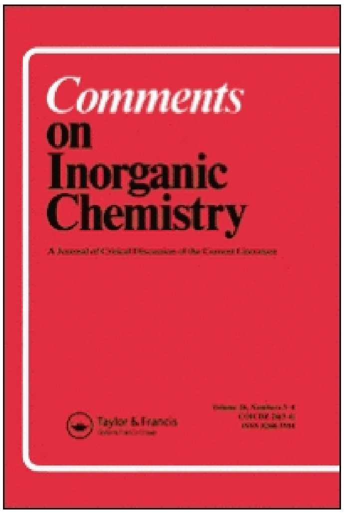

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(η^6-Cycloocta-1,3,5-Triene) (η^4-Cycloocta-1,5-Diene) Ruthenium (0) in the Development of Ruthenium Chemistry

Paolo Pertici[a]; Giovanni Vitulli[a]
[a] Centro di Studio del CNR per le Macromolecole Stereordinate ed Otticamente Attive, Dipartimento di Chimica e Chimica Industriale, Universitá di Pisa, Pisa, Italy

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(η^6-Cycloocta-1,3,5-Triene) (η^4-Cycloocta-1,5-Diene) Ruthenium (0) in the Development of Ruthenium Chemistry

The simple preparative route to the zero valent (η^6-cycloocta-1,3,5-triene) (η^4-cycloocta-1,5-diene)ruthenium complex, by reacting $RuCl_3 \cdot 3H_2O$ with cycloocta-1,5-diene in the presence of zinc powder, stimulated extensive studies on the chemistry of this compound. Its relevance and versatility as starting material in the preparation of new Ru complexes and as catalytic precursor in organic synthesis are reviewed and discussed.

Key Words: *ruthenium, organometallic synthesis, catalysis, organic reactions*

The discovery of metal complexes of special interest has often played a crucial role in the development of organometallic and catalytic chemistry.[1] $FeCp_2$ (Cp = cyclopentadienyl),[2] $Cr(C_6H_6)_2$,[3] $Ni(COD)_2$ (COD = cycloocta-1,5-diene),[4] $Pt(PPh_3)_3$,[5] $[RhCl(COD)]_2$,[6] $RhCl(PPh_3)_3$,[7] $IrCl(CO)(PPh_3)_2$,[8] for instance, are appropriate examples of such a pivotal function.

An additional complex which can be rightly included in this set of compounds is the zerovalent Ru(η^6-cycloocta-1,3,5-triene) (η^4-cycloocta-1,5-diene), Ru(η^6-C_8H_{10}) (η^4-C_8H_{12}), **1**. It was obtained for the first time in late 1963 by E. O. Fisher[9] by reduction of anhydrous ruthenium trichloride with isopropyl Grignard reagent under u.v. radiation in the presence of cycloocta-1,3,5-triene and cycloocta-1,5-diene. Because of the low reaction yield (ca. 6%)

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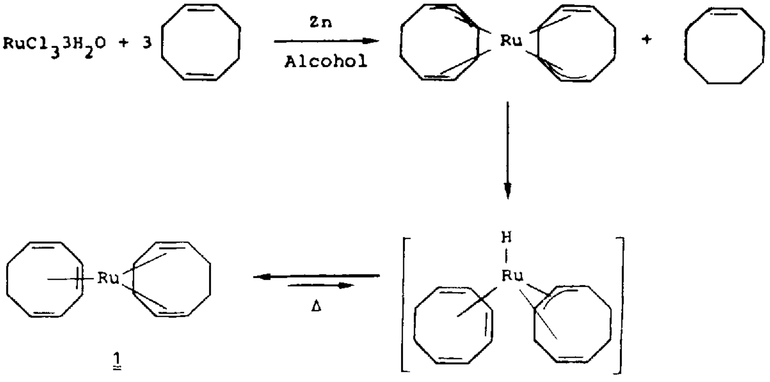
and the difficult preparative procedure, however, such a complex has been neglected for a long time, until 1975, when a very simple preparation method was acquired, reacting $RuCl_3\ 3H_2O$ with 1,5-cyclooctadiene in the presence of zinc powder (Eq. (1)).[10]

$$2RuCl_3 + 6C_8H_{12} + 3Zn \xrightarrow[\Delta]{\text{Ethanol}} 2|\underset{\mathbf{1}}{Ru(\eta^6\text{-}C_8H_{10})(\eta^4\text{-}C_8H_{12})}| + 3ZnCl_2 + 2C_8H_{14} \quad (1)$$

The reaction was performed in refluxing ethanol or tetrahydrofuran, giving **1** in yields of ca. 50%. The yields have been later improved to ca. 85% using ultrasound vibrations to activate the zinc powder.[11]

Cyclooctene was formed as a reaction product, suggesting a disproportionation reaction of the starting cycloocta-1,5-diene to cycloocta-1,3,5-triene, that remains bonded to the ruthenium, and free cyclooctene. Such a facile intermolecular hydride transfer reaction has been well proved by the isolation of the bis(1-3;5,6-η-cyclooctadienyl)Ru intermediate which easily isomerizes to complex **1** (Scheme 1).[11]

The molecular structure of **1** has been recently reported[12]: the



SCHEME 1

coordinated triene part of the η^6-C_8H_{10} ligand is characterized by C–C bond lengths not differing significantly from each other, indicating a substantial electron delocalization within the conjugated π-system. The η^4-C_8H_{12} ligand displays the normal tub configuration.

