta^6\text{-}C_6H_6)Ru(PMe_3)_2Cl]PF_6$, **68**, reacts with methyl lithium to give products arising from attack at both the metal centre and the arene ring. The cyclohexadienyl compound $[(\eta^5\text{-}C_6H_6Me)Ru(PMe_3)_2Me]$ is the major product of the reaction. Complex **68** also reacts with phenyl lithium (in the presence of LiBr) to give initially $[(\eta^5\text{-}C_6H_6Ph)Ru(PMe_3)_2Br]$, but with longer reaction times, the phenyl complex $[(\eta^5\text{-}C_6H_6Ph)Ru(PMe_3)_2Ph]$. $[(\eta\text{-}C_6H_6)Os(PMe_3)_2I]PF_6$, when treated with a range of alkylating agents LiR (R = Me, Et, Pr, Bu, Bu^t, Ph) also gives cyclohexadienyl compounds $[(\eta^5\text{-}C_6H_6R)Os(PMe_3)_2I]$, the substituent occupying the expected position *exo* to the metal atom. This has been confirmed by X-ray crystallography for $[(\eta^5\text{-}C_6H_6Bu)Os(PMe_3)_2I]$ [235].

The compounds $[(exo\text{-}6\text{-}R\text{-}\eta^5\text{-}C_6H_6)Os(PMe_3)_2I]$ react with $[CPh_3]PF_6$ in acetone to give the arene–osmium(II) complexes $[(\eta^6\text{-}C_6H_5R)Os(PMe_3)_2I]PF_6$ in quantitative yield [236]. A mechanism for hydride elimination involving (cyclohexadienyl)-hydrido osmium(IV) intermediates of the type $[(\eta^6\text{-}C_6H_6R)Os(H)(PMe_3)_2I]PF_6$ has been proposed [236].

Sodium borohydride reduction of the bis-arene cation $[(\eta^6\text{-}C_6H_3Me_3)Ru(\eta^6\text{-}C_6H_6)](BF_4)_2$ carried out in THF gives the neutral cyclohexadiene complex $[(\eta^6\text{-}C_6H_3Me_3)Ru(\eta^4\text{-}C_6H_8)]$. When performed in water the reduction yields the intermediate cyclohexadienyl complex $[(\eta^6\text{-}C_6H_3Me_3)Ru(\eta^5\text{-}C_6H_7)]X$ ($X = PF_6$, BPh_4) which on further treatment of $NaBH_4$ in THF as expected yields the η^4-cyclohexadiene complex [237].

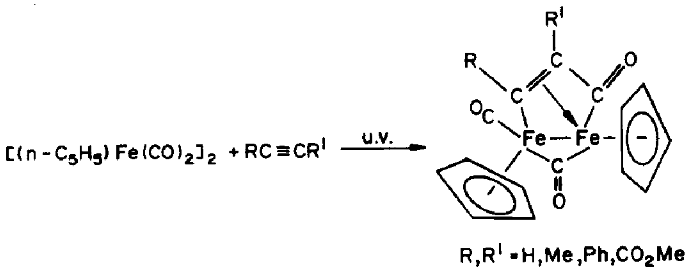
The cationic arene complex $[(\eta^6\text{-}C_6Me_6)Ru(\eta^6\text{-}C_6H_6)]^{2+}$ is readily reduced by $NaBH_4$ to the cyclohexadienyl complex $[(\eta^6\text{-}C_6Me_6)Ru(\eta^5\text{-}C_6H_7)]^+$ (yield 86%) [238,239] which further reacts under more forcing reducing conditions $(Na[AlH_2(OCH_2CH_2OMe)_2])$ to give the cyclohexadiene complex $[(\eta^6\text{-}C_6Me_6)Ru(\eta^4\text{-}C_6H_8)]$ [238]. Treatment of the latter either with HCl or $BF_3 \cdot H_2O$ liberates cyclohexene (Scheme 53).



Scheme 53.

D. DINUCLEAR COMPOUNDS

Whereas the complex $[(\eta\text{-}C_5H_5)_2Fe_2(CO)_4]$ reacts with a range of alkynes under UV irradiation to produce dinuclear complexes containing the dimetallacyclopentenone unit (Scheme 54), only diphenylacetylene produces



Scheme 54.

an analogous complex with $[(\eta\text{-}C_5H_5)_2Ru_2(CO)_4]$ [240]. Nevertheless, the product, $[(\eta\text{-}C_5H_5)_2Ru_2(CO)(\mu\text{-}CO)\{(\mu\text{-}C(O)C_2Ph_2\}]$, **69**, undergoes alkyne exchange with HC_2H, MeC_2Me, MeC_2H, PhC_2H or PhC_2Me on heating in toluene to afford the appropriate $[(\eta\text{-}C_5H_5)_2Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(O)C_2R_2\}]$ complexes as stable, orange, crystalline materials in near quantitative yields [240,241]. In the case of $MeO_2CC_2CO_2Me$, the dimetallacyclobutene complex *cis*-$[(\eta\text{-}C_5H_5)_2Ru_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C_2(CO_2Me)_2\}]$ (Fig. 17) is the only product of the reaction [241]. The X-ray crystal structure of **69** has been determined confirming the linking of alkyne and CO to produce the dimetallacyclopentenone ring, the bridging {C(O) C(Ph)C(Ph)} ligand being η^1-coordinated to one ruthenium atom and η^3-coordinated to the other (Fig. 18) [Ru–Ru′ 2.729, Ru–C_α 2.080, Ru′–C_α 2.158, Ru′–C_β 2.219, Ru′–CO 2.011 Å]. Compounds of the type $[(\eta\text{-}C_5H_5)_2Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(O)C(R^1)C(R^2)\}]$ in which $R^1 \neq R^2$, exist as isomers due to the linking of either end of the alkyne with CO. Steric factors apparently determine the relative stability of the isomers for terminal acetylenes but electronic factors are dominant for internal acetylenes. The iron and ruthenium complexes $[(\eta\text{-}C_5H_5)_2M_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(O)C_2R_2\}]$ exhibit an unprecedented fluxionality involving synchronous carbonyl "insertion" into, and elimination from, the dimetallacycle [240,241].

Protonation of $[(\eta\text{-}C_5H_5)_2Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(O)C_2R^1R^2\}]$ [**70**; $R^1R^2 = H_2$, Ph_2, H(Me), H(Ph)] with $HBF_4 \cdot OEt_2$ in acetone or CH_2Cl_2 solution results in facile carbon–carbon bond cleavage generating, essentially quantitatively, the μ-vinyl complexes $[(\eta\text{-}C_5H_5)_2Ru_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(R^1){=}CH(R^2)\}]BF_4$, **71**, in which the two R groups adopt a *cis* arrangement (Scheme 55) [242–244]. The action of $HBF_4 \cdot OEt_2$ on $[(\eta\text{-}$

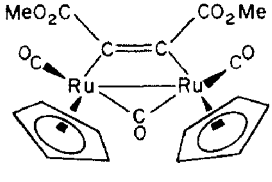
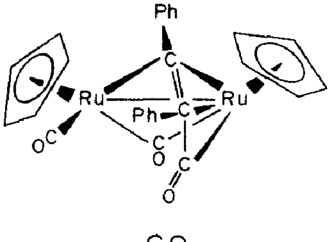
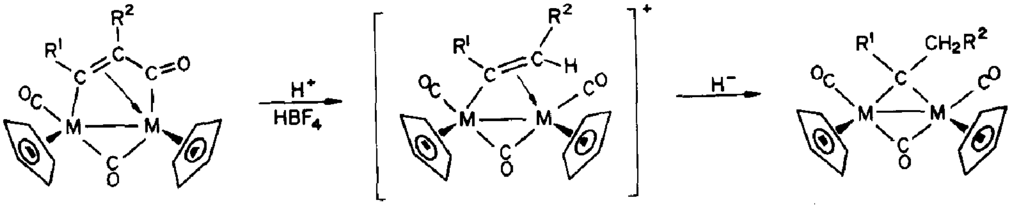


Fig. 17.



69

Fig. 18.

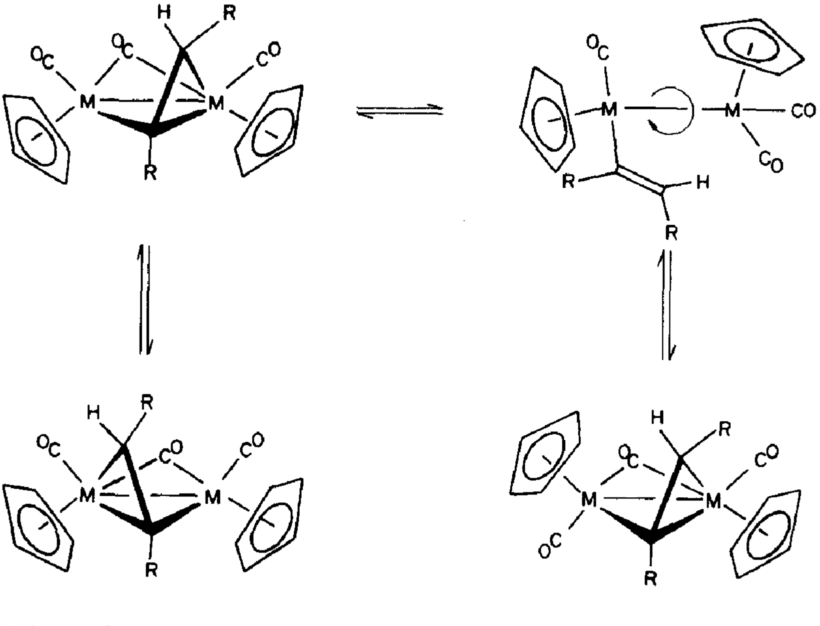


70

71

Scheme 55.

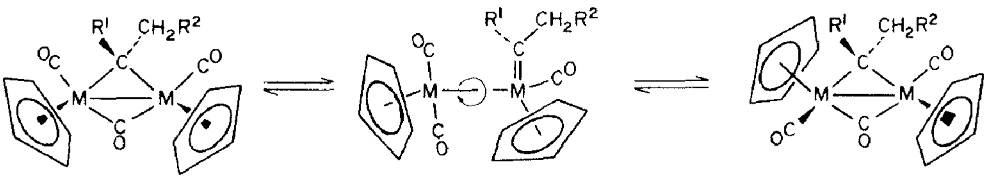
$C_5H_5)_2Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(O)C_2Me_2\}]$ produces first the intermediate cation $[(\eta\text{-}C_5H_5)_2Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(H)(O)C_2Me_2\}]^+$ which then isomerizes slowly in acetone at room temperature to the μ-vinyl complex $[(\eta\text{-}C_5H_5)_2Ru_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(Me)=C(H)Me\}]BF_4$. This unusual pathway may also be operative for the formation of the other μ-vinyl cations. Of a number of possible isomers, complexes **71** exist as a pair of interconverting *cis* and *trans* isomers in solution argued to take the form shown in Scheme 56 [242]. In addition, a μ-vinyl oscillation (σ, π interconversion) process was identified for the *cis* isomer (Scheme 56) [242]. A detailed analysis of the



Scheme 56.

infrared spectrum of $[(\eta\text{-}C_5H_5)_2Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHCH_2)]BF_4$ has been reported [243].

Treatment of the cations **71** with $NaBH_4$ in acetone at room temperature effects rapid hydride addition to the β-carbon of the μ-vinyl group generating the appropriate μ-alkylidene complexes $[(\eta\text{-}C_5H_5)_2Ru_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(R)CH_2R\}]$, **72** (Scheme 55). Anomalously no μ-carbene complex is obtained after addition of $NaBH_4$ to a solution of the cation $[(\eta\text{-}C_5H_5)_2Ru_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}CPh{=}CHPh\}]^+$. The μ-alkylidene complexes exist as interconvertable isomers with both *cis* and *trans* arrangements of CO and cyclopentadienyl ligands (Scheme 57) [242]. The proposed mechanism



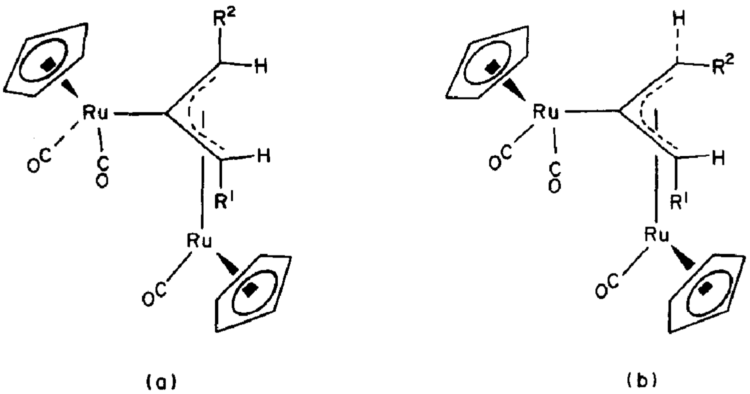
Scheme 57.

envisages a concerted bridge opening process to form a transient terminal carbene complex which undergoes rotation about the metal–metal bond followed by bridge closure [242,245]. The X-ray crystal structure of $[(\eta\text{-}C_5H_5)_2Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CMe_2)]$ has been determined [245]. The two ruthenium atoms are 2.712 Å apart and are essentially symmetrically bridged by the carbonyl and dimethylcarbene ligands [mean Ru–C(carbene) separation 2.113 Å]. The cyclopentadienyl ligands adopt an eclipsed *cis* orientation skew to the Ru–Ru axis.

While the μ-carbene complexes appear to be formed by nucleophilic attack on the β-carbon of the μ-vinyl ligand in **71**, there is also some evidence for hydride attack on the α-carbon of the μ-vinyl group: the ethylene complex $[(\eta\text{-}C_5H_5)_2Ru_2(CO)(C_2H_4)(\mu\text{-}CO)_2]$ is also obtained as a product of the sodium borohydride treatment of $[(\eta\text{-}C_5H_5)_2Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH{=}CH_2)]^+$ [246].

