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Indenyl complexes of Group 8 metals

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Abstract

The present review article is concerned with the state of the art of the chemistry of indenyl Group 8 metal complexes which has undergone significant progress during the last decade. It deals mainly with complexes of the types: (a) bis(indenyl) sandwich compounds $[M(\eta^5\text{-}C_9H_{7-x}R_x)_2]$ (R = H, Me); (b) half-sandwich derivatives $[M(\eta^5\text{-}C_9H_{7-x}R_x)(CO)_2]_2$ and $[M(\eta^5\text{-}C_9H_{7-x}R_x)XL_2]$ (X = halides, H, alkyl, acetylide; L = two electron donor ligands); (c) cationic complexes $[M(\eta^5\text{-}C_9H_{7-x}R_x)L_2L']^+$ (L, L′ = two electron donor ligands). A detailed account of the synthesis, structural and reactivity aspects is presented including kinetic studies and catalytic processes. A discussion of the structural features and coordination modes of the indenyl group with special attention to its distortion parameters is presented. The reactivity studies include redox (chemical and electrochemical) processes, insertion reactions, ring transformations as well as ligand exchange processes in half-sandwich derivatives $[M(\eta^5\text{-}C_9H_{7-x}R_x)XL_2]$. In particular, a detailed discussion of the ability of the moiety $[M(\eta^5\text{-}C_9H_{7-x}R_x)L_2]$ to stabilize unsaturated carbene groups such as vinylidene (C=CR$_2$, allenylidene =C=C=CR$_2$ and α,β-unsaturated alkenyl carbene =C(H)C(R^1)=CRR′ complexes is presented. The influence of the indenyl ring on the regio- and stereoselective nucleophilic additions to these carbene groups allows selective synthesis leading to either allenyl or functionalized alkynyl complexes. A large number of the latter have been synthesized some of them showing excellent non-linear optical properties.

Keywords: Indenyl complexes; Iron, ruthenium and osmium complexes; Indenyl metal alkynyl complexes; Indenyl metal carbene complexes

1. Introduction

The indenyl anion $C_9H_7^-$ belongs to the series of six electron groups such as cyclopentadienyl, pentamethylcyclopentadienyl and tris–pyrazolylborate which form one of the most typical ligands in organometallic chemistry. In contrast to the extensively used cyclopentadienyl metal fragments $[M(\eta^5\text{-}C_5H_5)L_n]$, the analogous indenyl derivatives $[M(\eta^5\text{-}C_9H_7)L_n]$ have attracted comparatively less attention. However, the last decade has witnessed a rapid development in the chemistry of indenyl transition metal complexes mainly raised by the nowadays well known enhanced reactivity of these derivatives.

This typical behaviour was first described by Mawby and co-workers in studies on the kinetics and mechanisms of the methyl migration in $[Mo(\eta^5\text{-}C_9H_7)(Me)(CO)_3]$ [1a]. Similarly, CO substitution by phosphines in $[Mo(\eta^5\text{-}C_9H_7)X(CO)_3]$ (X = Cl, Br, I) [1b] and $[Fe(\eta^5\text{-}C_9H_7)I(CO)_2]$ [2] was found to proceed at a faster rate compared with the corresponding cyclopentadienyl analogues. More significantly, remarkable rate increasing effects of ca. 10^8 times were observed by Basolo and co-workers in the replacement reactions of CO of the indenyl complex $[Rh(\eta^5\text{-}C_9H_7)(CO)_2]$ with respect to the analogous cyclopentadienyl complex. This large rate enhancement is now widely referred to as the *indenyl effect*. Kinetic studies show that the processes proceed via an associative mechanism through the initial formation of an unsaturated η^3-indenyl complex to which the entering ligand is bonded. The driving force responsible for the higher reactivity of these processes has been explained on the basis of the special ability of the indenyl group to undergo a slippage from the η^5- to η^3-coordination which is favored by the generation of the aromaticity in the fused benzene ring [3].