Complex **1** has been an actractive starting point for organometallic and catalytic studies.

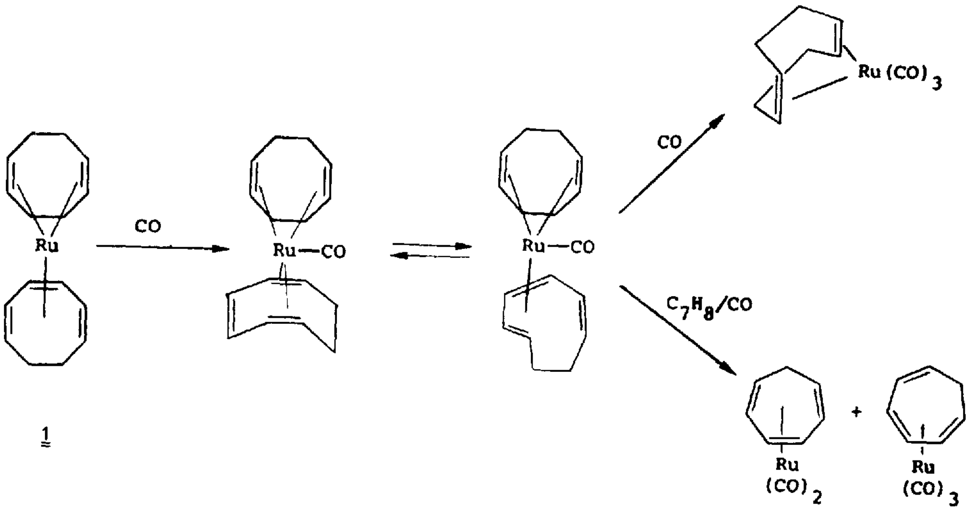
ORGANOMETALLIC CHEMISTRY

Ru(η^6-C_8H_{10})(η^4-C_8H_{12}), **1**, is a widely reactive compound. It easily undergoes ligand displacement reactions, molecular hydrogen promoted cycloolefin replacement and protonation reactions, allowing the entrance of a broad range of new ruthenium compounds.

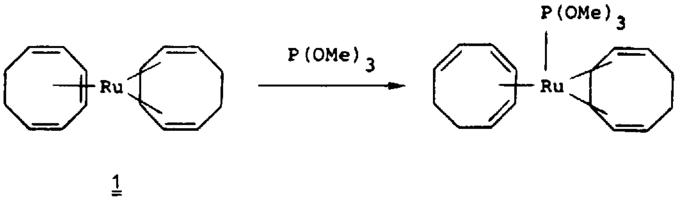
(a) Ligand Displacement Reactions

1 readily reacts with carbon monoxide at room temperature and atmospheric pressure of CO to give Ru(CO) (η^4-C_8H_{10})(η^4-C_8H_{12}) as a first reaction product, and by further reaction, $Ru(CO)_3$(η^4-C_8H_{12}), in almost quantitative yield.[13] In the presence of C_7H_8, (C_7H_8 = cycloheptatriene), the reaction affords $Ru(CO)_3$(η^4-C_7H_8) and $Ru(CO)_2$(η^6-C_7H_8) as major products (Scheme 2). The reaction provides a valid entry to compounds of interest in studying the reactivity of coordinated olefin molecules, not easily accessible by alternative methods.[14]

The tendency for cycloocta-1,3,5-triene to give bidentate coordination, which plays an active role in determining the reactivity of **1**, has been well focused in the reaction with a stoichiometric amount of $P(OMe)_3$[15] (Scheme 3). The molecular structure of the resulting {Ru(η^4-C_8H_{10})(η^4-C_8H_{12}) [$P(OMe)_3$]} is shown in Fig. 1. The cycloocta-1,3,5-triene is bonded by its buta-1,3-diene moiety; the increasing Ru–C distances from C(15) to C(12) (2.04, 2.16, 2.18 and 2.23 Å) indicates an interesting decreasing bond strength which could account for the easier replacement of the η^4-cycloocta-1,3,5-triene with respect to η^4-cycloocta-1,5-diene in the presence of excess ligand.