Heating $[(\eta\text{-}C_5H_5)_2Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(O)C_2Ph_2\}]$, **69**, with an allene $R^1CH{=}C{=}CHR^2$ (R^1, R^2 = H or Me; R^1 = H, R^2 = Me) in toluene at 100°C results in diphenylacetylene displacement, metal–metal bond rupture and the formation of the allyl complexes $[(\eta\text{-}C_5H_5)Ru(CO)\{\eta^3\text{-}C_3H_{4-n}Me_n[2\text{-}Ru(CO)_2(\eta\text{-}C_5H_5)]\}]$ (**73**, $n = 0$–2) [245,247,248]. The compounds obtained from buta-1,2-diene and penta-2,3-diene exist as isomers of the form shown in Fig. 19. Protonation of **73** with $HBF_4 \cdot OEt_2$ regenerates the metal–metal bond giving the μ-vinyl complexes $[(\eta\text{-}C_5H_5)_2Ru_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(CHR^2)CHR^1\}]BF_4$ in near quantitative yield, complexes obtained also by protonation of the compounds $[(\eta\text{-}C_5H_5)_2Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(O)C_2R^1R^2\}]$ (see above). Accordingly, μ-carbene complexes can also be obtained by the successive treatment of **73** with $HBF_4 \cdot OEt$ and $NaBH_4$. (Surprisingly, though, the μ-CEt_2 complex could not be synthesized in this manner.)

Minor products of the synthesis of $[(\eta\text{-}C_5H_5)_2Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CMe_2)]$



(a) (b)

Fig. 19.

are the isomers $[(\eta\text{-}C_5H_5)_2Ru_2(CO)_2(\mu\text{-}H)\{\mu\text{-}C(Me)CH_2\}]$ and $[(\eta\text{-}C_5H_5)_2Ru_2(CO)_2(\mu\text{-}H)\{\mu\text{-}CHC(H)Me\}]$. The former is the dominant species in solution while X-ray diffraction has shown the latter to be the solid state structure (Fig. 20) [245]. The ruthenium–ruthenium bond (2.857 Å) is bridged by the hydrido and 2-methylvinyl ligands [Ru–H 1.764, Ru′–H 1.648, Ru–C_α 2.189, Ru–C_β 2.275, Ru′–C_α 2.013 Å].

On heating in boiling toluene the complexes $[(\eta\text{-}C_5H_5)_2Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(O)C_2HR\}]$ (R = H, Ph) isomerize slowly to the μ-vinylidene complexes $[(\eta\text{-}C_5H_5)_2Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CCHR)]$. Each exists as *cis*- and *trans*-isomers separable by chromatography; at room temperature both *cis*- and *trans*- $[(\eta\text{-}C_5H_5)_2Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CCH_2)]$ slowly transform to an equilibrium mixture of the two while isomerization of *cis*-$[(\eta\text{-}C_5H_5)_2Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CCHPh)]$ occurs at a significant rate only at 70 °C. It is likely that this mechanism of interconversion involves bridge-opening to produce transient terminal vinylidene complexes followed by rotation about the metal–metal bond and bridge-closure. A deuterium labelling experiment has led to the mechanism shown in Scheme 58 being proposed to account for the formation of the vinylidene complexes from the dimetallacycles. The X-ray crystal structure of *cis*-$[(\eta\text{-}C_5H_5)_2Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CCH_2)]$ has been determined [246]; a detailed analysis of the infrared spectrum of $[(\eta\text{-}C_5H_5)_2Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CCH_2)]$ has also been reported [243]. The

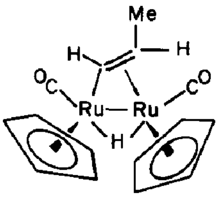
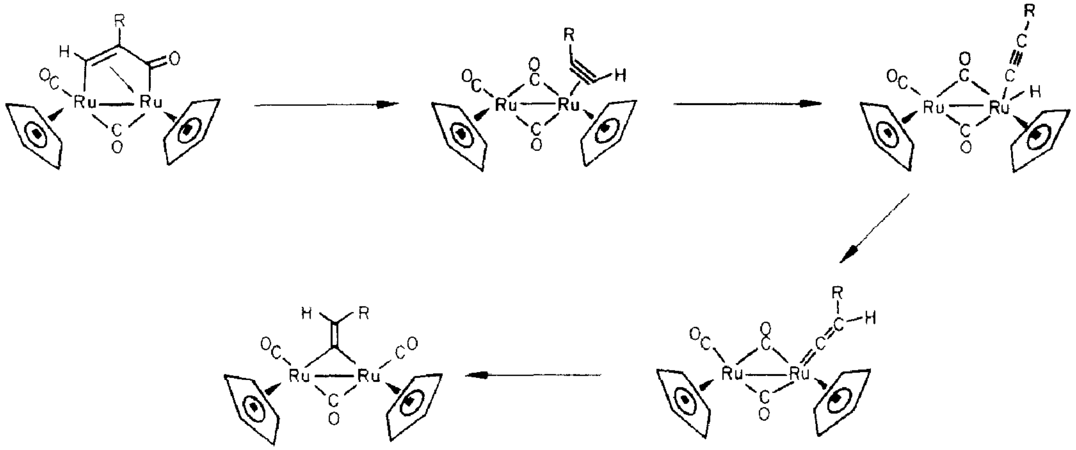
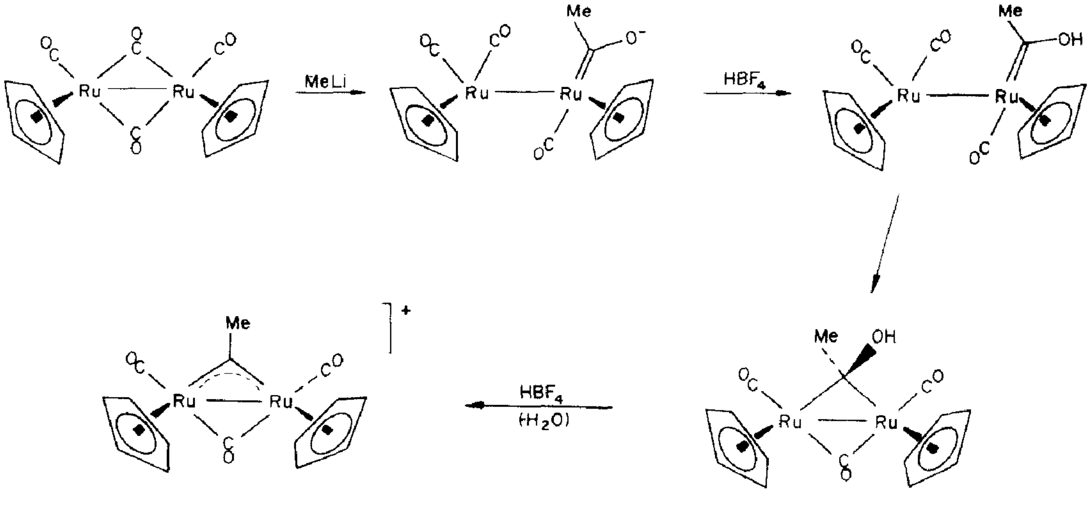


Fig. 20.



Scheme 58.

complex $[(\eta\text{-}C_5H_5)_2Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CCH_2)]$ is converted quantitatively to the μ-ethylidyne species $[(\eta\text{-}C_5H_5)_2Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CMe)]^+$ upon protonation with $HBF_4 \cdot OEt_2$. The X-ray crystal structure of this complex has been determined [246]. The methyl group of the μ-CMe ligand has a fairly high acidity, and the μ-vinylidene complex can readily be regenerated on treatment with water, Et_3N or methyl lithium. Treatment of the μ-CMe cation with $NaBH_4$, however, results in hydride attack at the bridging carbon atom forming the μ-ethylidene complex $[(\eta\text{-}C_5H_5)_2Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHMe)]$ [246]. The μ-CMe complex can also be synthesized in high yield by the successive treatment of $[(\eta\text{-}C_5H_5)_2Ru_2(CO)_4]$ with MeLi and $HBF_4 \cdot OEt_2$. A proposed mechanism for this transformation is outlined in Scheme 59. Detailed analyses of the IR spectra of both $[(\eta$-



Scheme 59.

$C_5H_5)_2Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CMe)]BF_4$ and $[(\eta\text{-}C_5H_5)_2Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHMe)]$ have been reported [244].

Heating $[(\eta\text{-}C_5H_5)_2Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(O)C_2Ph_2\}]$, **69**, with an ylide, $Ph_3P{=}CHR$, in toluene readily yields the μ-alkylidene complexes $[(\eta\text{-}C_5H_5)_2Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHR)]$ (R = H, Me, Et, Ph). The complex $[(\eta\text{-}C_5H_5)_2Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_2)]$ exists as *cis* and *trans* isomers which interconvert in solution too rapidly to allow their separation by chromatography. The structure of the *cis* isomer has been determined by X-ray crystallography (Fig. 21) [249]. The ruthenium–ruthenium bond (2.707 Å) is symmetrically bridged by a carbonyl and the methylene fragment [Ru–C(methylene) 2.078 Å]. An analogous reaction of **69** with $Ph_3P{=}CHCH{=}CH_2$ gave a low yield of the complex $[(\eta\text{-}C_5H_5)_2Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHCHCH_2)]$, the major product being the isomeric substituted allyl complex $[(\eta\text{-}C_5H_5)Ru(CO)\{\eta^3\text{-}C_3H_4[1\text{-}Ru(CO)_2(\eta\text{-}C_5H_5)]\}]$ (Scheme 60). Upon UV irradiation the latter undergoes rearrange-

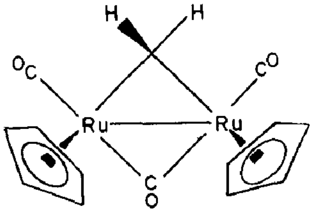
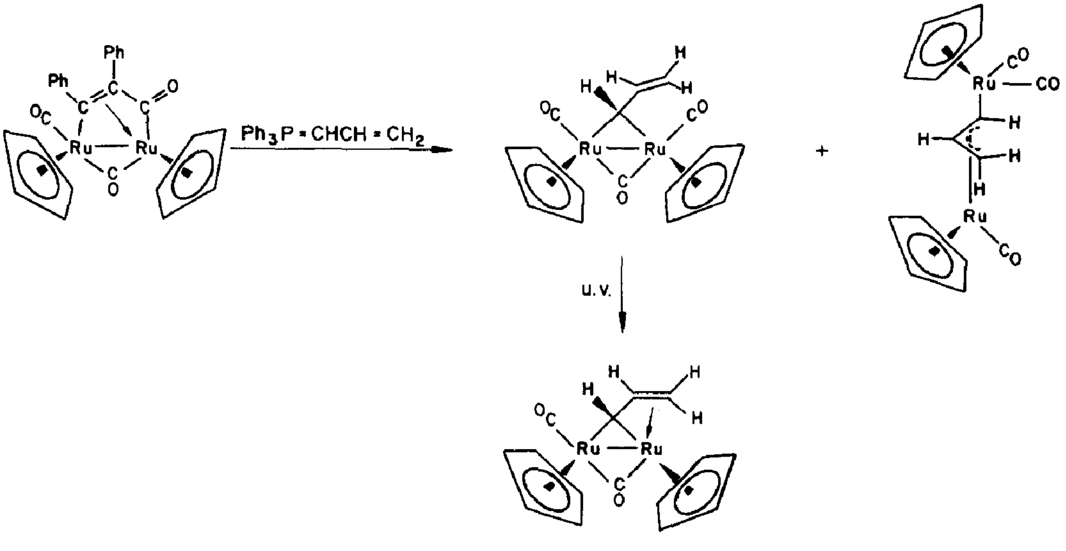
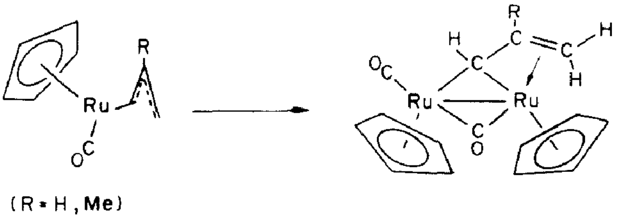


Fig. 21.



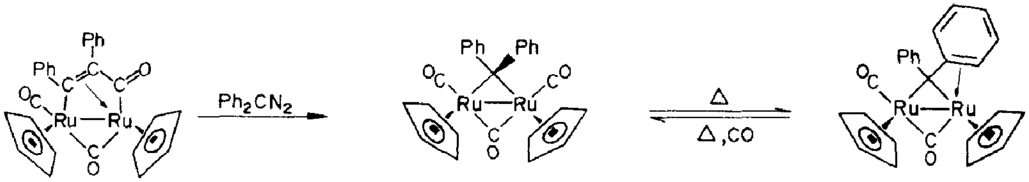
Scheme 60.

ment, with ruthenium–ruthenium bond formation, to the former. Further irradiation of $[(\eta\text{-}C_5H_5)_2Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHCHCH_2)]$ results in carbonyl displacement and π-coordination of the alkylidene vinyl substituent (Scheme 60) [249]. The synthesis of this class of compound containing bridging η^1,η^3-allylidene ligands had first been reported from the photolytic reaction of $[(\eta\text{-}C_5H_5)_2Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CMe)]BF_4$ with ethylene or propene [250]. Eisenstadt and Efraty [251] have described the remarkable conversion of $[(\eta\text{-}C_5H_5)Ru(CO)(\eta^3\text{-}C_3H_5)]$ to the parent μ-η^1,η^3-allylidene complex $[(\eta\text{-}C_5H_5)_2Ru_2(CO)(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^3\text{-}CHCHCH_2)]$ (Scheme 61), achieved simply by passing an acetone–hexane solution of the allyl complex down a column of deactivated silica gel. Further studies [251] have also suggested the generality of the allyl to bridging allylidene conversion, but at present the mechanistic features of this reaction are obscure.



Scheme 61.