The interest raised by the enhanced reactivity of transition metal indenyl complexes versus cyclopentadienyl derivatives has motivated the rapid development of both experimental and theoretic studies [4][1]. In particular, for most transition metals a wide number of half-sandwich type derivatives $[M(\eta^5\text{-}C_9H_7)]$ have been described. However, in spite of bis(indenyl) sandwich compounds $[Fe(\eta^5\text{-}C_9H_7)_2]$ [5] and $[Ru(\eta^5\text{-}C_9H_7)_2]$ [6] being synthesized soon after ferrocene [7] and ruthenocene [8] the chemistry of indenyl Group 8 metal complexes has remained less known [9] compared to that of the corresponding cyclopentadienyl complexes. This is especially remarkable in osmium for which the first derivatives $[Os(\eta^5\text{-}C_9H_7)_2]$ and $[Os(\eta^5\text{-}C_9H_7)\ X\ L_2]$ were prepared in 1996.

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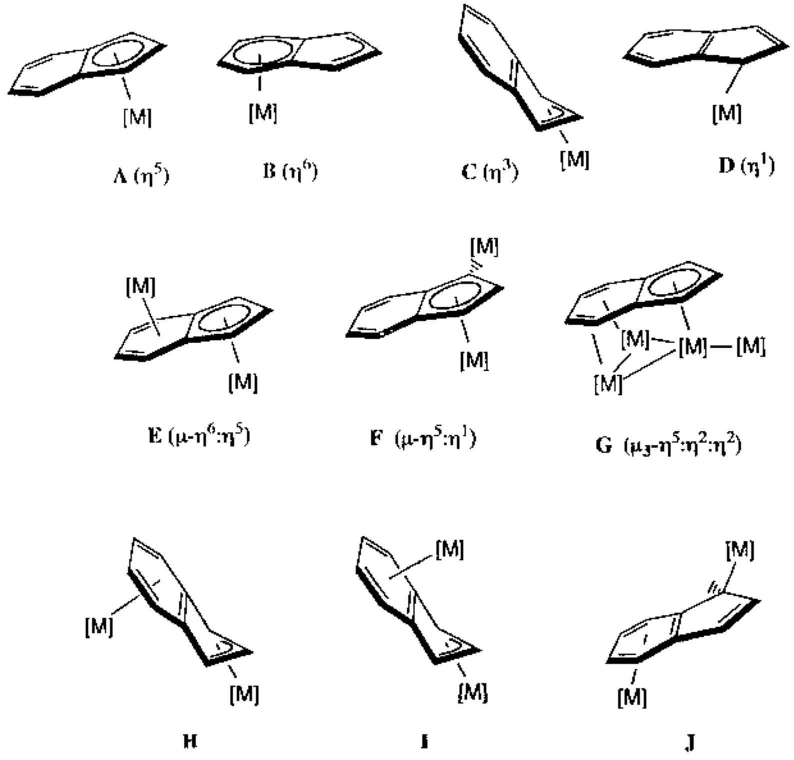
[1] Applications of indenyl transition metal complexes as efficient catalysts are known for a number of processes such as: (i) selective carbon–carbon coupling reactions; (ii) redox isomerization of allyl and propargyl alcohols; (iii) stereoselective polymerizations of olefins.

This review deals with indenyl Group 8 metal complexes including selected aspects of the synthetic, structural and reactivity studies. Coverage is mainly devoted to the discussion of the role played by the bonding modes of the indenyl ligand as well as to the influence of their electronic and/or steric properties on the reactivity of the complexes. Kinetic and mechanistic studies, which are of special importance for the rationalization of this reactivity, are also presented.

2. Coordination modes and structural studies

A comprehensive list of mono- and polynuclear indenyl complexes of iron, ruthenium and osmium (including also ring substituted complexes) is collected in Table 1. Literature has been reviewed up to 1998.

A total of at least ten coordination modes have been described for the C_9H_7 ligand (Chart I), although the types **H**, **I** and **J** are not known for Group 8 metals[2].



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[2] For examples of coordination modes H–J see Ref. [9j].