SCHEME 2



SCHEME 3

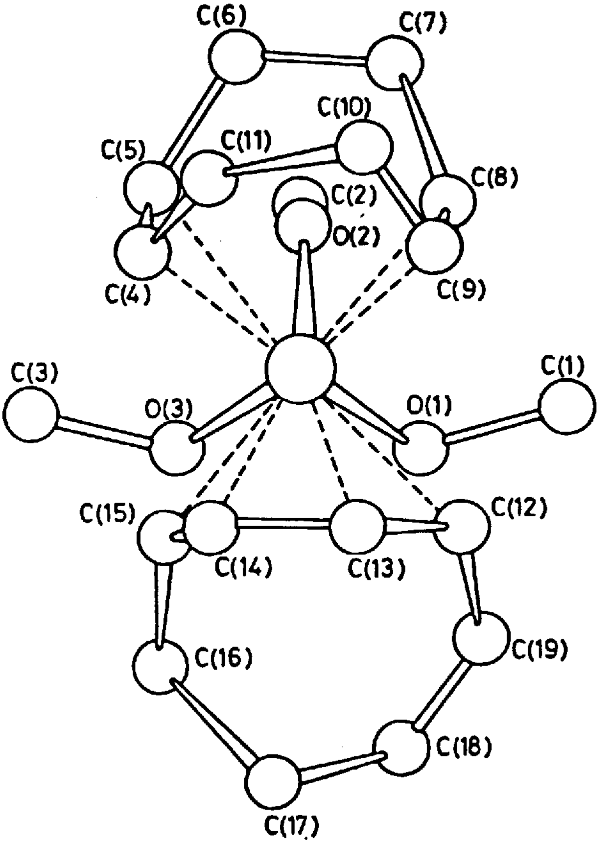
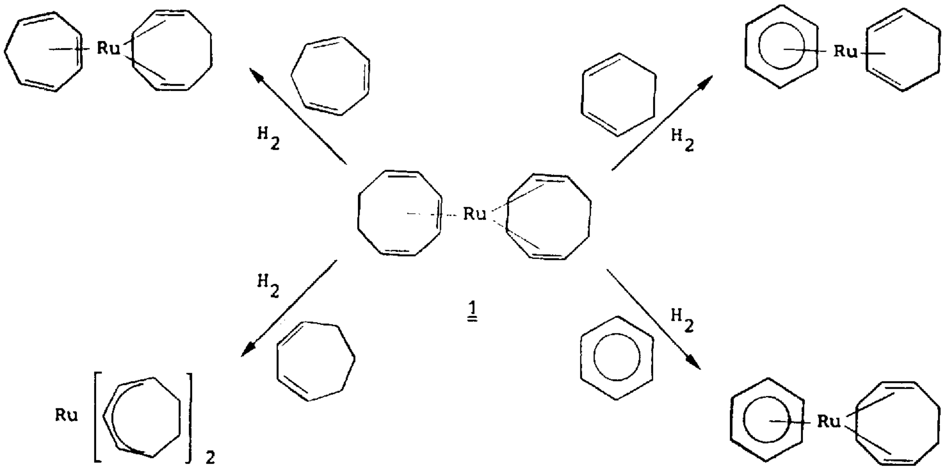


FIGURE 1 The molecular structure of $\{Ru(\eta^4\text{-}C_8H_{10})(\eta^4\text{-}C_8H_{12})|P(OMe)|\}$ viewed along the P–Ru bond.



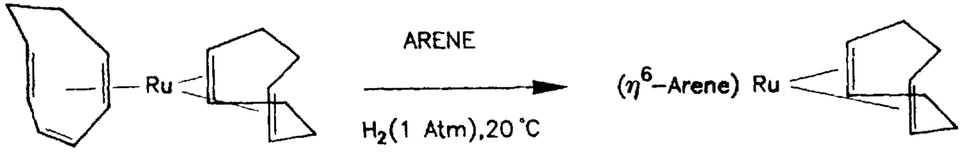
SCHEME 4

(b) Molecular Hydrogen Promoted Cycloolefin Replacement Reactions

(i) Reactions with cycloolefins and aromatic hydrocarbons. Ligand displacement or exchange reactions are strongly activated by molecular hydrogen. Under atmospheric pressure of hydrogen, **1** rapidly reacts with cycloolefins and arenes at room temperature, affording Ru(0) or Ru(II) complexes in which one or both the original ligands have been replaced[16] (Scheme 4). Since no cyclooctatriene was detected in the mother liquor of the reaction, a possible mechanism for the formation of the new complexes probably involves the hydrogenation of the bonded cyclooctatriene to give a coordinatively unsaturated ruthenium complex which undergoes a ligand exchange reaction in the presence of cycloolefins or arenes. No ligand displacement reaction takes place in the absence of molecular hydrogen, even at high temperature. On heating under nitrogen, **1** slightly isomerizes to the bis-cyclooctadienyl compound, $Ru(1\text{-}5\text{-}\eta\text{-}C_8H_{11})_2$.[16]