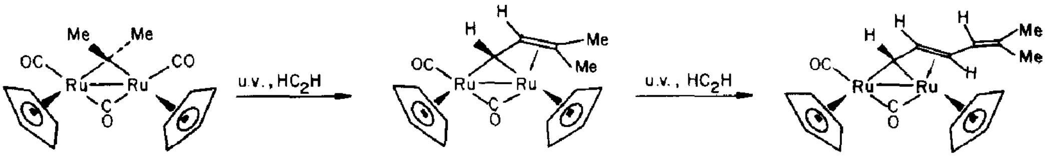
Although the conditions necessary to achieve the displacement of diphenylacetylene from $[(\eta\text{-}C_5H_5)_2Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(O)C_2Ph_2\}]$ precludes the synthesis of $[(\eta\text{-}C_5H_5)_2Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_2)]$ by reaction with diazomethane, other more thermally stable diazoalkanes react smoothly. Thus for instance, ethyldiazoacetate generates in 90% yield *cis* and *trans* $[(\eta\text{-}C_5H_5)_2Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHCO_2Et)]$. The reaction with diphenyldiazomethane yields aside from the expected product $[(\eta\text{-}C_5H_5)_2Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CPh_2)]$ (the *cis* isomer), the decarbonylated material $[(\eta\text{-}C_5H_5)_2Ru_2(CO)(\mu\text{-}CO)(\mu\text{-}CPh_2)]$, the best representation of which is probably as a μ-η^1,η^3-allylidene complex (Scheme 62) [249].



Scheme 62.

It has been reported [252,253] that $[(\eta\text{-}C_5H_5)_2Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHMe)]$ reacts under UV irradiation with ethyne giving the complex $[(\eta$-

$C_5H_5)_2Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}\eta^1,\eta^3\text{-}CHCHCH(Me)\}]$ as a result of stereospecific alkyne "insertion". On the other hand treatment of the complex $[(\eta\text{-}C_5H_5)_2Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CMe_2)]$, **74**, with ethyne under the same conditions results in the stereospecific insertion of two molecules of alkyne (Scheme 63). X-ray crystallography has confirmed that the product, $[(\eta\text{-}$

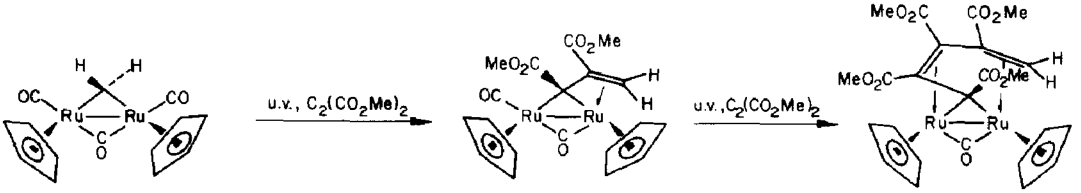


74

Scheme 63.

$C_5H_5)_2Ru_2(CO)(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^3\text{-}C_4H_4CMe_2)]$, is to be considered as a complex of the same type as **74** simply with an extended carbon chain [Ru–Ru′ 2.716, Ru–C_α 2.118, Ru′–C_α 2.022, Ru–C_β 2.141, Ru–C_γ 2.239 Å] [253].

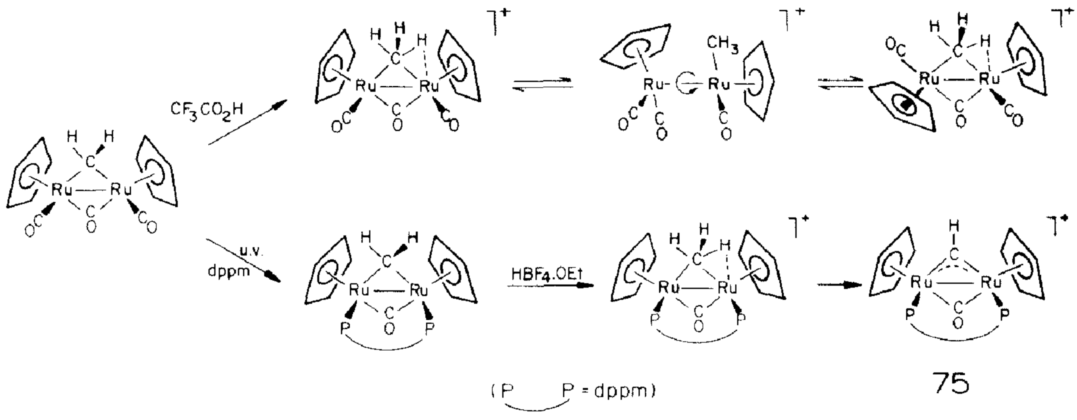
Treatment of $[(\eta\text{-}C_5H_5)_2Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_2)]$ with dimethylacetylenedicarboxylate under UV irradiation also gives a double insertion product, $[(\eta\text{-}C_5H_5)_2Ru_2(\mu\text{-}CO)\{\mu\text{-}C_4(CO_2Me)_4CH_2\}]$ (Scheme 64). X-ray



Scheme 64.

crystallography has been used to establish the geometry of the five carbon chain shown. The differing reactivity patterns and stereochemistry of the carbon chains is attributed to the differing steric demands of the carbene substituents. It is interesting to note here that preliminary results describing the further insertion of alkyne (three and four molecules) have been briefly discussed [254]. These observations may have some significance to alkyne polymerization chemistry [253].

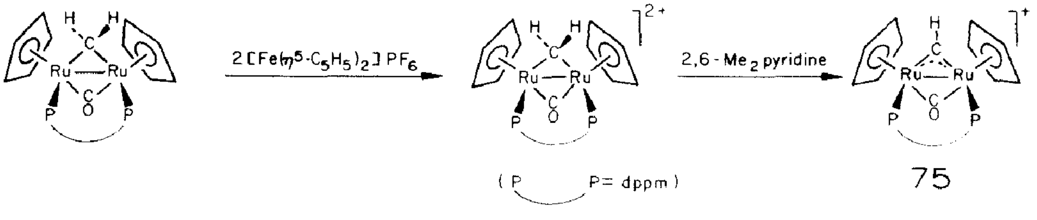
Protonation of $[(\eta\text{-}C_5H_5)_2Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_2)]$ (CF_3CO_2H in dichloromethane) yields *cis* and *trans* isomers of the μ-methyl cation $[(\eta\text{-}C_5H_5)_2Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_3)]^+$ [255]. The high field chemical shift of the μ-methyl group signals (*cis*, -1.09; *trans*, -0.98 ppm) is typical of this ligand coordinated in the agostic mode. The *cis* and *trans* isomers interconvert on the NMR timescale ($\Delta G^{\neq}$ ca. 55 kJ mol^{-1}) via an intermediate



Scheme 65.

proposed to contain a terminally bound methyl group (Scheme 65). Protonation of the substituted μ-methylene complex $[(\eta\text{-}C_5H_5)_2Ru_2(\mu\text{-dppm})(\mu\text{-}CO)(\mu\text{-}CH_2)]$ with $HBF_4 \cdot OEt_2$ has given the μ-methyl cation *cis*-$[(\eta\text{-}C_5H_5)_2Ru_2(\mu\text{-dppm})(\mu\text{-}CO)(\mu\text{-}CH_3)]^+$. Slow crystallization from tetrahydrofuran–hexane, however, gave low yields of the diruthenium complex $[(\eta\text{-}C_5H_5)_2Ru_2(\mu\text{-dppm})(\mu\text{-}CO)(\mu\text{-}CH)]^+$, **75**, containing a bridging methyne ligand. The structure of this unusual complex has been determined by X-ray crystallography [255]; the cyclopentadienyl ligands lie mutually *cis* (due to the steric demands of the dppm ligand) about the slightly puckered central $\{Ru_2(\mu\text{-}C)_2\}$ core [Ru–Ru′ 2.716, Ru–C(H) 1.937, Ru–C(O) 2.028 Å].

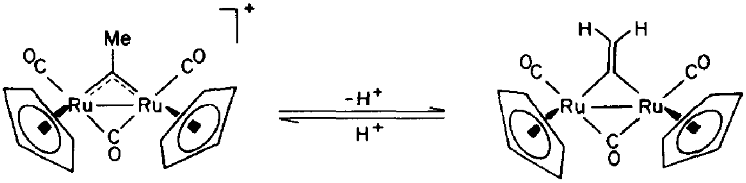
While the mechanism of the conversion of μ-methyl to μ-methyne is at present obscure, one possible process involves the loss of the agostic hydrogen as a radical generating a radical cation intermediate $[(\eta\text{-}C_5H_5)_2Ru_2(\mu\text{-dppm})(\mu\text{-}CO)(\mu\text{-}CH_2)]^+$. This cation has in fact been generated essentially quantitatively by the electrochemical oxidation of $[(\eta\text{-}C_5H_5)_2Ru_2(\mu\text{-dppm})(\mu\text{-}CO)(\mu\text{-}CH_2)]$. The cation is further oxidized to the dication $[(\eta\text{-}C_5H_5)_2Ru_2(\mu\text{-dppm})(\mu\text{-}CO)(\mu\text{-}CH_2)]^{2+}$ which subsequently deprotonates to give $[(\eta\text{-}C_5H_5)_2Ru_2(\mu\text{-dppm})(\mu\text{-}CO)(\mu\text{-}CH)]^+$, **75**. This sequence has also been performed by chemical oxidation using 2 equivalents of $[Fe(\eta\text{-}C_5H_5)_2]PF_6$ in the presence of a base, 2,6-dimethylpyridine, and giving near quantitative yields of **75** (Scheme 66) [256].



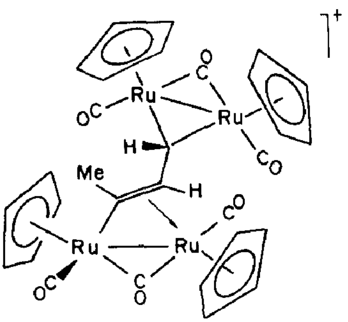
Scheme 66.

The cation **75** reacts readily with nucleophiles ($NaBH_4$, MeLi, NEt_3) providing a route to functionalized μ-methylene ligands, and with dihydrogen (150 atm.) to afford the μ-methyl complex $[(\eta\text{-}C_5H_5)_2Ru_2(\mu\text{-dppm})(\mu\text{-}CO)(\mu\text{-}CH_3)]^+$. The EEC (electrochemical–electrochemical–chemical) mechanism by which **75** is obtained from $[(\eta\text{-}C_5H_5)_2Ru_2(\mu\text{-dppm})(\mu\text{-}CO)(\mu\text{-}CH_2)]$ is also observed in other di-ruthenium systems. $[(\eta\text{-}C_5H_5)_2Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHMe)]$ is oxidized by $AgBF_4$ affording the μ-vinyl complex $[(\eta\text{-}C_5H_5)_2Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHCH_2)]BF_4$, **76**, in high yield. Complex **76** in turn also reacts with nucleophiles giving for example $[(\eta\text{-}C_5H_5)_2Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHEt)]$ with methyl lithium [256].

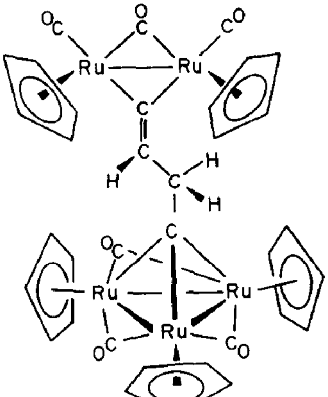
The μ-ethylidyne cation $[(\eta\text{-}C_5H_5)_2Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CMe)]^+$ and the μ-vinylidene complex $[(\eta\text{-}C_5H_5)_2Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CCH_2)]$ are readily interconverted via deprotonation/protonation steps (Scheme 67) [257]. The deprotonation of $[(\eta\text{-}C_5H_5)_2Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CMe)]^+$ also gives two minor products of formulation $[\{(\eta\text{-}C_5H_5)_2Ru_2(CO)_3\}_2(\mu\text{-}CMeCHCH)]BF_4$, **77**, and $[\{(\eta\text{-}C_5H_5)_3Ru_3(CO)_3\}(\mu\text{-}CCH_2CHC)\{Ru_2(CO)_3(\eta\text{-}C_5H_5)_2\}]$, **78**. Both **77** and **78** have been characterized by X-ray crystallography establishing the structures shown in Fig. 22. The complex **78** consists of



Scheme 67.



77



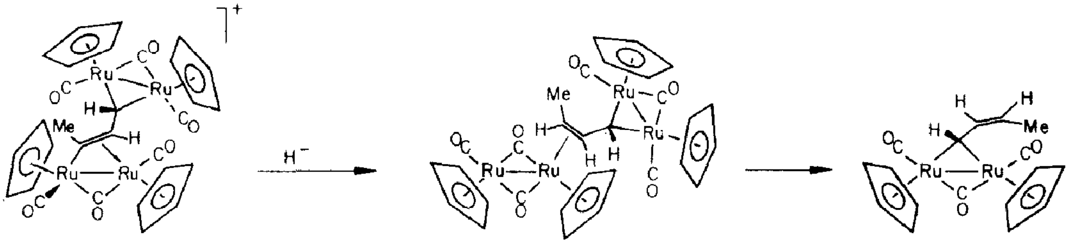
78

Fig. 22.

$\{(\eta\text{-}C_5H_5)_3Ru_3(CO)_3\}$ and $\{(\eta\text{-}C_5H_5)_2Ru_2(CO)_2(\mu\text{-}CO)\}$ fragments linked by a $CCH_2C{=}C$ chain which at the one end caps the tri-ruthenium unit as a μ_3-alkylidene ligand and at the other bridges the di-ruthenium unit as a μ-vinylidene. The complex **77** also contains a four carbon link, but now between two $\{(\eta\text{-}C_5H_5)_2Ru_2(CO)_2(\mu\text{-}CO)\}$ units, bridging the one as a μ-vinyl, and the other as a μ-alkylidene. While the mechanism of formation of **78** remains obscure, it seems likely that **77** arises via electrophilic attack of $[(\eta\text{-}C_5H_5)_2Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CMe)]^+$ on $[(\eta\text{-}C_5H_5)_2Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CCH_2)]$ followed by an alkylidyne to vinyl (via a hydrogen shift process) isomerization [257].

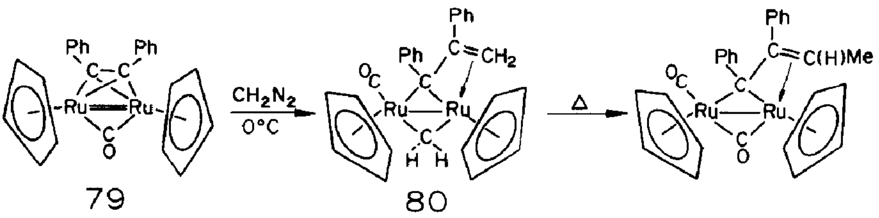
In the solid state the alkylidene bridged di-ruthenium unit in **77** adopts a configuration with mutually *cis* cyclopentadienyl moieties, while the vinyl bridged di-ruthenium unit has a *trans* disposition of cyclopentadienyl groups (the *cis–trans* isomer of **77**). In solution there is NMR evidence that two (the *cis–trans* and the *cis–cis*) isomers exist in almost equal proportions interconverting via *cis* ⇌ *trans* isomerization of the vinyl bridged di-ruthenium unit [257].