Table 1
Indenyl complexes of Group 8 metals

Compound	Ref.
η^5-Sandwich complexes	
$[Fe(\eta^5\text{-}C_9H_7)_2]^c$	[5b,d,10,11]
$[Fe(\eta^5\text{-}C_9H_7)(\eta^6\text{-}C_9H_8)][PF_6]$	[12,13]
$[Fe(\eta^5\text{-}C_9H_6Me)_2]$	[14]
$[Fe(\eta^5\text{-}C_9H_5Me_2)_2][PF_6]^c$	[15]
$[Fe(\eta^5\text{-}C_9Me_7)_2]^c$	[5d,16]
$[Fe(\eta^5\text{-}C_9Me_7)_2][PF_6]$	[17]
$[Fe(\eta^5\text{-}C_9HMe_6)_2]$	[18]
$[Fe\{(\eta^5\text{-}C_9Me_6)_2SiMe_2\}]^c$	[18]
$[Fe(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_5H_5)]$	[19,13]
$[Fe(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_5H_4Me)]$	[14]
$[Fe(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_5Me_5)]$	[20,21]
$[Fe(\eta^5\text{-}C_9H_6Me)(\eta^5\text{-}C_5H_5)]$	[14]
$[Fe(\eta^5\text{-}C_9H_7)H(Et_2C_2B_4H_4)]$	[22]
$[Fe(\eta^5\text{-}C_9H_7)(Et_2C_2B_4H_4)]$	[22]
$[Fe(\eta^5\text{-}C_9Me_7)_2][A]$ (A = TCNE, TCNQ^c, DDQ)	[23]
$[Fe(\eta^5{:}\eta^5\text{-}C_9H_6C_5H_4)]_2{}^c$	[24]
$[Fe(\eta^5\text{-}C_9H_7)(Et_2C_2B_4H_4)]_2$	[22]
$[Fe(\eta^5\text{-}C_9H_7)(Et_2C_2B_4H_4)Ni(Et_2MeC_3B_2Et_2)Co(\eta^5\text{-}C_5H_5]$	[22]
$[Ru(\eta^5\text{-}C_9H_7)_2]^c$	[6a,b,25,26,27]
$[Ru(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_5H_5)]$	[21]
$[Ru(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_5Me_5)]^c$	[27,28]
$[Ru(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_6H_7)]$	[29]
$[Ru(\eta^5\text{-}C_9H_7)(Me_3tacn)][PF_6]^c$ (Me_3tacn = 1,4,7-trimethyl-1,4,7-triazacyclononane)	[30]
$[Ru(\eta^5\text{-}C_9H_7)(\eta^6\text{-}C_6H_6)]^+$	[29,31]
$[\{Ru(\eta^5\text{-}C_9H_7)\}_2(\mu\text{-}\eta^5{:}\eta^5\text{-}C_6H_6C_6H_6)]$	[29]
$[Os(\eta^5\text{-}C_9H_7)_2]$	[32]
Iron mononuclear η^5 half-sandwich complexes	
$[Fe(\eta^5\text{-}C_9H_7)LL'X]$	
$[Fe(\eta^5\text{-}C_9H_7)Br(CO_2)]$	[33]
$[Fe(\eta^5\text{-}C_9H_7)I(CO_2)]$	[2,34]
$[Fe(\eta^5\text{-}C_9H_7)H(CO_2)]$	[35,36]
$[Fe(\eta^5\text{-}C_9H_7)(Me)(CO)_2]$	[37]
$[Fe(\eta^5\text{-}C_9H_6R)(Me)(CO)_2]$ (R = Me, ^{t}Bu)	[38]
$[Fe(\eta^5\text{-}C_9H_6R)(Me)(CO)\{Ph_2PN(Me)CH(Me)(Ph)\}]$ (R = Me, ^{t}Bu)	[38]
$[Fe(\eta^5\text{-}C_9H_6E)(Me)(CO)_2]$ (E = $SiMe_3$, Si_2Me_5, Si_3Me_7, Si_4Me_9, $Si(SiMe_3)_3$, Si_6Me_{11})	[39]
$[Fe(\eta^5\text{-}C_9H_7)(CHMe_2)(CO)_2]$	[40]
$[Fe(\eta^5\text{-}C_9H_7)(CH_2OMe)(CO)_2]$	[41]
$[Fe(\eta^5\text{-}C_9H_7)(CH_2Ph)(CO)_2]$	[42]
$[Fe(\eta^5\text{-}C_9H_7)\{CH_2N(OCC_6H_4CO)\}(CO)_2]$	[43]
$[Fe(\eta^5\text{-}C_9H_7)(CH_2SiMe_2SiMe_3)(CO)_2]$	[44]
$[Fe(\eta^5\text{-}C_9H_7)(CH_2SiMe_2SiMe_2SiMe_3)(CO)_2]$	[45]
$[Fe(\eta^5\text{-}C_9H_7)(R)(CO)_2]$ R = Et, C_3H_5, $CH_2C(Me){=}CH_2$	[46]
$[Fe(\eta^5\text{-}C_9H_7)(C_8H_4ClN_2)(CO)_2]^c$	[47]
$[Fe(\eta^5\text{-}C_9H_7)\{CH(Ph)OMe\}(CO)_2]$	[48]
$[Fe(\eta^5\text{-}C_9H_7)(CH_2OR)(CO)_2]$ (R = Me, Et)	[49]
$[Fe(\eta^5\text{-}C_9H_7)\{CH(OEt)Me\}(CO)_2]$	[49]