The reaction with arenes under hydrogen is remarkable, allowing the preparation of a large number of Ru(η^6-arene) (η^4-C_8H_{12}) complexes, **2**, including those containing arenes with bulky or functional groups and polinuclear aromatic ligands[17] (Scheme 5). Several complexes **2** are of great interest for structural studies and in preparative chemistry and catalysis. Complexes **2(l–r)**, for instance, containing chiral substituents on the arene ring, show in their ^{1}Hnmr spectra an unusual inequivalence of the ortho and meta protons of the aromatic ligands.[17,18] The ^{1}Hnmr spectrum of the aromatic protons of complex **2l** is reported in Fig. 2, for example. The chemical shifts of such protons result in a singular relationship $\Delta\delta Ho \cong \Delta\delta Hm'$ and $\Delta\delta Ho' \cong \Delta\delta Hm$, which can be related to the presence of rotameric conformations generating similar environments for the protons Ho, Hm' and, separately, Ho', Hm, as pictured in Fig. 3.[18]

Among complexes **2**, Ru(η^6-naphthalene) (η^4-cycloocta-1,5-diene), **2s**, is also worthy of mention. The easy displacement of the bonded naphthalene, even at room temperature, in the presence of stoichiometric amounts of CH_3CN ($CH_3CN/Ru = 3$), makes this compound very attractive as a new starting material in preparative chemistry and catalysis.[19]



1

2

ARENE = C_6H_6(a), $CH_3C_6H_5$(b), 1,4–$Me_2C_6H_4$(c),
1,3,5–$Me_3C_6H_3$(d), $C_2H_5C_6H_5$(e), $Me_2CHC_6H_5$(f)
$Et_2CHC_6H_5$(g), $C_6H_5(CH_2)_3C_6H_5$(h), $C_6H_5C_6H_5$(i),
$CH_3OC_6H_5$(j), $CH_3COC_6H_5$(k), $C_2H_5CH(Me)C_6H_5$(l),
$Me_2CHCH(Me)C_6H_5$(m), $Me_3CH(Me)C_6H_5$(n),
p–$C_2H_5CH(Me)C_6H_4Me$(o), $C_2H_5OCH(Me)C_6H_5$(p),
$C_2H_5CH(Me)OC_6H_5$(q), $NH_2CH(Me)C_6H_5$(r), $C_{10}H_8$(s).

SCHEME 5

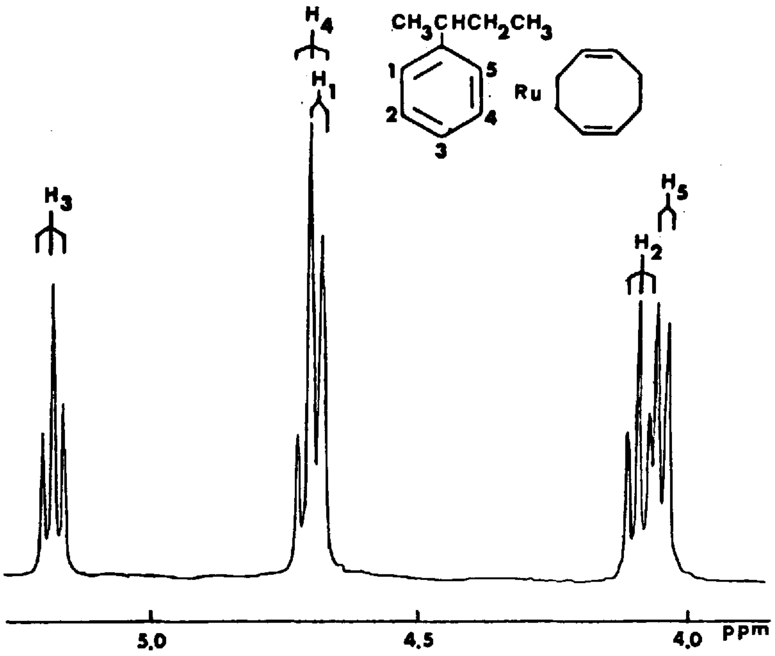


FIGURE 2 Hnmr spectrum (aromatic protons) of the complex **21** at 270 MHz and full assignment.

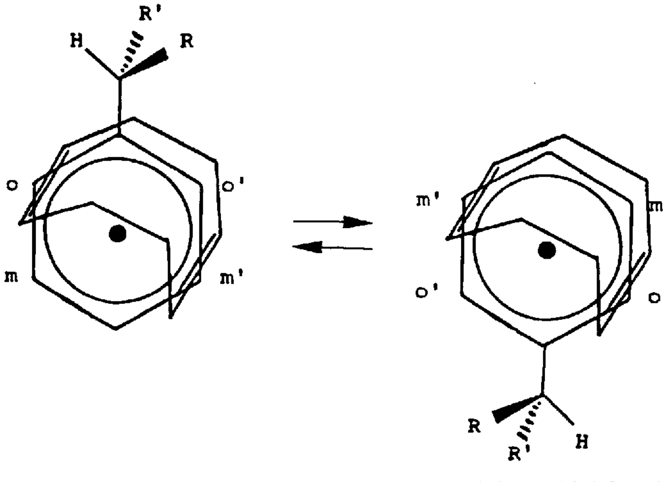


FIGURE 3 Possible rotamers of the chiral complexes Ru(η^6-arene)(η^4-C_8H_{12}), **21–r**, present in solution.