Surprisingly hydride attack on **77** does not occur at the β-carbon of the vinyl substituent to give a μ-alkylidene complex, but rather at the α-carbon atom, giving ultimately the complex $[(\eta\text{-}C_5H_5)_2Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHCHCHMe)]$ (Scheme 68). This effect has been attributed to steric crowding about the β-carbon site [257].



Scheme 68.

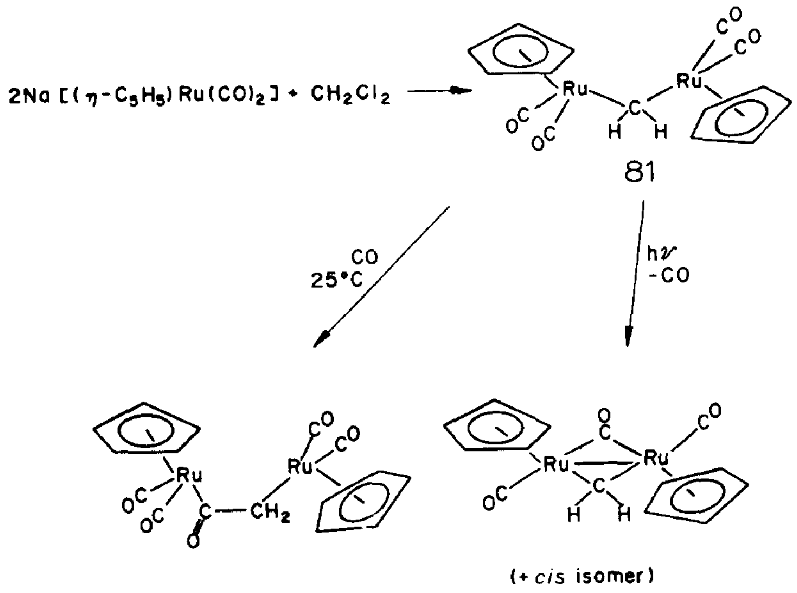
The metal–metal double-bonded μ-alkyne complex $[(\eta\text{-}C_5H_5)_2Ru_2(\mu\text{-}CO)(\mu\text{-}C_2Ph_2)]$, **79**, reacts with diazomethane to give the complex $[(\eta\text{-}C_5H_5)_2Ru_2(CO)(\mu\text{-}CH_2)\{\mu\text{-}C(Ph)C(Ph)CH_2\}]$, **80**, arising from the incorporation of two methylene units, one bridging the two metal atoms, the other linking with the alkyne (Scheme 69) [258]. Heating **80** alone in boiling xylene or with CO (10 atm, 140°C) gives $[(\eta\text{-}C_5H_5)_2Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(Ph)C(Ph)CHMe\}]$ (Scheme 69). The X-ray crystal structures of both **79** and **80** have been determined; in the case of the former establishing a di-ruthenium unit bridged transversely by a diphenylacetylene molecule and also by a carbonyl ligand. The ruthenium–ruthenium distance of 2.505 Å is



Scheme 69.

significantly shorter than typical Ru–Ru single bonds and together with the 18-electron rule, is consistent with formal double bonding. In the case of **80** the structure shows the α-carbon atom of the bridging $\{C(Ph)C(Ph)CH_2\}$ ligand to be equidistant from each ruthenium suggesting the bonding representation shown in Scheme 69 [258].

Reacting $Na[(\eta\text{-}C_5H_5)Ru(CO)_2]$ with CH_2Cl_2 (2:1 molar ratio) at $-35\,°C$ in THF has given the μ-methylene complex $[\{(\eta\text{-}C_5H_5)Ru(CO)_2\}_2(\mu\text{-}CH_2)]$, **81**, containing no metal–metal bond and shown by X-ray crystallography to have a symmetrical disposition of the two $\{(\eta\text{-}C_5H_5)Ru(CO)_2\}$ groups about the methylene units [259]. Photolysis of **81** gave an 80% yield of the *cis* and *trans* isomers of the metal–metal bonded dimer $[(\eta\text{-}C_5H_5)_2Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_2)]$, while carbonylation of **81** occurred readily at room temperature to give the μ-acyl complex $[(\eta\text{-}C_5H_5)_2Ru_2(CO)_4\{\mu\text{-}C(O)CH_2\}]$ (Scheme 70). Treatment of **81** with excess



Scheme 70.

PMe_3 at room temperature gave the substituted μ-acyl species $[(\eta\text{-}C_5H_5)_2Ru_2(CO)_3(PMe_3)\{\mu\text{-}C(O)CH_2\}]$ [259].

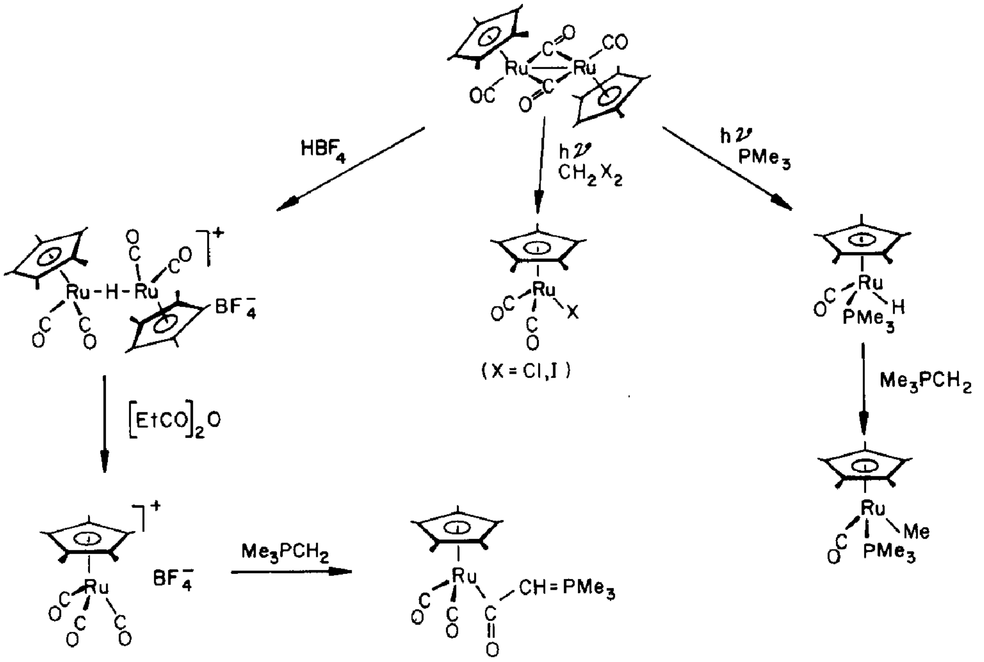
A range of dimeric complexes $[\{(\eta\text{-}C_5H_5)Ru(CO)_2\}_2\{\mu\text{-}(CH_2)_n\}]$ ($n = 2$, 3, 4) [259,260] has been synthesized in an analogous fashion, and the hydrocarbon products of the thermal and photochemical decomposition of $[\{(\eta\text{-}C_5H_5)Ru(CO)_2\}_2\{\mu\text{-}(CH_2)_n\}]$ ($n = 3$, 4) and $[\{(\eta\text{-}C_5H_5)Ru(CO)_2\}\{(\eta\text{-}C_5H_5)Fe(CO)_2\}\{\mu\text{-}(CH_2)_3\}]$ have been determined [260]. The results have been interpreted in terms of dimetallacyclic intermediates which undergo decomposition via β-elimination and reductive elimination processes. Strong supporting evidence is provided by the corresponding iron systems, except for the complex $[\{(\eta\text{-}C_5H_5)Fe(CO)_2\}_2\{\mu\text{-}(CH_2)_5\}]$ for which a radical mechanism appears to dominate [260].

An extensive chemistry of the di-ruthenium centre in $[(\eta\text{-}C_5H_5)_2Ru_2(CO)_4]$ has been established in recent years (see above). On the other hand, it is well documented that the pentamethylcyclopentadienyl ligand has substantially different steric and electronic properties compared with the cyclopentadienyl ligand.

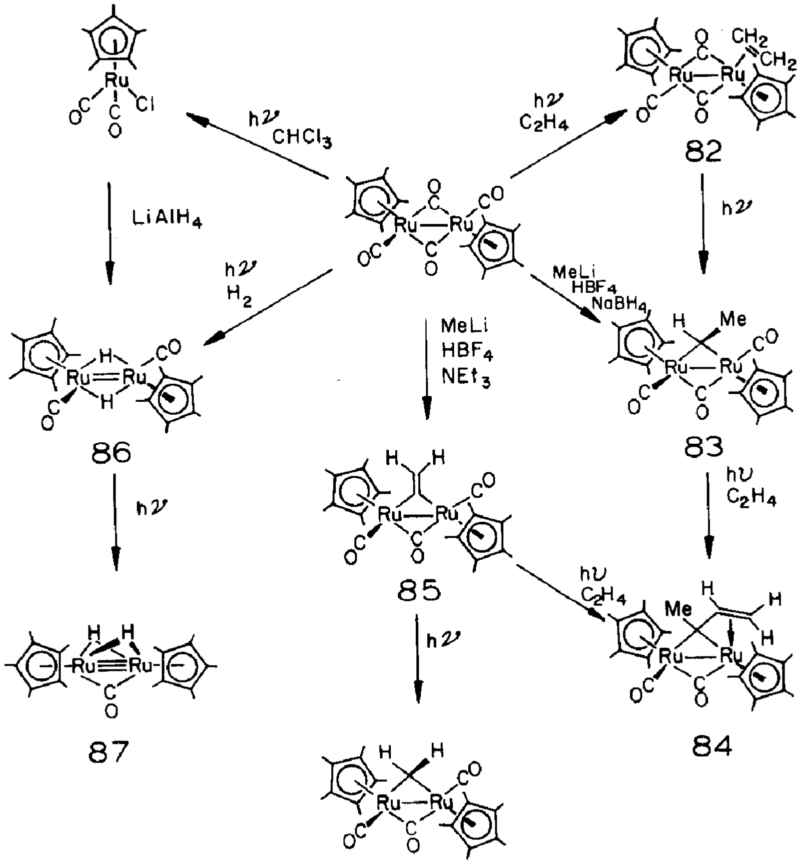
The dimeric complex $[(\eta\text{-}C_5Me_5)_2Ru_2(CO)_4]$ may be synthesized by the direct treatment of $[Ru_3(CO)_{12}]$ with pentamethylcyclopentadiene, or reaction of $[\{Ru(CO)_3Cl_2\}_2]$ with NaC_5Me_5 [261].

Treatment of $[(\eta\text{-}C_5Me_5)_2Ru_2(CO)_4]$ with HBF_4 in CH_2Cl_2 yields the hydrido-bridged dinuclear complex $[(\eta\text{-}C_5Me_5)_2Ru_2(CO)_4H]BF_4$, which when heated under reflux in propionic anhydride gives the mononuclear cation $[(\eta\text{-}C_5Me_5)Ru(CO)_3]^+$ (Scheme 71) [261]. The UV irradiation of $[\{(\eta\text{-}C_5Me_5)Ru(CO)_2\}_2]$ in the presence of CH_2X_2 ($X = Cl$, I) gives $[(\eta\text{-}C_5Me_5)Ru(CO)_2X]$, while irradiation of a benzene solution in the presence of PMe_3 gives $[(\eta\text{-}C_5Me_5)Ru(CO)(PMe_3)H]$ in good yield. The diverse chemistry of some of these mononuclear systems has been briefly communicated [261]; this is summarized in Scheme 71.

Knox and co-workers [116] have reported preliminary studies which show that the effects of the pentamethylcyclopentadienyl ligand on the organic chemistry of the di-ruthenium centre in $[(\eta\text{-}C_5Me_5)_2Ru_2(CO)_4]$ is quite significant. The results of these studies are summarized in Scheme 72. UV irradiation of a toluene solution of $[(\eta\text{-}C_5Me_5)_2Ru_2(CO)_4]$ while purging with ethylene yields the complexes $[(\eta\text{-}C_5Me_5)_2Ru_2(CO)(C_2H_4)(\mu\text{-}CO)_2]$, **82**, (22% yield), $[(\eta\text{-}C_5Me_5)_2Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHMe)]$, **83**, (6%) and $[(\eta\text{-}C_5Me_5)_2Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(Me)CHCH_2\}]$, **84**, (28%). It has been established that these products are formed in the sequence **82** → **83** → **84**; while the reagent-induced alkene to alkylidene transformation is known, the mechanistic details of the **82** → **83** isomerization are still obscure. Complex **84** is probably formed through initial substitution of a CO ligand in **83** by ethylene, which if followed by the formation of a dimetallacyclopentane ring



Scheme 71.



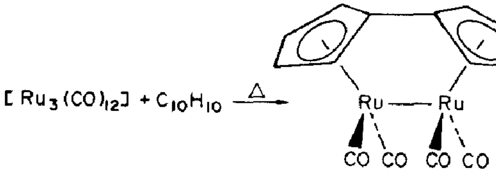
Scheme 72.

and β-elimination processes, can be envisaged to lead to **84**.

Sequential treatment of $[(\eta\text{-}C_5Me_5)_2Ru_2(CO)_4]$ with MeLi, HBF_4 and NEt_3 has given the μ-vinylidene complex $[(\eta\text{-}C_5Me_5)_2Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CCH_2)]$, **85**, a pattern of reactivity entirely parallel to the corresponding cyclopentadienyl system. Complex **85** reacts with ethylene under UV irradiation to give **84** (labelled **85** containing $\mu\text{-}^{13}C{=}CH_2$ gave a $\mu\text{-}^{13}C(Me)CHCH_2$ ligand in **84**) probably proceeding via an initial olefin coordination to ruthenium prior to C–C bond formation and H-transfer. UV irradiation of **85** in toluene over several days gave the μ-methylene complex $[(\eta\text{-}C_5Me_5)_2Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_2)]$ in 20% yield. The use of labelled precursors $[\mu\text{-}C{=}C(^2H)_2$ and $\mu\text{-}^{13}C{=}CH_2]$ indicated that the methylene fragment did not appear to arise as a consequence of cleaving the vinylidene C=C bond, and at present the mechanistic details of this process await elucidation.