Table 1 (Continued)

Compound	Ref.
$[Fe(\eta^5-C_9H_7)(COMe)(CO)_2]$	[37]
$[Fe(\eta^5-C_9H_7)\{CH(OSiMe_3)R\}(CO)_2]$ ($R = Ph$, Me, C_6H_4OMe-4)	[50]
$[Fe(\eta^5-C_9H_7)\{COCH(R)OSiMe_3\}(CO)_2]$ ($R = Ph$, C_6H_4OMe-4)	[48]
$[Fe(\eta^5-C_9H_7)\{COCH(Ph)OMe\}(CO)_2]$	[48]
$[Fe(\eta^5-C_9H_7)(COCH_2OR)(CO)_2]$ ($R = Me$, Et)	[49]
$[Fe(\eta^5-C_9H_7)\{COCH(OEt)Me\}(CO)_2]$	[49]
$[Fe(\eta^5-C_9H_7)(E)(CO)_2]$ ($E = SiMe_3{}^c$, $Si_2Me_5{}^c$, $SiMe(SiMe_3)_2{}^c$)	[51]
$[Fe(\eta^5-C_9H_7)(SiMe_2CH_2SiMe_3)(CO)_2]$	[44]
$[Fe(\eta^5-C_9H_7)(SiMe_2CH_2SiMe_2SiMe_3)(CO)_2]$	[45]
$[Fe(\eta^5-C_9H_7)(E)(CO)_2]$ ($E = SiMe_3$, Si_2Me_5, Si_3Me_7, $SiMe_2(SiMe_2)_2SiMe_3SiMe(SiMe_3)_2$, $Si(SiMe_3)_3$, Si_6Me_{11})	[39]
$[Fe(\eta^5-C_9H_7)(E)(CO)_2]$ ($E = SiPh_3$, $SiMe_2Ph$, $SiMePh_2$, $SiPh_2SiMe_2PhSiMePhSiMePh_2$, $SiMe_2SiPh_3$)	[52]
$[Fe(\eta^5-C_9H_7)(SiMe_2CH_2SiMe_2SiMe_3)(CO)_2]$	[45]
$[Fe(\eta^5-C_9H_7)\{S(O)_2CH_2C_6H_5\}(CO)_2]$	[42]
$[Fe(\eta^5-C_9H_7)(SnX_3)(CO)_2]$ ($X = Cl$, Br, I)	[34]
$[Fe(\eta^5-C_9H_7)$ $(SnR_3)(CO)_2]$ ($R = Ph$, Me)	[53]
$[Fe\{\eta^5-C_9H_6E\}(SnPh_3)(CO)_2]$ ($E = SiMe_3$, Si_2Me_5, $SiMe(SiMe_3)_2$)	[39]
$[Fe\{\eta^5-C_9H_5(SiMe_3)(SnPh_3)\}(E)(CO)_2]$ ($E = Me$, $SnPh_3$)	[39]
$[Fe(\eta^5-C_9H_7)I(CO)(PR_3)]$ ($R = Ph$, CH_2Ph)	[55]
$[Fe(\eta^5-C_9H_7)I(CO)(L)]$ ($L = PMe_2Ph$, $PMePh_2$)	[55]
$[Fe(\eta^5-C_9H_7)I(CO)\{P(OR)_3\}]$ ($R = Me$, ${}^iPr$, C_6H_4Me-2)	[55]
$[Fe(\eta^5-C_9H_7)I(CO)\{P(OR)_3\}]$ ($R = Et$, Ph)	[2,55]
$[Fe(\eta^5-C_9H_7)I(CO)(L)]$ ($L = P(OMe)Ph_2$, $P(OMe)_2Ph$)	[55]
$[Fe(\eta^5-C_9H_7)(Me)(CO)(PPh_3)]$	[37]