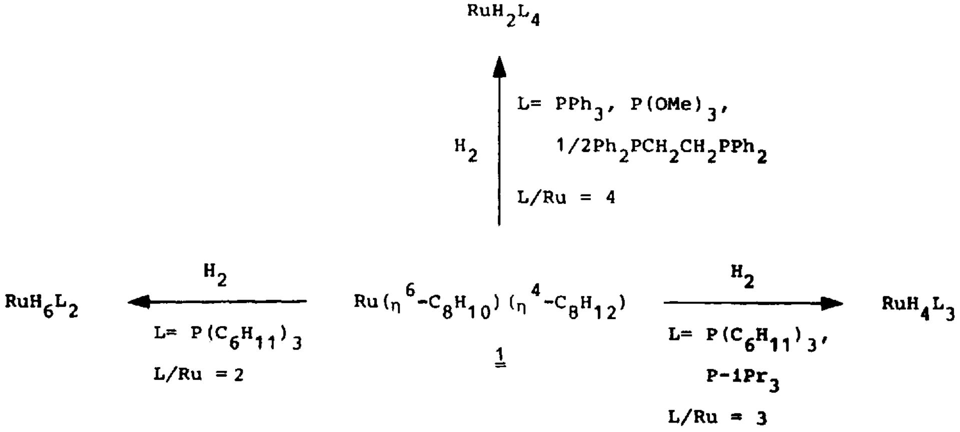
It is also worthwhile to note that the yellow solution of **2** in acetone or THF readily turns red on addition of HCl, giving, in quantitative yields, $[RuCl_2\ (\eta^6\text{-Arene})]_2$ compounds,[17] many of which cannot be obtained by alternative routes.[20] Further treatment of such compounds with olefins in the presence of Na_2CO_3 and isopropyl alcohol allows us to prepare the corresponding $Ru(\eta^6\text{-Arene})(\eta^2\text{-Olefin})_2$ complexes.[18,21] The ensemble of these two reactions provides access to complexes containing a broad range of arene and olefin ligands.

(ii) Reactions with phosphorous ligands. The reaction of **1** with hydrogen and trivalent phosphorous compounds allows us to prepare, in high yields, ruthenium–hydride phosphine complexes. The η^4-cycloocta-1,5-diene and the η^6-cycloocta-1,3,5-triene are hydrogenated to a mixture of cyclooctene and cyclooctane, and the vacant coordination positions on ruthenium are refilled by the phosphorus ligand and hydrogen atoms. According to the ligand and to the reaction conditions, complexes of the type RuH_2L_4, RuH_4L_3 and RuH_6L_2 are formed (Scheme 6).[22,23] Complexes RuH_4L_3 and RuH_6L_2, $[L = P(C_6H_{11})_3]$, previously described as polyhydrido complexes, have been recently reinvestigated and reformulated as η^2-dihydrogen complexes.[24]

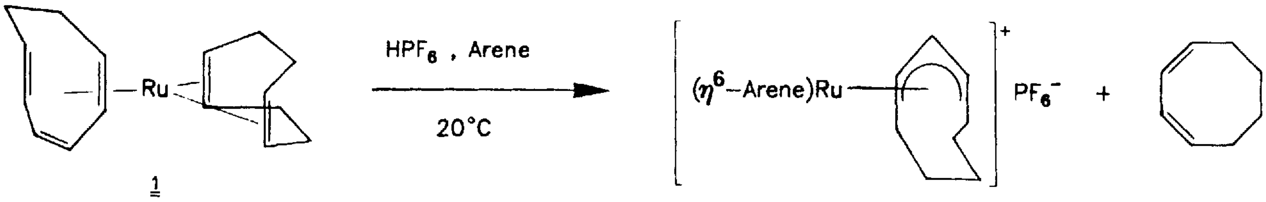
(c) Protonation Reactions

Protonation of **1** with HPF_6 in aromatic solvents affords $[Ru(\eta^6\text{-Arene})(\eta^5\text{-cyclooctadienyl})]PF_6$ complexes in almost quantitative yield, along with free cycloocta-1,3-diene, the neat result of protonation being the displacement of a bonded cycloolefin by the coordinating solvents[25] (Scheme 7).