Treatment of $[(\eta\text{-}C_5Me_5)_2Ru_2(CO)_4]$ with dihydrogen under UV irradiation produces the multiply metal–metal bonded species $[(\eta\text{-}C_5Me_5)_2Ru_2(CO)_2(\mu\text{-}H)_2]$, **86**, and $[(\eta\text{-}C_5Me_5)_2Ru_2(\mu\text{-}CO)(\mu\text{-}H)_2]$, **87**, both of which find their counterparts in pentamethylcyclopentadienyl osmium chemistry [118]. Complex **86** is obtained in greatly improved yield by the $LiAlH_4$ mediated reduction of $[(\eta\text{-}C_5Me_5)Ru(CO)_2Cl]$, and **87** can be obtained in quantitative yield by the UV irradiation of **86** (Scheme 72) [116].

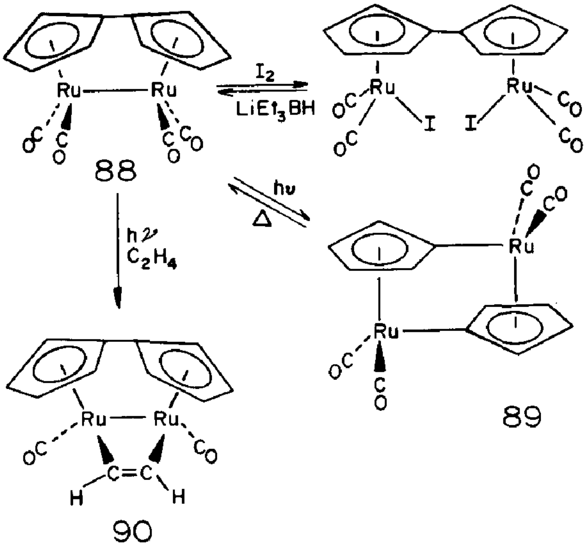
Vollhardt and Weideman have reported the high yield synthesis of the $\eta^5{:}\eta^5$ fulvalene dinuclear complex $[(\eta^5{:}\eta^5\text{-}C_{10}H_8)Ru_2(CO)_4]$, **88**, by the reaction of dihydrofulvalene with $[Ru_3(CO)_{12}]$ in glyme (Scheme 73)



88

Scheme 73.

[262–264]. The X-ray crystal structure of **88** [262] reveals the significant deformation of the hydrocarbon ligand from ideal planarity, a feature that is necessary in order to meet the requirements for metal–metal bonding (Ru–Ru 2.821, Ru–Cp(centroid) 1.894, 1.896 Å). The carbonyl ligands can only adopt an eclipsed conformation. Iodine readily cleaves the ruthenium–ruthenium bond in **88** to give the diiodide complex which when treated with $LiEt_3BH$ (even at −60°C) gives instead of the expected dihydride species $[(\eta^5{:}\eta^5\text{-}C_{10}H_8)\{Ru(CO)_2H\}_2]$, complex **88**, indicating the probable operation of an unusual, very fast intramolecular H_2 elimination process. Irradiation of **88** (350 nm or sunlight) in the absence of donor ligands gives the remarkable dinuclear oxidative addition product **89** (Scheme 74) characterized by X-ray crystallography [Ru · · · Ru 3.456, Ru–Cp

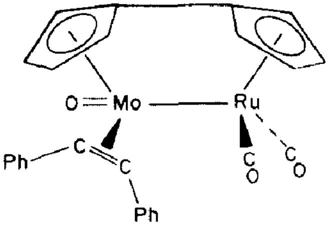


Scheme 74.

(centroid) 1.88, Ru–C 2.077 Å]. Complex **89** converts thermally back to **88** following first-order kinetics in THF, a process which has also been observed to occur in the solid state at 208 ° C. Irradiation of an ethyne purged THF solution of **88** gives the diruthenacylobutene **90** in which the alkyne is bound in the "parallel" μ-η^2 mode as shown by X-ray structural investigation [Ru–Ru 2.719, Ru–C(alkyne) 2.089, 2,095, C–C(alkyne) 1.268 Å]. Similar complexes are afforded by the reaction of **88** with diphenylacetylene and dimethylacetylenedicarboxylate.

The synthesis of the heterobimetallic $\eta^5 : \eta^5$ fulvalene complex [($\eta^5 : \eta^5$-$C_{10}H_8$)RuMo(CO)$_5$], **91**, by the addition of dihydrofulvalene to a boiling glyme solution of [$Ru_3(CO)_{12}$] and [$Mo(CO)_6$] has also been reported [262,264]. Irradiation of **91** with diphenylacetylene gives the novel product **92** containing an oxo ligand derived from traces of water in the reaction medium [263]. Complex **92** has been fully characterized by X-ray crystallography [Ru–Mo 2.859, Mo–O 1.698, Mo–C(alkyne) 2.073, 2.092 Å] (Fig. 23). The most unusual feature of this complex is the oxo ligand found in conjugation with the alkyne ligand. In this regard it is interesting to note that **92** is an active alkyne polymerization catalyst. Hydrogenation of **92** in the presence of CO regenerates **91** [263].

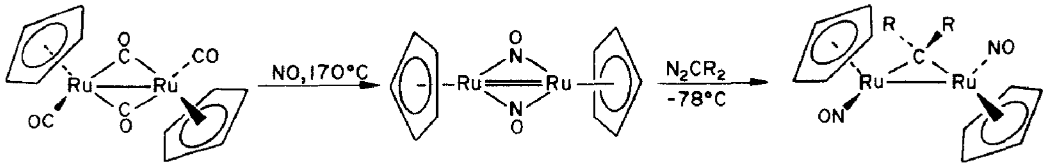
Treatment of [(η-C_5H_5)$_2$Ru$_2$(CO)$_4$] with nitrogen monoxide in *n*-decane



92

Fig. 23.

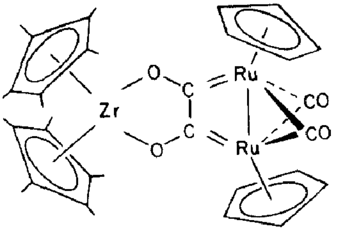
at 170°C gives, in good yield, the black, air-stable nitrosyl complex $[(\eta\text{-}C_5H_5)_2Ru_2(NO)_2]$, **93**, in 78–80% yield (Scheme 75) [265]. Complex **93** has its analogue in iron chemistry and similarly requires a formal metal–metal double bond to achieve an inert gas electronic configuration. In support of this **93** readily adds carbene ligands in a bridging mode. The complexes $[(\eta\text{-}C_5H_5)_2Ru_2(NO)_2(\mu\text{-}CR_2)]$ ($R = H$, Me) have been obtained in excellent yield by the treatment of **93** with diazomethane and 2-diazopropane in THF at −78°C (Scheme 75) [265].



95

Scheme 75.

The reaction of $[\{(\eta\text{-}C_5Me_5)_2Zr(N_2)\}_2(\mu\text{-}N_2)]$ with $[(\eta\text{-}C_5H_5)_2Ru_2(CO)_4]$ has been briefly reported to give the complex $[(\eta\text{-}C_5Me_5)_2Zr(CO)_4Ru_2(\eta\text{-}C_5H_5)_2]$ (**94**) (Fig. 24), arising from a coupling of two carbonyl ligands [266]. This chemistry is paralleled in iron chemistry by the reactions of $[(\eta\text{-}$



94

Fig. 24.

$C_5H_4R)_2Fe_2(CO)_4]$ (R = H, Me) with the same zirconium dinitrogen species and also with $[\{(\eta\text{-}C_5Me_5)_2Hf(N_2)\}_2(\mu\text{-}N_2)]$ [266].

It is remarkable that since the first reported synthesis of $[(\eta\text{-}C_5H_5)_2Os_2(CO)_4]$ by Fischer and Bittler [267] in 1962 there has been virtually no reported interest in the chemistry of this molecule and its congeners [268]. Fischer et al. [269] reported an improved, modified synthesis in 1967, and also commented on the unusual unbridged structure observed by IR spectroscopy found in both the solid state and in solution for this molecule. While, as far as we are aware, this anomaly has not been examined in detail, the analogue $[(\eta\text{-}C_5Me_5)_2Os_2(CO)_4]$ (obtained by heating the complex $[(\eta\text{-}C_5Me_5)Os(COD)H]$ (COD = cycloocta-1,5-diene) in boiling decane with a CO purge for 12 h) has, on the basis of IR spectroscopy (ν(CO) 1890, 1680 cm^{-1}) a bridged dicarbonyl structure. This has been confirmed for *trans*-$[(\eta\text{-}C_5Me_5)_2Os_2(CO)_2(\mu\text{-}CO)_2]$ by X-ray crystallography [Os–Os′ 2.763(1), Os–Cp(centroid) 1.904(10), Os–C(bridging) 2.064(11), Os–C(terminal) 1.820(15) Å; Os–Os′–C-(bridging) 46.8(3).Os–C (bridging)–Os′ 85.1(5)°] [270].

When $[(\eta\text{-}C_5Me_5)Os(CO)_2H]$ is photolyzed with a continuous purge of dihydrogen, the three products $[(\eta\text{-}C_5Me_5)Os(CO)H_3]$, **95**, $[(\eta\text{-}C_5Me_5)_2Os_2(CO)_2(\mu\text{-}H)_2]$, **96**, and $[(\eta\text{-}C_5Me_5)_2Os_2(\mu\text{-}CO)(\mu\text{-}H)_2]$, **97**, are formed [118]. Optimum yields of each of these compounds can be obtained by varying the experimental conditions. Complex **95** apparently arises via a photolyzed CO dissociation from $[(\eta\text{-}C_5Me_5)Os(CO)_2H]$ followed by reaction with dihydrogen

$$[(\eta\text{-}C_5Me_5)Os(CO)_2H] \xrightarrow{h\nu} [(\eta\text{-}C_5Me_5)Os(CO)H] + CO$$

$$[(\eta\text{-}C_5Me_5)Os(CO)H] + H_2 \underset{h\nu}{\rightleftharpoons} [(\eta\text{-}C_5Me_5)Os(CO)H_3]$$

The processes which lead to **96** and **97** are obscure, but may involve the following sequence of steps

$$[(\eta\text{-}C_5Me_5)Os(CO)H] + [(\eta\text{-}C_5Me_5)Os(CO)H_3]$$
$$\rightarrow [(\eta\text{-}C_5Me_5)_2Os_2(CO)_2(\mu\text{-}H)_2] + H_2$$

$$2[(\eta\text{-}C_5Me_5)Os(CO)H] \rightarrow [(\eta\text{-}C_5Me_5)_2Os_2(CO)_2(\mu\text{-}H)_2]$$

$$[(\eta\text{-}C_5Me_5)_2Os_2(CO)_2(\mu\text{-}H)_2] \xrightarrow{h\nu} [(\eta\text{-}C_5Me_5)_2Os_2(\mu\text{-}CO)(\mu\text{-}H)_2] + CO$$

The last step has been demonstrated by irradiation of N_2 or H_2 purged solutions of **96** which give **97** and some measure of decomposition, while the irradiation of **95** affords **96** in good yield.

The inert gas formalism applied to the dimer **96** requires a double bond between the osmium atoms. This is a feature supported by X-ray crystallography [118] which reveals a striking resemblance of the central $\{Os(\mu\text{-}H)_2Os\}$ core (Os–Os 2.6773 Å) to the $\{Os(\mu\text{-}H)_2Os\}$ portion of $[Os_3(CO)_{10}(\mu\text{-}H)_2]$ (Os–Os 2.681 Å) [271]. The third product of the irradiation of $[(\eta\text{-}C_5Me_5)Os(CO)_2H]$ with H_2 purge, **97**, would on the basis of the 18-electron formalism, require a triple bond between the osmium atoms [118].

It is notable that while a wide diversity of cyclopentadienyl homometallic ruthenium (and to a lesser extent osmium) dinuclear complexes are known, relatively few heterometallic complexes have been reported.

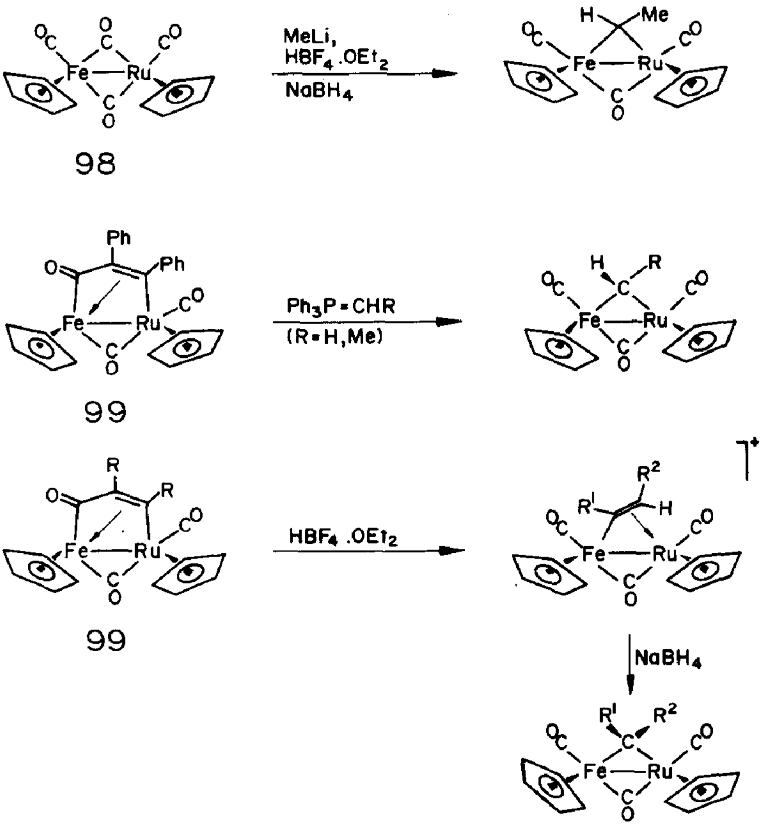
Knox and co-workers [272,273] and Allcock and co-workers [274] have independently reported the synthesis of the cyclopentadienyl iron-ruthenium complex $[(\eta\text{-}C_5H_5)_2FeRu(CO)_4]$, **98**. The compound is obtained from the reaction of $Na[(\eta\text{-}C_5H_5)Fe(CO)_2]$ with $[(\eta\text{-}C_5H_5)Ru(CO)_2I]$ [272,273] or from the reaction of $Na[(\eta\text{-}C_5H_5)Ru(CO)_2]$ with $[(\eta\text{-}C_5H_5)Fe(CO)_2I]$ [273,274], the former providing the superior synthetic route (yield 60%). The X-ray crystal structure of *trans*-$[(\eta\text{-}C_5H_5)_2FeRu(CO)_2(\mu\text{-}CO)_2]$ has been determined (Fe–Ru 2.626 Å). In solution the *cis* isomer is dominant, and the molecule has been shown by ^{13}C NMR to be undergoing *cis–trans* isomerization with bridge-terminal exchange at room temperature. At −80°C the molecule is static. The energy barrier to isomerization appears to be similar to that in $[(\eta\text{-}C_5H_5)_2Fe_2(CO)_4]$ and higher than that in $[(\eta\text{-}C_5H_5)_2Ru_2(CO)_4]$.