$[Fe(\eta^5-C_9H_7)(CH_2OMe)(CO)(PPh_3)]$	[56]
$[Fe(\eta^5-C_9H_7)\{\kappa^2-(C,O)-C(Me)=C(Me)COMe\}(CO)]$	[57]
$[Fe(\eta^5-C_9H_7)\{\kappa^2-(C,O)-CH=C({}^tBu)COMe\}(CO)]$	[57]
$[Fe(\eta^5-C_9H_7)(Me)(CO)\{Ph_2PN(Me)CH(Me)Ph\}]^c$	[58a]
$[Fe(\eta^5-C_9H_7)(COR)(CO)\{Ph_2PN(Me)CH(Me)Ph\}]$ ($R = Me$, Et, $CHMe_2$, CH_2Ph)	[58b]
$[Fe(\eta^5-C_9H_7)(COCH_2SiMe_2SiMe_2SiMe_3)(CO)(PPh_3)]$	[45]
$[Fe(\eta^5-C_9H_7)(COMe)(CO)(PPh_3)]^c$	[37,43,56]
$[Fe(\eta^5-C_9H_7)(COR)(CO)(PPh_3)]$ ($R = Et$, ${}^nPr$)	[43]
$[Fe(\eta^5-C_9H_7)(COR)(CO)(PPh_3)]$ ($R = CH(Me)Et$, CH_2OMe, $CH_2CH(OH)Me$)	[43]
$[Fe(\eta^5-C_9H_7)(COCHMe_2)(CO)(PR_3)]$ ($R = Me$, ${}^nBu$, Ph^c, Cy, C_6H_4Me-3, C_6H_4Me-4,C_6H_4OMe-4, $C_6H_4NMe_2$-4, $C_6H_4CF_3$-4, C_6H_4Cl-4, C_6H_4F-4)	[40]
$[Fe(\eta^5-C_9H_7)(COMe)(CO)(PMe_3)]$	[59]
$[Fe(\eta^5-C_9H_7)(COMe)(CO)(PR_3)]$ ($R = Cy$, C_6H_4Me-3, C_6H_4Me-4, C_6H_4OMe-4, $C_6H_4NMe_2$-4,$C_6H_4CF_3$-4, C_6H_4Cl-4, C_6H_4F-4)	[40]
$[Fe(\eta^5-C_9H_7)(COCHMe_2)(CO)(PR_2Ph)]$ ($R = Me$, Et)	[40]
$[Fe(\eta^5-C_9H_7)(COCHMe_2)(CO)(PPh_2R)]$ ($R = Me$, Bz)	[40]
$[Fe(\eta^5-C_9H_7)(COMe)(CO)(PMe_2Ph)]$	[59]
$[Fe(\eta^5-C_9H_7)(COMe)(CO)(PEt_2Ph)]$	[40]
$[Fe(\eta^5-C_9H_7)(COMe)(CO)(PMePh_2)]$	[59]
$[Fe(\eta^5-C_9H_7)(COMe)(CO)(PPh_2Bz)]$	[40]
$[Fe(\eta^5-C_9H_7)(COMe)(CO)\{P(OR)_3\}]$ ($R = Et$, Ph)	[40]
$[Fe(\eta^5-C_9H_7)(COCHMe_2)(CO)\{P(OR)_3\}]$ ($R = Et$, ${}^nBu$, Ph)	[40]
$[Fe(\eta^5-C_9H_7)(COCHMe_2)(CO)\{P(OCH_2)_3CEt\}]$	[40]
$[Fe(\eta^5-C_9H_7)(COCH_2SiMe_2SiMe_2SiMe_3)(CO)(PPh_3)]$	[45]
$[Fe(\eta^5-C_9H_7)(SiMe_2CH_2SiMe_2SiMe_3)(CO)(PPh_3)]$	[45]