If the protonation of **1** is performed at −80°C using $HBF_4 \cdot Et_2O$ as protonating agent, the thermally unstable hydrido complex $[RuH(1\text{-}6\text{-}\eta\text{-}C_8H_{10})\ (1,2{:}5,6\text{-}\eta\text{-}C_8H_{12})]BF_4$ can be isolated. On warming at room temperature this complex isomerizes to $[Ru(1\text{-}5\text{-}\eta\text{-}C_8H_{11})(1,3\text{-COD})]BF_4$ and easily undergoes ligand exchange reactions in the presence of ligands such as pentamethylcyclopentadiene and phosphorous compounds[26] (Scheme 8). Complexes like $[RuH(1\text{-}6\text{-}\eta\text{-}C_8H_{10})\ (1,2{:}5,6\text{-}\eta\text{-}C_8H_{12})]BF_4$ and $[Ru\ (1\text{-}5\text{-}\eta\text{-}C_8H_{11})(1\text{-}4\text{-}\eta\text{-}C_8H_{12})]BF_4$ (Scheme 8) can be considered as possible


RuH_2L_4
H_2
L= PPh_3, $P(OMe)_3$,
$1/2Ph_2PCH_2CH_2PPh_2$
L/Ru = 4
RuH_6L_2
H_2
L= $P(C_6H_{11})_3$
L/Ru = 2
$Ru(\eta^6-C_8H_{10})(\eta^4-C_8H_{12})$
1
H_2
L= $P(C_6H_{11})_3$,
$P-iPr_3$
L/Ru = 3
RuH_4L_3

SCHEME 6



ARENE = C_6H_6, 1,4-$Me_2C_6H_4$, 1,3,5-$Me_3C_6H_3$, ClC_6H_5

SCHEME 7

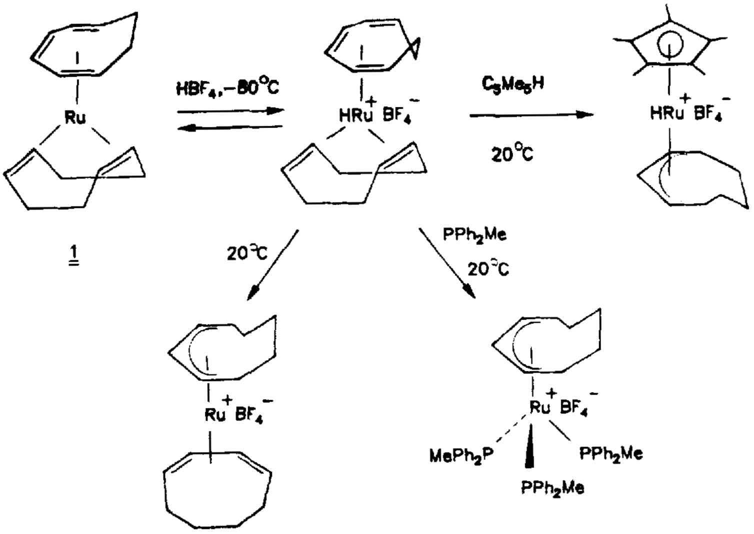
intermediates in the protonation at room temperature of **1** with HPF_6 in aromatic solutions to $|Ru(\eta^6\text{-Arene})(1\text{-}5\text{-}\eta\text{-}C_8H_{11})|PF_6$ compounds.[25]

The protonation of **1** with 3-butenoic acid in the presence of aryl tertiary phosphines, PR_3, has been reported to afford η^3-allylcarboxylatoruthenium(II) complexes.[27]

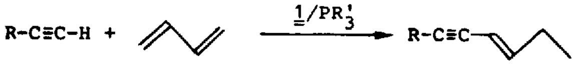
$Ru(\eta^6\text{-}C_8H_{10})(\eta^4\text{-}C_8H_{12})$ IN CATALYSIS

1. Organic Synthesis Catalyzed by 1 and Its Derivatives

Low valent transition metal complexes, apt to generate coordinatively unsaturated species, are of great relevance in catalysis.[28] Complex **1** is really promising form this point of view, and interesting organic reactions catalyzed by this compound and its derivatives have been recently developed.[29] Selected examples include: (a) the linear codimerization of terminal acetylenes with 1,3-dienes, (b) the addition of carboxilic acids to acetylenes, (c) [2 + 2] cross cycloaddition of norbornenes with acetylenes dicarboxylate, (d) the



SCHEME 8



R' = Et, t-Bu, n-C_8H_{17}

SCHEME 9

synthesis of allylsylanes, (e) the selective hydrogenation of polyolefins to monoolefins.

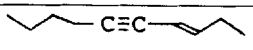
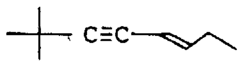
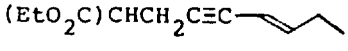
(a) Linear Codimerization of 1,3-Dienes with Terminal Acetylenes Catalyzed by **1**/PR_3 Systems

1,3-dienes have been found to react with terminal acetylenes in the presence of catalytic amounts of **1** and PR_3, as additional ligand, to give linear codimers with high chemo-, regio- and stereoselectivity[30] (Scheme 9). Some results are summarized in Table I.