The $\{(\eta\text{-}C_5H_5)Fe\text{–}Ru(\eta\text{-}C_5H_5)\}$ unit in **98** has proved to be sufficiently robust to accommodate a substantial organometallic chemistry which, broadly speaking, parallels that of the corresponding di-iron and di-ruthenium systems. UV irradiation of **98** with a variety of alkynes $R^1C_2R^2$ ($R^1 = R^2 =$ H, Me, Ph, CO_2Me; $R^1 =$ Me or Ph, $R^2 =$ H) over 1–16 h produces the complexes $[(\eta\text{-}C_5H_5)_2FeRu(CO)(\mu\text{-}CO)\{\mu\text{-}C(O)CR^1CR^2\}]$, **99**, in 20–65% yield. These reactions closely parallel those of the di-iron centres rather than those of di-ruthenium (for which a similar product has only been obtained with diphenylacetylene). However in contrast to the iron systems the fluxional process in which CO molecules move synchronously in and out of the dimetallacycle is not observed below 80°C (at which point decomposition in the heterometallic systems sets in). It is interesting to note that the absence of homonuclear products in the reactions of **98** with alkynes rules out the intermediacy of radical intermediates in these reactions and strongly suggests the unsaturated species $[(\eta\text{-}C_5H_5)_2FeRu(CO)_3]$ as a more likely candidate. Another general observation is that the heteronuclear system **98** reacts much faster with alkynes than do the corresponding ruthenium (when applicable) and iron systems (e.g. order FeRu (16 h) > Ru_2 (2 d) > Fe_2 (28 d) for diphenylacetylene).

As in the di-iron and di-ruthenium systems, the heterometallic complexes **99** undergo ready cleavage of the carbonyl–alkyne link. Thus for instance,

99 (R^1, $R^2 = CO_2Me$) isomerizes on heating in toluene to the dimetallacyclobutene complex $[(\eta\text{-}C_5H_5)_2FeRu(CO)_2(\mu\text{-}CO)\{\mu\text{-}C_2(CO)_2Me)_2\}]$, while treatment of **99** (R^1, $R^2 = Ph$) with but-2-yne gave **99** (R^1, $R^2 = Me$).

Three routes to μ-alkylidene complexes have been explored (Scheme 76).

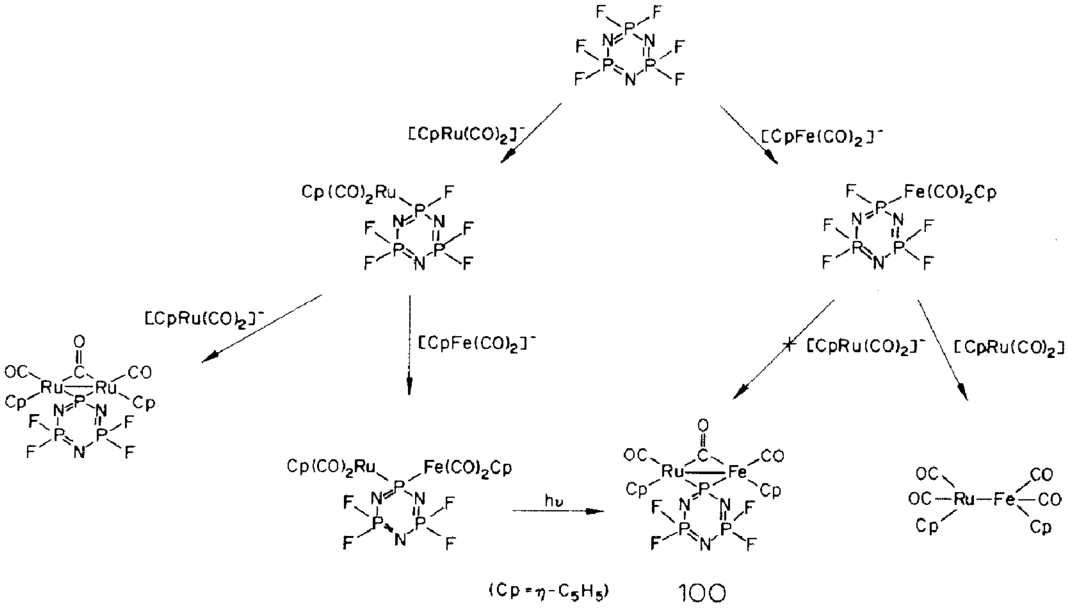


Scheme 76.

Treatment of **98** with methyl lithium followed by $HBF_4 \cdot OEt_2$ and $NaBH_4$ gave the μ-ethylidene complex $[(\eta\text{-}C_5H_5)_2FeRu(CO)_2(\mu\text{-}CO)(\mu\text{-}CHMe)]$ in good yield. The μ-methylene complex $[(\eta\text{-}C_5H_5)_2FeRu(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_2)]$ is obtained from the sequential addition of $LiBHEt_3$ and water to **98** in toluene. Secondly, heating **99** (R^1, $R^2 = Ph$) with the appropriate ylide $Ph_3P{=}CHR$ ($R = H$, Me) in toluene gives the complexes $[(\eta\text{-}C_5H_5)_2FeRu(CO)_2(\mu\text{-}CO)(\mu\text{-}CHR)]$ ($R = H$, Me) in good yield. Heating **99** (R^1, $R^2 = Ph$) with $CH(CO_2Et)N_2$ affords $[(\eta\text{-}C_5H_5)_2FeRu(CO)_2(\mu\text{-}CO)(\mu\text{-}CHCO_2Et)]$. Finally, addition of $HBF_4 \cdot OEt_2$ to a suspension of **99** (R^1, $R^2 = H$, Me; $R^1 = H$, $R^2 = Me$) yields the μ-vinyl cations $[(\eta\text{-}C_5H_5)_2FeRu(CO)_2(\mu\text{-}CO)(\mu\text{-}CR^1{=}CHR^2)]^+$ in a carbon–carbon bond cleavage reaction which mirrors di-iron and di-ruthenium chemistry. On the basis of the IR spectra there are both *cis* and *trans* isomers of each of these complexes. Treatment of the cations with $NaBH_4$ gives the μ-alkylidene complexes $[(\eta\text{-}C_5H_5)_2FeRu(CO)_2(\mu\text{-}CO)(\mu\text{-}CR^1R^2)]$ ($R^1 = H$, $R^2 = Me$; $R^1 = H$, $R^2 = Et$; $R^1 = Me$, $R^2 = Et$) resulting from hydride attack on the β-carbon of the μ-vinyl group.

In common with the di-iron analogues, the complexes $[(\eta\text{-}C_5H_5)_2FeRu(CO)_2(\mu\text{-}CO)(\mu\text{-}CHR^1)]$ (R^1 = H, Me) react under UV irradiation with only one molecule of alkyne giving products of alkyne–alkylidene linking $[(\eta\text{-}C_5H_5)_2FeRu(CO)_2(\mu\text{-}CO)(\mu\text{-}CR^3CR^2CHR^1)]$ (R^1 = H, Me; $R^2 = R^3$ = H, Me, Ph, CO_2Me; R^1 = H, Me; R^2 = Me, Ph; R^3 = H). These exist as non-interconverting isomers in which the new C_3 ligand is either η^1 bound to iron and η^1,η^3 bound to ruthenium or vice versa [273].

The $\{(\eta\text{-}C_5H_5)Fe\text{-}Ru(\eta\text{-}C_5H_5)\}$ core has also been obtained in a study of the reactions of $[(\eta\text{-}C_5H_5)M(CO)_2](M = Fe, Ru)$ anions with $(NPF_2)_3$ (Scheme 77) [274]. Treatment of $(NPF_2)_3$ with $K[(\eta\text{-}C_5H_5)Ru(CO)_2]$ followed by $K[(\eta\text{-}C_5H_5)Fe(CO)_2]$ and exposure to light gives the phosphazene bridged species **100** (Scheme 77). The X-ray crystal structure of **100** has been determined [274] confirming the metal–metal bond (Ru–Fe 2.698 Å) and the *cis* disposition of the cyclopentadienyl groups.



Scheme 77.

There is considerable interest in the synthesis of heterobimetallic complexes containing direct early–late transition metal bonds. For a variety of reasons, most not always clearly understood, this goal has been fraught with more difficulties than at first anticipated. Nevertheless it is interesting that a number of successful examples of these syntheses feature the $\{(\eta\text{-}C_5H_5)Ru(CO)_2\}$ unit.

Casey and Jordan [275] reacted $[(\eta\text{-}C_5H_5)_2Zr(CH_3)Cl]$ with one equivalent of $K[(\eta\text{-}C_5H_5)Ru(CO)_2]$ in THF (25°C, 1 h) and obtained a yellow crystalline solid formulated as $[(\eta\text{-}C_5H_5)_2Zr(CH_3)Ru(CO)_2(\eta\text{-}C_5H_5)]$, **101**, on the basis of IR and ^{13}C NMR spectroscopy, and proposed to contain a Zr–Ru bond. While being thermally stable, **101** is rapidly hydrolyzed to $[\{(\eta\text{-}C_5H_5)_2Zr(CH_3)\}_2O]$ and $[(\eta\text{-}C_5H_5)Ru(CO)_2H]$ on exposure to air. The more hydrolytically stable $[(\eta\text{-}C_5H_5)_2Zr(OBu^t)Ru(CO)_2(\eta\text{-}C_5H_5)]$, **102**, was synthesized by the reaction of $K[(\eta\text{-}C_5H_5)Ru(CO)_2]$ with $[(\eta\text{-}C_5H_5)_2Zr(OBu^t)Cl]$ in THF. Spectroscopic data are again consistent with a metal–metal bonded structure, a feature confirmed in this case by X-ray crystallography (Ru–Zr 2.910 Å). Compounds **101** and **102** are also prepared by halide substitution reactions involving the intact bimetallic framework of $[(\eta\text{-}C_5H_5)_2Zr(Cl)Ru(CO)_2(\eta\text{-}C_5H_5)]$, **103**, (prepared from $[(\eta\text{-}C_5H_5)_2ZrCl_2]$ and $K[(\eta\text{-}C_5H_5)Ru(CO)_2]$ in THF). Treatment of **103** with MeLi gave **100**, and addition of $KOBu^t$ to **103** gave **102** [275].

Sartain and Selegue [276] have reported the synthesis of the dinuclear complex $[(\eta\text{-}C_5H_5)Ru(CO)_2Ti(NMe_2)_3]$, **104**, by the reaction of $[(\eta\text{-}C_5H_5)Ru(CO)_2H]$ with $[Ti(NMe_2)_4]$

$$[(\eta\text{-}C_5H_5)Ru(CO)_2H] + [Ti(NMe_2)_4]$$
$$\rightarrow [(\eta\text{-}C_5H_5)Ru(CO)_2Ti(NMe_2)_3] + NH_3$$

Spectroscopic characterization (specifically the absence of a band at ca. 1600 cm^{-1} in the infrared spectrum characteristic of an isocarbonyl linkage [277]) suggested the formation of a direct Ti–Ru bond, a feature confirmed by X-ray crystallography (Ti–Ru 2.663 Å) [276].

A series of compounds similar to **104** has been synthesized by reacting $[(\eta\text{-}C_5H_5)Ru(CO)_2H]$ with $[Ti(NMe_2)_n(OCHMe_2)_{4-n}]$ ($n = 1\text{–}3$) in a 1 : 1 molar ratio [276]

$$[(\eta\text{-}C_5H_5)Ru(CO)_2H] + [Ti(NMe_2)_n(OCHMe_2)_{4-n}]$$
$$\rightarrow [(\eta\text{-}C_5H_5)Ru(CO)Ti(NMe_2)_{n-1}(OCHMe_2)_n] + NH_3$$

Remarkably these compounds are liquids, with a high thermal stability. As expected though, the ruthenium–titanium bond is readily cleaved by moisture, air and other agents such as alcohols [276].

The reaction of $[(\eta\text{-}C_5Me_5)_2ZrH_2]$ with $[(\eta\text{-}C_5H_5)Ru(CO)_2H]$ in heptane gives the heterobimetallic complex $[(\eta\text{-}C_5H_5)Ru(H)(CO)_2Zr(\eta\text{-}C_5Me_5)_2]$, **105**, in 59% isolated yield [278]. Complex **105** can also be prepared from $[(\eta\text{-}C_5H_5)Ru(CO)_2H]$ and $[\{(\eta\text{-}C_5Me_5)_2Zr(N_2)\}_2N_2]$. On the basis of spectroscopic evidence **105** is proposed to have the structure shown in Fig. 25. A reaction occurs between $[(\eta\text{-}C_5H_5)Ru(PMe_3)(CO)H]$ and $[(\eta\text{-}C_5Me_5)_2ZrH_2]$ in the presence of PMe_3 to give a compound formulated as $[(\eta\text{-}$

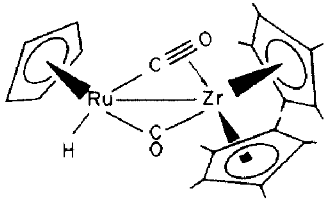


Fig. 25.