Table 1 (Continued)

Compound	Ref.
[Fe(η^5-C_9H_7)(E)(CO)(PPh_3)] (E = $SiMe_3$[c], Si_2Me_5[c], $SiMe(SiMe_3)_2$[c])	[51]
[Fe(η^5-C_9H_7)(SnR_3)(CO)(olefin)] (R = Ph, Me; olefin = C_2H_4, C_3H_6)	[53]
[Fe(η^5-C_9H_7)(CO_2SnPPh_3)(CO)(PPh_3)][c]	[54]
[Fe(η^5-C_9H_7)(η^3-C_3H_5)(CO)]	[60]
[Fe(η^5-C_9H_7)Br{κ^2-(*P*,*P*)-dppe}]	[a]
[Fe(η^5-C_9H_7)LL′L″]$^+$	
[Fe(η^5-C_9H_7)$(CO)_3$][X] X = BF_4, PF_6[c]	[33,61]
[Fe(η^5-C_9H_7)(olefin)$(CO)_2$][BF_4] (olefin = C_2H_4, C_3H_6, $(Me)_2C{=}CH_2$, $^iC_4H_8$)	[46]
[Fe(η^5-C_9H_7)$(CO)_2${=C(OEt)Me}][PF_6]	[49]
[Fe(η^5-C_9H_7)$(CO)_2$(RCN)][BF_4] (R = Me, Ph)	[33]
[Fe(η^5-C_9H_7)$(CO)_2$(C_5H_5N)][BF_4]	[33]
[Fe(η^5-C_9H_7)$(CO)_2$(PR_3)][BF_4] (R = Me, Ph)	[62]
[Fe(η^5-C_9H_7)$(CO)_2$(PR_3)][BF_4] (R = ^{i}Pr, $C_6H_4CH_3$-4, $C_6H_4OCH_3$-2, C_6H_4Cl-3)	[33,62]
[Fe(η^5-C_9H_7)$(CO)_2$(PPh_2Me)][BF_4]	[62]
[Fe(η^5-C_9H_7)$(CO)_2${$P(C_2H_4CN)_3$}][BF_4]	[61]
[Fe(η^5-C_9H_7)$(CO)_2${$P(^nBu)_3$}][BF_4]	[33]
[Fe(η^5-C_9H_7)$(CO)_2$(κ-*P*-diphos)][BF_4]	[61]
[Fe(η^5-C_9H_7)$(CO)_2${κ-*P*-$Ph_2P(CH_2)_nPPh_2$}][BF_4] (n = 1, 2, 4, 6, 8)	[62]
[Fe(η^5-C_9H_7)$(CO)_2${κ-(*As*)-$Me_2As(CH_2)_5AsMe_2$}][BF_4]	[62]
[Fe(η^5-C_9H_7)$(CO)_2${{κ-(*As*)-$Ph_2As(CH_2)_2AsPh_2$}][BF_4]	[62]
[Fe(η^5-C_9H_7)$(CO)_2${$P(OR)_3$}][BF_4] (R = Me, Et, Ph)	[33]
[Fe(η^5-C_9H_7)$(CO)_2$($SbPh_3$)][BF_4]	[62]
[Fe(η^5-C_9H_7)$(CO)_2$($AsPh_3$)][BF_4]	[61]
[Fe(η^5-C_9H_7)(CO){κ^2-(*P*,*P*)-$Ph_2P(CH_2)_nPPh_2$}][BF_4] (*n* = 1[c], 2, 4, 6, 8)	[62]
[Fe(η^5-C_9H_7)(CO){κ^2-(*As*,*As*)-$Ph_2As(CH_2)_2AsPh_2$}][BF_4]	[62]