As shown in Table I, 1-hexyne, 3,3-dimethyl-1-butyne and 4,4-dicarboethoxy-1-butyne readily react with 1,3-butadiene to give (E)-3-decen-5-yne, (E)-7,7-dimethyl-3-octen-5-yne and ethyl-(E)-2-ethoxycarbonyl-6-nonen-4-ynoate, respectively. The stereochemistry of the olefinic group is completely *trans* and neither the

TABLE I

Codimerization of acetylenes and 1,3-butadiene catalyzed by Ru(η^6-cycloocta-1,3,5-triene)(η^4-cycloocta-1,5-diene)/P-nBu$_3^*$

Acetylene	1/P-nBu$_3$ (mmol/mmol)	Product	Yield (%)
1-Hexyne	0.1/0.2		94
3,3-Dimethyl-1-butyne	0.1/0.2		96
4,4-Dicarboethoxy-1-butyne	0.2/0.4	 $(EtO_2C)CHCH_2C\equiv C$	80

*Acetylene (10 mmol); 1,3-butadiene (20 mmol); solvent, benzene (5 ml); temperature, 80°C; time, 4 h (from Ref. 25).

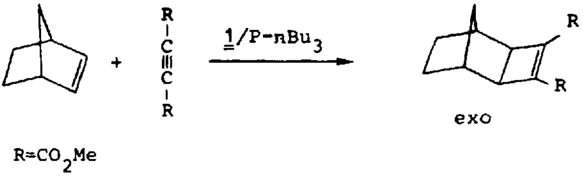
branched isomers nor the cyclic oligomers are formed. A possible reaction mechanism could involve an oxidative addition of acetylenes to a zero valent ruthenium complex followed by diene insertion in the ruthenium–carbon bond and further reductive elimination, providing the organic products and regenerating the catalytic Ru(0) specie.[30]

(b) [2 + 2] Cross Cycloaddition of Norbornenes with Dimethylacetylendicarboxylate

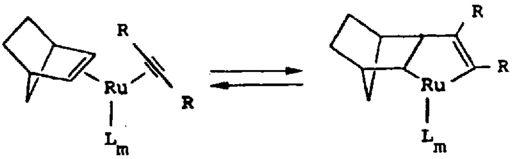
Complex **1** is an effective catalyst for the [2 + 2] cross addition of norbornene derivatives to dimethylacetylenedicarboxylate, affording *exo*-tricyclo[4,2,1,0]non-3-ene systems with selectivity over the 95%[31] (Scheme 10). A Ru(0) ⇄ Ru(II) catalytic cycle has been postulated, involving the intermediate species reported in Scheme 11.

(c) Synthesis of Enol Esters by Addition of Carboxylic Acids to Acetylenes

As already mentioned, **1** easily isomerizes on heating in hydrocarbon solvents to the bis-cyclooctadienyl complex Ru(1-5-η-



SCHEME 10



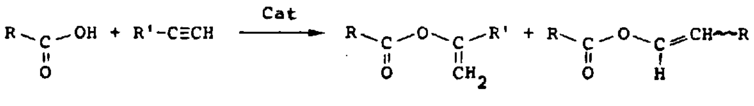
SCHEME 11

$C_8H_{11})_2$.[16] This complex, when treated with trialkyl phosphines and maleic anhydride, affords an extremely versatile catalytic system for the preparation of enol esters through the addition of carboxylic acids to terminal alkynes[32] (Scheme 12). The regio selectivity of the reaction is controlled by the phosphine; selectivities >90% in the enol ester having the methylene group have been obtained using $P(n\text{-}Bu)_3$. The presence of maleic anhydride, an electron deficient olefin probably acting as a π-acid ligand, is essential to have the reaction of the alkyne with saturated carboxylic acids. α, β-unsaturated acids or benzoic acid react with acetylenes even in the absence of such a catalytic component. Kinetic studies on the addition reaction suggest alkyne coordination to ruthenium as a first step with further addition of carboxylic acid to the coordinated alkyne and attachment of the proton to the ruthenium atom, followed by reductive elimination.[32]

(d) Synthesis of Allylsylanes

The sylilation of olefins at 60–140°C takes place easily in the presence of catalytic amounts of **1**, giving allylsylanes in high yields and good selectivities[33] (Scheme 13). Hydrogen is not evolved in such a reaction and hydrogenation of the starting olefin also occurs. Dialkyl ruthenium(II) intermediates have been suggested, evolving by hydrogen transfer reaction to allylsylane derivatives, hydrogenated olefin and Ru(0) catalytic species, as shown in Scheme 14.

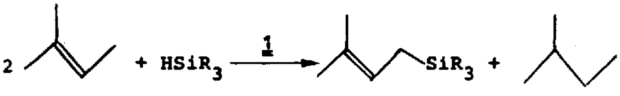
The observation that 2-methyl-1-butene and 3-methyl-1-butene give, by reaction with trialkylsylanes, the same product 3-methyl-1-trialkylsylil-2-butene suggests that isomerization of the starting olefin before sylilation also occurs.