$C_5H_5)Ru(PMe_3)_2(\mu\text{-}CH_2O)Zr(H)(\eta\text{-}C_5Me_5)_2]$, which has its better characterized analogue in iron chemistry [278].

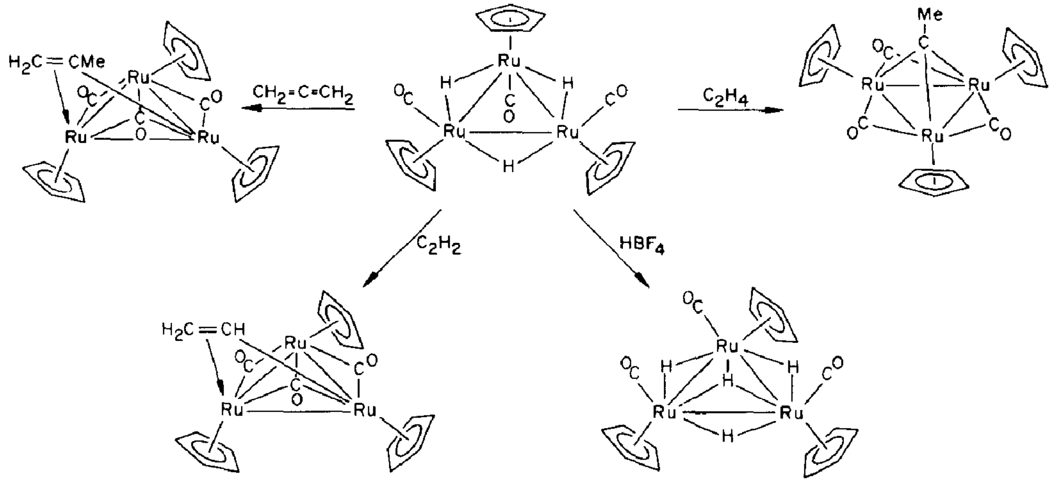
Perhaps the most remarkable examples of heterobimetallic dinuclear compounds involving the $\{(\eta\text{-}C_5H_5)Ru(CO)_2\}$ fragment reported to date are the complexes $[(\eta\text{-}C_5Me_5)_2Th(X)Ru(CO)_2(\eta\text{-}C_5H_5)]$ obtained by the reaction of $[(\eta\text{-}C_5Me_5)_2ThX_2]$ ($X = Cl$, I) with $Na[(\eta\text{-}C_5H_5)Ru(CO)_2]$ in THF [279]. X-ray crystallography has established (for $X = I$) the existence of direct, unsupported actinide to ruthenium bonds (Ru–Th 3.0277 Å), the first examples thereof. With regard to the reactivity of the Ru–Th bond, *t*-butanolysis of $[(\eta\text{-}C_5Me_5)_2Th(I)Ru(CO)_2(\eta\text{-}C_5H_5)]$ rapidly gives $[(\eta\text{-}C_5Me_5)_2Th(I)(OBu^t)]$ and $[(\eta\text{-}C_5H_5)Ru(CO)_2H]$. Reactions with carbon monoxide and dihydrogen have also been observed but details are not yet available [279].

The reaction of $[(\eta\text{-}C_5H_5)Ru(PPh_3)_2Cl]$ with $Tl[Co(CO)_4)]$ in tetrahydrofuran [280,281] gives a number of products including one of formulation $[(\eta\text{-}C_5H_5)Ru(PPh_3)_2Co(CO)_4]$ believed to be a metal–metal bonded dinuclear complex, and one shown by X-ray crystallography to be the ionic complex $[(\eta\text{-}C_5H_5)Ru(PPh_3)_2(CO)][Co(CO)_4]$ [281].

E. POLYNUCLEAR COMPLEXES

Compared to the chemistry of mono- and dinuclear ruthenium and osmium cyclopentadienyl complexes, relatively little has been reported on higher nuclearity complexes containing pentadienyl moieties, and with few exceptions [282,283], this has been restricted to ruthenium. This is a somewhat surprising observation considering the ability of the cyclopentadienyl ring to coordinate in a wide range of ligand and metal environments and the well-known propensity of ruthenium and osmium to form cluster complexes [284, 285].

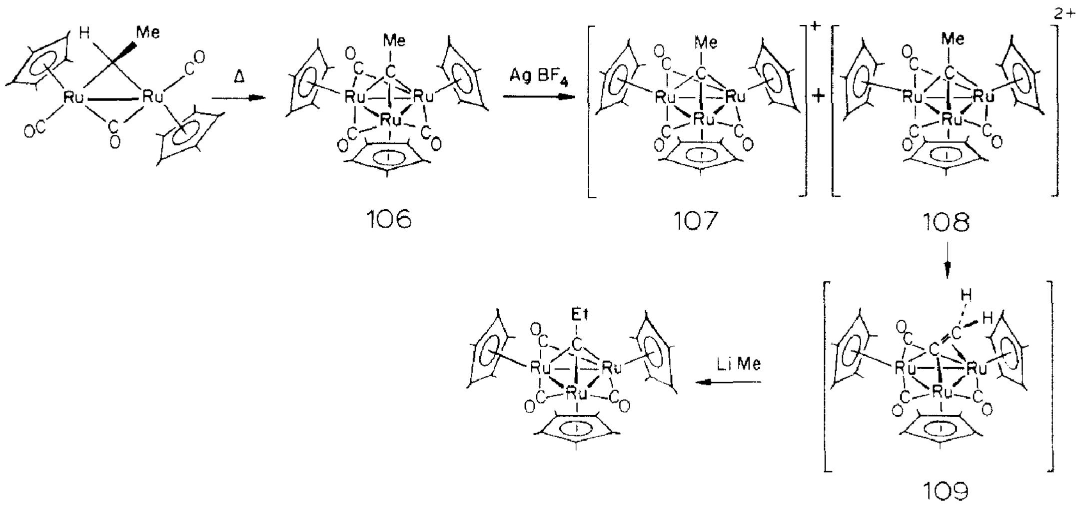
Knox and co-workers have accumulated perhaps the largest body of knowledge to date on polynuclear cyclopentadienyl ruthenium complexes, featuring in particular the trinuclear clusters $[(\eta\text{-}C_5H_5)_3Ru_3(\mu\text{-}CO)_3(\mu_3\text{-}CR)]$ (containing a triply-bridging alkylidiyne unit) and $[(\eta\text{-}C_5H_5)_3Ru_3H_3(CO)_3]$ (containing three bridging hydrido ligands) [254,286]. These two compounds



Scheme 78.

have provided a ready entry into $\{(\eta\text{-}C_5H_5)_3Ru_3\}$ chemistry (Scheme 78), developments recently surveyed in some detail by Knox [254]. In contrast though, trinuclear ruthenium complexes containing the pentamethylcyclopentadienyl ligand are more difficult to come by; one important compound $[(\eta\text{-}C_5Me_5)_3Ru_3(\mu\text{-}CO)_3(\mu_3\text{-}CMe)]$, **106**, has been obtained by thermolysis of the dinuclear complex $[(\eta\text{-}C_5Me_5)_2Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHMe)]$ at 200 °C [254]. (This result should be compared with unsuccessful attempts to synthesize $[(\eta\text{-}C_5Me_5)_3Ru_3H_3(\mu\text{-}CO)_3]$ by photolysis of $[(\eta\text{-}C_5Me_5)_2Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHMe)]$, a reaction which gave instead the dinuclear multiply ruthenium–ruthenium bonded species $[(\eta\text{-}C_5Me_5)_2Ru_2(CO)_2(\mu\text{-}H)_2]$ and $[(\eta\text{-}C_5Me_5)_2Ru_2(\mu\text{-}CO)(\mu\text{-}H)_2]$ [254].) Oxidation of **106** with $AgBF_4$ (one or two equivalents) yields $[(\eta\text{-}C_5Me_5)_3Ru_3(\mu\text{-}CO)_3(\mu_3\text{-}CMe)]^+$, **107**, and $[(\eta\text{-}C_5Me_5)_3Ru_3(\mu\text{-}CO)_3(\mu_3\text{-}CMe)]^{2+}$, **108** (Scheme 79) [287]. Regeneration of **106** from **107** and **108** can be achieved with $LiBHEt_3$. The X-ray crystal structures of both **106** and **107** have been determined confirming that only slight distortions of the metal–metal and metal–ligand bonding are observed on oxidation. Complex **108** readily deprotonates, either in the solid state or more rapidly in nitromethane to give the μ_3-vinylidene complex $[(\eta\text{-}C_5Me_5)_3Ru_3(\mu\text{-}CO)_3(\mu\text{-}CCH_2)]BF_4$, **109**, in good yield. In turn, **109** reacts readily with $NaBH_4$ to regenerate **106**, or with methyllithium to give the μ_3-propylidyne complex $[(\eta\text{-}C_5Me_5)_3Ru_3(\mu\text{-}CO)_3(\mu_3\text{-}CEt)]$ (Scheme 79) [287].

The deprotonation of $[(\eta\text{-}C_5H_5)_2Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CMe)]^+$ with triethylamine, methyllithium or water gives as the major product $[(\eta\text{-}C_5H_5)_2Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CCH_2)]$ together with two minor products $[\{(\eta\text{-}C_5H_5)_2Ru_2(CO)_3\}_2(\mu\text{-}CMeCHCH)][BF_4]$, **77**, and $[\{(\eta\text{-}C_5H_5)_3Ru_3(CO)_3\}$

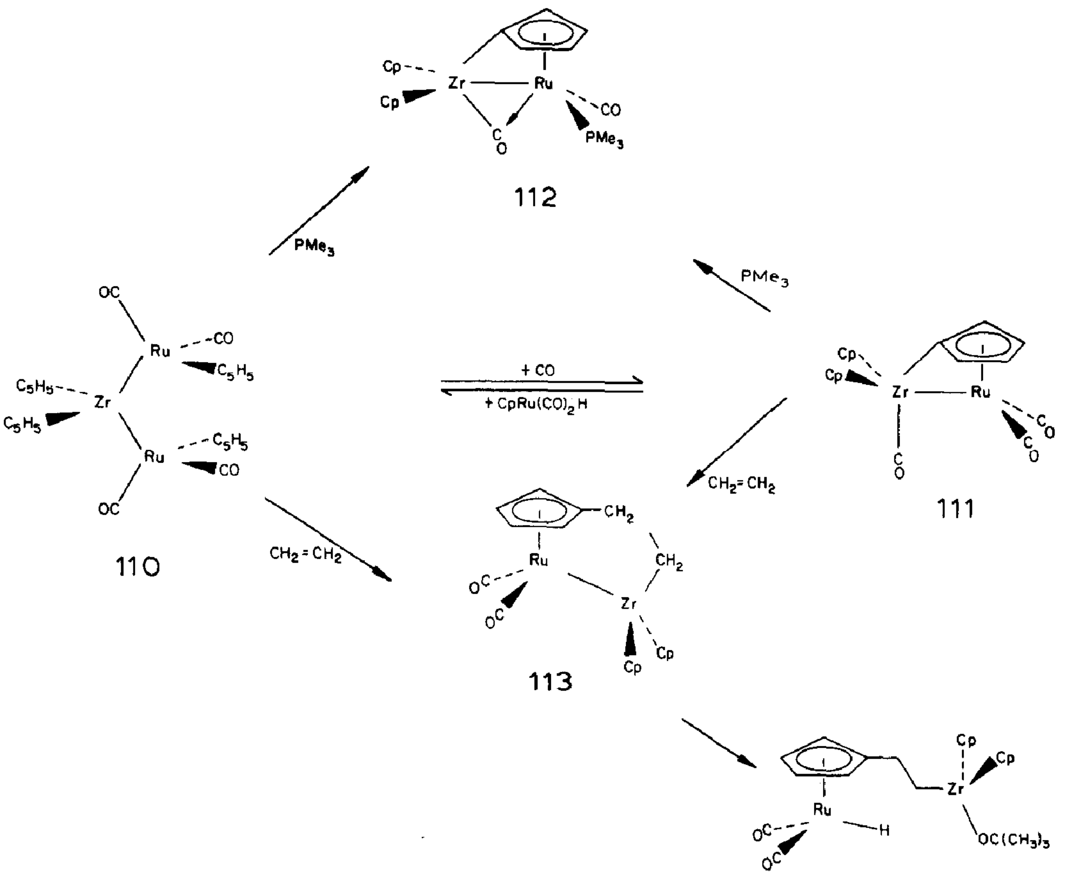


Scheme 79.

(μ-CCH$_2$CHC){(η-C$_5$H$_5$)$_2$Ru$_2$(CO)$_3$}], **78**, [257] (Fig. 20).

Formally related to the {(η-C$_5$H$_5$)$_3$Ru$_3$} type complexes synthesized by Knox and co-workers [254] is the heterometallic complex [{(η-C$_5$H$_5$)$_2$Ru$_2$} {(η-C$_5$Me$_5$)Co}(μ-CO)$_3$(μ_3-CO)] obtained by the UV irradiation of [(η-C$_5$H$_5$)$_2$Ru$_2$(CO)$_4$] together with [(η-C$_5$Me$_5$)Co(C$_2$H$_4$)$_2$] in toluene [288]. Unfortunately little is known of the properties or chemistry of this compound.