Cat = Ru(1-5-η-cyclooctadienyl)$_2$, PR_3,
maleic anhydride

R= nBu, Ph, Cy

SCHEME 12



R = Me,Et

SCHEME 13

(e) Selective Hydrogenation of Polyolefins to Monoolefins

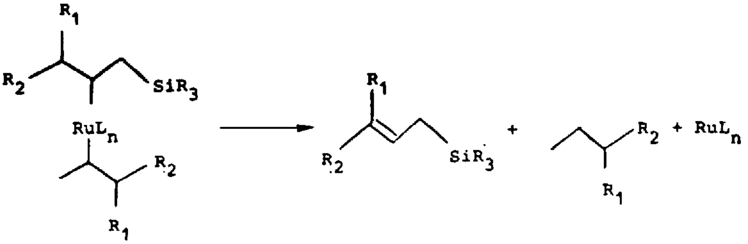
Polyolefins, such as cycloocta-1,3,5-triene and cycloheptatriene, are easily hydrogenated in the presence of catalytic amounts of **1** at room temperature under 1 atm of hydrogen.[34] In hydrocarbon solvents the reduction is very selective, giving the monoolefin as the only reduction product.

2. Ru(η^6-C_8H_{10})(η^2-C_8H_{12}) in the Preparation of Heterogeneous Catalysts

Complex **1** has also proved to be valuable material in the preparation of very active heterogeneous catalysts containing small ruthenium aggregates supported on organic aromatic polymers or inorganic matrices.

(a) Polystyrene/Ruthenium System

The reaction of **1** with polystyrene in THF solution under hydrogen atmosphere (P = 1 atm) at 20°C proceeds with complete displacement of the cycloolefinic ligands to give insoluble polystyrene/



SCHEME 14

ruthenium derivatives[35] (Scheme 15). EXAFS, TEM, IR and Raman spectroscopic studies indicate a structure based on small metal clusters bound to the polymer by single ruthenium–arene binding, as schematically represented in Fig. 4.[36]

These systems are very active catalysts for the hydrogenation of a large variety of unsaturated groups such as olefinic double bonds, mononuclear aromatic hydrocarbons, ketones, nitriles, nitroaromatic compounds and oxymes.[37]

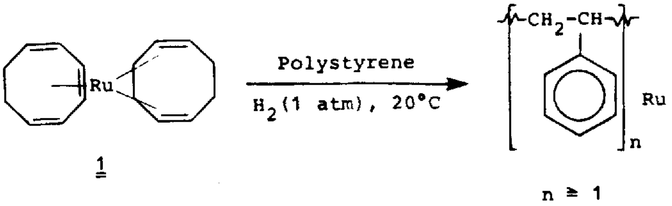
(b) Ruthenium Supported on SiO_2

A highly dispersed ruthenium catalyst supported in SiO_2 (particle size < 10 Å) has been obtained by treatment of the support with **1**, followed by hydrogenolysis.[38] The ruthenium dispersion is very high even at loadings up to ca. 5%, in contrast with that found using $RuCl_3$ aqueous solution for the preparation of SiO_2 supported catalysts.

CONCLUSIONS

It appears from the reported examples that Ru(η^6-cycloocta-1,3,5-triene)(η^4-cycloocta-1,5-diene) is a highly versatile starting compound in the preparation of new complexes and in catalysis. Its wide chemistry is largely far to be completed, and the aim of this review is to stimulate studies on new reactions involving this compound and its derivatives.

For instance, by reaction of **1** with other appropriate complexes, such as $RhClL_3$, $IrCl(CO)L_2$ (L = phosphine), $[RhCl(COD)]_2$, heterometallic new complexes probably could be obtained. Moreover, the reaction of **1** with polystyrene, which affords polymers



SCHEME 15

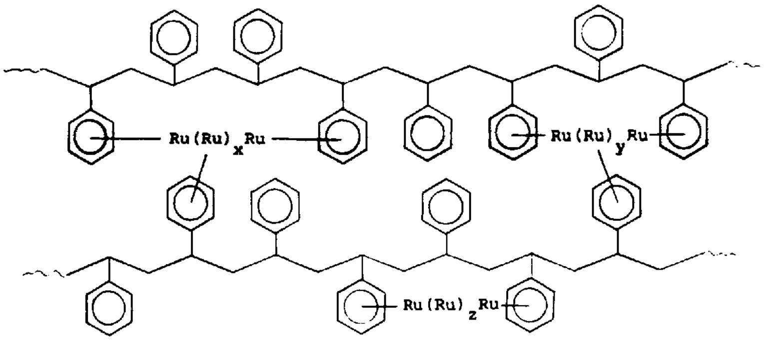


FIGURE 4 Schematic representation of some possible structures of ruthenium clusters coordinated to polystyrene.

containing materials and could offer fair perspective in the polymers containing metals field.[39]

PAOLO PERTICI and GIOVANNI VITULLI
Centro di Studio del CNR
per le Macromolecole Stereordinate ed Otticamente Attive,
Dipartimento di Chimica e Chimica Industriale,
Universitá di Pisa,
via Risorgimento 35,
56100 Pisa, Italy

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