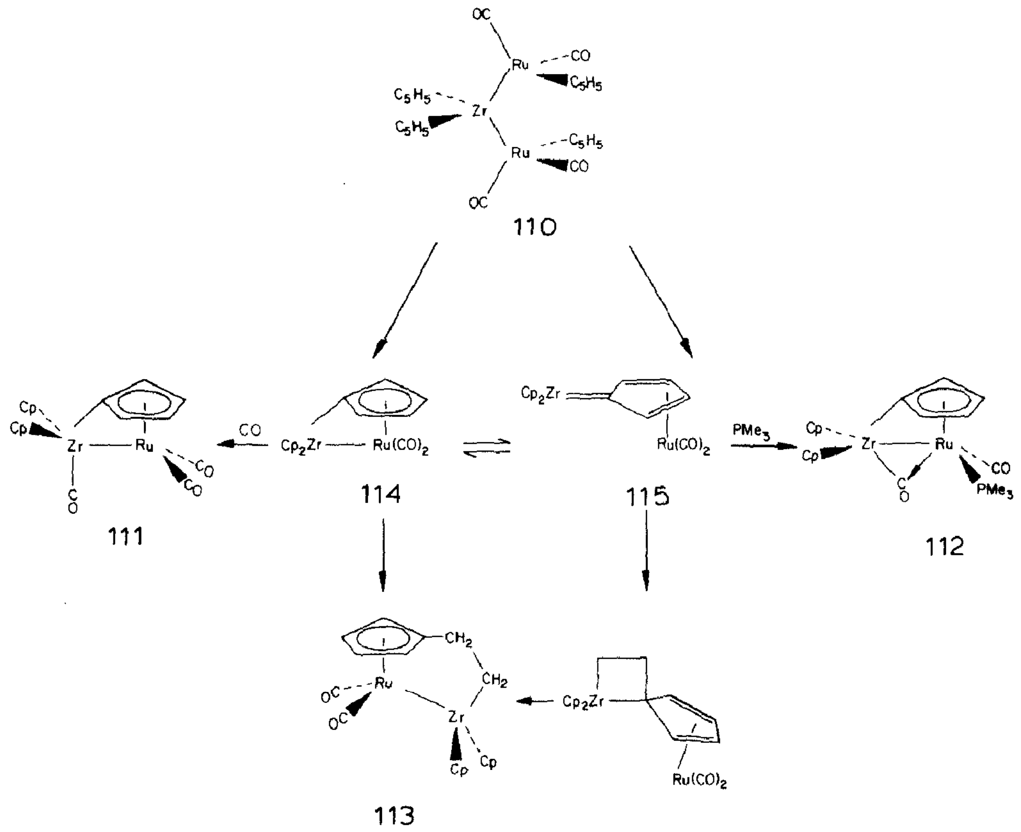
The reaction between K[(η-C$_5$H$_5$)Ru(CO)$_2$] and [(η-C$_5$H$_5$)$_2$ZrI$_2$] in THF at 25°C gives, in 90% yield, the trinuclear acyclic cluster [284] complex [(η-C$_5$H$_5$)$_2$Zr{(η-C$_5$H$_5$)Ru(CO)$_2$}$_2$], **110** [289]. The X-ray crystal structure of this molecule has been determined confirming the presence of direct metal–metal bonding (Zr–Ru 2.938, 2.948 Å; Ru–Zr–Ru 100.5°). An interesting dynamic process (observed by ^{13}C NMR) which causes the carbonyl ligands to become equivalent has been ascribed to rotation about the Zr–Ru bonds, turning the cyclopentadienyl ligands past one another [289]. It is interesting to note that the {(η-C$_5$H$_5$)Ru(CO)$_2$} groups in **110** are readily exchangeable with halide and {(η-C$_5$H$_5$)M(CO)$_2$} ligands of other zirconium complexes. For example, reaction of **110** with [(η-C$_5$H$_5$)$_2$ZrCl$_2$] gave the dinuclear complex [(η-C$_5$H$_5$)$_2$Zr(Cl){(η-C$_5$H$_5$)Ru (CO)$_2$}] in quantitative yield, while reaction with [(η-C$_5$H$_5$)$_2${(CH$_3$)$_2$ CO)}Zr–Fe(CO)$_2$(η-C$_5$H$_5$)] gave a quantitative yield of [(η-C$_5$H$_5$)$_2$Zr {(CH$_3$)$_2$CO)}–Ru(CO)$_2$(η-C$_5$H$_5$)] and a mixture of by-products dominated by [(η-C$_5$H$_5$)$_2$Fe$_2$(CO)$_4$] [289]. **110** also undergoes reaction with added ligands that lead to the expulsion of [(η-C$_5$H$_5$)Ru(CO)$_2$H] and formation of {C$_5$H$_4$Zr} products or intermediates (Scheme 80) [290]. With CO, [(η-C$_5$H$_5$)Ru(CO)$_2$H] together with the heterobimetallic complex **111** are formed. With PMe_3, **112** is formed, while **110** also reacts with ethylene to give **113**. The structures of both **111** and **112** have been determined by X-ray crystallography, while **113** has been characterized by spectroscopy and by derivatization with *t*-butanol (Scheme 80). In both **111** and **112** direct



Scheme 80.

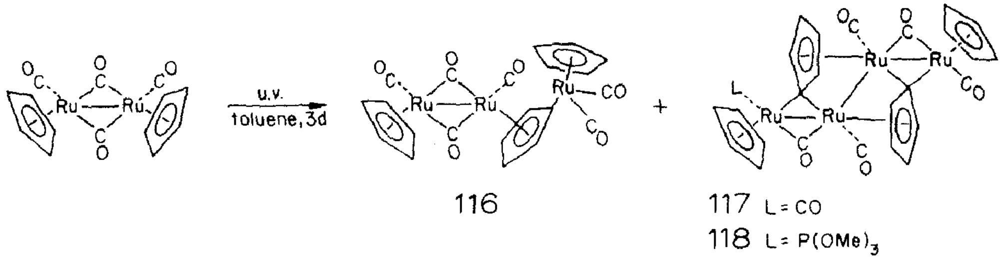
metal–metal bonds (3.064(1) and 3.080(1) Å respectively) are observed. **111** is particularly reactive (Scheme 80) and when treated with $[(\eta\text{-}C_5H_5)Ru(CO)_2H]$ regenerates **110** in greater than 50% yield. A common intermediate **114** is proposed in the formation of **111**–**113** (Scheme 81) and may possibly be generated by elimination of $[(\eta\text{-}C_5H_5)Ru(CO)_2H]$ or via the migration of Zr to the C_5H_5 ligand bound to the ruthenium atom followed by β-hydride elimination to give **115** and ring closure to **114** [290].

UV irradiation of $[(\eta\text{-}C_5H_5)_2Ru_2(CO)_4]$ in the absence of ligands gives the tri- and tetra-ruthenium complexes **116** and **117** (Scheme 82) [291], the former also having been observed as a side-product of the photochemical reaction between $[(\eta\text{-}C_5H_5)_2Ru_2(CO)_4]$ and diphenylacetylene [241]. Although suitable crystallographic crystals of **117** could not be obtained, the

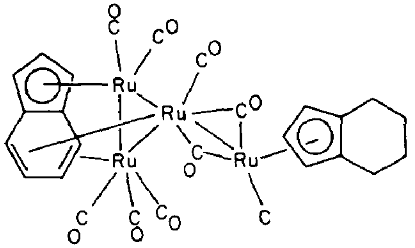


Scheme 81.

substituted derivative $[(\eta\text{-}C_5H_5)_2Ru_4(CO)_5\{P(OMe)_3\}(\mu_3\text{-}C_5H_4)_2]$, **118**, (obtained from the photochemical reaction between **117** and $P(OMe)_3$ in which the terminal CO on Ru(1) is substituted) has been structurally characterized by X-ray crystallography. The molecule consists of a Z-shaped Ru_4 backbone [Ru(1)–Ru(2)–Ru(3) 101.7, Ru(2)–Ru(3)–Ru(4) 99.6°]. The central Ru(2)–Ru(3) bond length (2.887 Å) was found to be significantly longer than the outer ones [Ru(1)–Ru(2) 2.755, Ru(3)–Ru(4) 2.767 Å]. An



Scheme 82.



119

Fig. 26.

unusual feature of the photochemical reaction of $[(\eta\text{-}C_5H_5)_2Ru_2(CO)_4]$ leading to **116** and **117** is the apparently facile attack of $\{(\eta\text{-}C_5H_5)Ru(CO)_2\}$ radicals on cyclopentadienyl rings. Two isomers of **117** are observed by ^1H NMR in solution; the first is assigned a terminal carbonyl stereochemistry similar to that observed by X-ray crystallography for **118** i.e. *trans* about Ru(3)–Ru(4) and *cis* about Ru(1)–Ru(2). The second is assigned a *trans–trans* configuration. These isomers are partially separable by chromatography but interconvert slowly on heating [291].

The reaction of indene with $[Ru_3(CO)_{12}]$ in methylcyclohexane gives a low yield of two products, $[(\eta^5\text{-}C_9H_7)_2Ru_2(CO)_4]$ (C_9H_7 = indenyl) and the tetranuclear cluster complex $[Ru_4(CO)_7(\mu\text{-}CO)_2(\eta^5\text{-}C_9H_7)(\eta\text{-}C_9H_9)]$ (**119**; C_9H_9 = dihydroindenyl) [292]. While the yield of the dinuclear product can be significantly improved (to ca. 65%) in methylisobutylketone as solvent, the yield of the cluster (ca. 5%) remains disappointingly low, apparently irrespective of the reaction conditions. Complex **119** has been completely characterized by X-ray crystallography and consists of a tri-ruthenium core with one pendant ruthenium atom (Fig. 26); remarkable features of this molecule include the near planarity of the Ru_4 framework, and the formal Ru → Ru donor bond (2.972 Å) [292].

F. CONCLUSIONS

On the basis of the survey presented above, several general conclusions can be drawn.

(i) Metallocenes

The chemistry of ruthenocenes and osmocenes forms one of the largest bodies of information on cyclopentadienyl-ruthenium and -osmium complexes [7]. Nevertheless, it still falls far short of the extensive chemistry associated with ferrocene [293,294]. This may partly be attributed to the lack of suitable synthetic procedures which give ruthenocenes and osmocenes in high yield, and possibly also to the more significant cost of ruthenium and osmium relative to iron. The recently published new syntheses of ruthenocenes and osmocenes [14,17] should therefore benefit the development of this area, specifically the substitution chemistry of the metallocene core and the medical and technological applications of these metallocenes.

(ii) Half-sandwich compounds

Cyclopentadienyl half-sandwich compounds of ruthenium and osmium form, without doubt, the most extensively studied class of cyclopentadienyl-ruthenium and -osmium complexes. The spectrum of reactivity and chemical properties established to date for these systems is remarkable, especially considering the limited number of synthetic precursors (traditionally $[(\eta\text{-}C_5H_5)Ru(CO)_2X]$ and $[(\eta\text{-}C_5H_5)Ru(PPh_3)_2Cl]$) which have been utilized so far [7]. Perhaps then the most significant recent developments in cyclopentadienyl-ruthenium and -osmium chemistry relate to the preparation of the new generation of highly reactive precursors $[(\eta\text{-}C_5R_5)Ru(\eta\text{-diolefin})X]$ ($R = H$, Me; diolefin is typically cycloocta-1,5-diene; $X = H$, Cl, Br, I), compounds which are showing some completely unanticipated, and remarkable reactivity patterns [12–14,16,128,157,220].

Another significant recent development which should have far reaching implications relates to the organometallic chemistry of the ruthenium- and osmium(IV) oxidation state [126–129]. Stabilization of the +IV oxidation state seems to be particularly favourable in the environment created by the cyclopentadienyl ligand and several recent reports in this area strengthen the case for an extensive organometallic chemistry of this oxidation state.

One of the most strikingly neglected aspects of cyclopentadienyl-ruthenium and -osmium chemistry relates to involving the cyclopentadienyl ligand in more of the reactivity of the complex. This might for instance be achieved simply by suitable ring functionality [295] (including electron-withdrawing substituents and cyclometallation), or by the use of polycyclic cyclopentadienyl ligands typified by indenyl and fluorenyl systems which have been shown with other transition metals to possess some very interesting chemical properties.

(iii) Dinuclear compounds

Perhaps the most striking aspect of the chemistry of dinuclear cyclopentadienyl-ruthenium and -osmium complexes is that it, almost without exception, revolves around the single synthetic precursor $[(\eta\text{-}C_5H_5)_2Ru_2(CO)_4]$. In this respect the organic chemistry of this compound developed largely by Knox and his co-workers [254], is outstanding. However, very little has to date been reported on the chemistry of the corresponding osmium complex $[(\eta\text{-}C_5H_5)_2Os_2(CO)_4]$, and almost nothing on either ruthenium or osmium systems containing cyclopentadienyl ligands other than the basic C_5H_5. Few attempts have been made to introduce reactivity, via the cyclopentadienyl ligands, into what are apparently rather unreactive dimetal fragments. (The work of Vollhardt and Weideman [262–264] with the fulvalene diruthenium complexes is a significant exception.)

More generally though, the ruthenium(I) and osmium(I) oxidation states have, over the years, remained sadly neglected, and there is no a priori reason why there should not be a more extensive organometallic chemistry of such dimetal centres, utilizing for instance functionalized or reactive cyclopentadienyl ligands, or only a single cyclopentadienyl ligand.

(iv) Polynuclear compounds

Considering the stabilizing properties of the cyclopentadienyl ligand, and considering also the well-known propensity of both ruthenium and osmium for forming metal–metal bonds and therefore clusters, it is remarkable that, to date, almost no cluster compounds of these metals bearing cyclopentadienyl ligands have been reported. Notable exceptions are the polynuclear systems developed by Knox and co-workers [254]. However, it is apparent that there is still much to be desired in terms of reactivity, and alternative synthetic strategies might focus on ways of introducing reactive functionality, very much in the same way as has been achieved with half-sandwich cyclopentadienyl complexes, into the polynuclear systems.

(v) General

There is a noticeable lack of emphasis on osmium chemistry in all four of the above categories of compounds. There are reasons for this, such as the lower kinetic lability of osmium relative to ruthenium, and possibly the greater cost of osmium, but with greater emphasis being placed on the development of new synthetic precursors, this imbalance may soon be redressed. Also, the catalytic chemistry of cyclopentadienyl-ruthenium and -osmium complexes is at present not very important. However, one interesting report has shown that suitable catalyst/ligand design can be used to overcome some of the inhibiting aspects of the essentially stabilizing cyclopentadienyl ligand. One thinks particularly in terms of the more reactive cyclopentadienyl ligands already mentioned above with respect to half-sandwich compounds. Finally, there have been few systematic attempts to compare the structures and properties of substituted (e.g. peralkyl) and conventional cyclopentadienyl-ruthenium and -osmium complexes.

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