[Fe(η^5-C_9H_7)(CO){κ^2-(*As*,*As*)-$Me_2As(CH_2)_5AsMe_2$}][BF_4]	[62]
[Fe(η^5-C_9H_7)($C{=}C{=}CPh_2$){κ^2-(*P*,*P*)-dppe}][BF_4]	[a]
Iron di and polynuclear complexes	
[Fe(η^5-C_9H_7)(CO_2)]$_2$	[2,43,63]
[Fe_2{(η^5-C_9H_6)$_2$E}$(CO)_2$(μ-CO)$_2$] (E = Me_2Si[c], $Me_2SiOSiMe_2$)	[64]
[Fe_2{(η^5-C_9H_6)$_2$$Me_2SiSiMe_2$}$(CO)_2$($\mu$-CO)$_2$][c]	[65]
[Fe_2{μ-η^5:η^1-κ^2-(*C*,*Si*)-$C_9H_6SiMe_2$}$_2$$(CO)_4$][c]	[65]
[Fe(η^5-C_9H_7)(CO)(μ-CO)(μ-CH_2)Fe(η^5-C_5H_5)(CO)]	[41]
[PPN][Fe(η^5-C_9H_7)(COMe)(μ-CO)$_2$Fe(η^5-C_9H_7)(CO)]	[41]
[Na][Fe(η^5-C_9H_7)(COR)(μ-CO)$_2$Fe(η^5-C_5H_5)(CO)] (R = Me, CH_2OMe)	[41]
[PPN][Fe(η^5-C_5H_5)(COMe)(μ-CO)$_2$Fe(η^5-C_9H_7)(CO)][c]	[41]
Na[Fe(η^5-C_9H_7)(CO)(μ-CO)$_2$Fe(η^5-C_9H_7)($COCH_2OR$)] (R = Me, Et)	[49]
Na[Fe(η^5-C_9H_7)(CO)(μ-CO)$_2$Fe(η^5-C_9H_7){COCH(OEt)Me}]	[49]
[{Fe(η^5-C_9H_7)$(CO)_2$}$_2$(SnX_2)] (X = Cl, Br, I)	[34]
[Fe(η^5-C_9H_7)(CO)(μ-CO)$_2$Co$(CO)_3$][c]	[66,67]
[Fe(η^5-C_9H_7)$(CO)_2$Re$(CO)_5$]	[68]
[Fe(η^5-C_9H_7)$(CO)_2$Re$(CO)_{5-x}(CNR)_x$)] (x = 1, 2, 3; R = ^{t}Bu, $C_6H_3Me_2$-2,6)	[68]
[Fe(η^5-C_9H_7)$(CO)_2$(μ-η^1:η^6-Ph)Cr$(CO)_3$][c]	[69]
[Fe(η^5-C_9H_7)($Et_2C_2B_4H_4$)Ni(η^5-C_5Me_5)][c]	[22]
[Fe(η^5-C_9H_7){$C{\equiv}CC_4H_2SC{\equiv}C$-Mo($\eta^5$-$C_5H_5$)$(CO)_3$}$(CO)_2$]	[70]
[{Fe(η^5-C_9H_7)$(CO)_2$}{Fe(η^5-C_5H_5)$(CO)_2$}(SnX_2)] (X = Cl, Br, I)	[34]
[{Fe(η^5-C_9H_7)$(CO)_2$}$_3$(SnX)] X = F, Br	[34]
[{Fe(η^5-C_9H_7)$(CO)_2$}$_2$$\mu$-{$Ph_2P(CH_2)_nPPh_2$}][$BF_4$]$_2$ (*n* = 1, 2, 4, 6, 8)	[62]
[{Fe(η^5-C_9H_7)$(CO)_2$}$_2$$\mu$-{$Me_2As(CH_2)_5AsMe_2$}][$BF_4$]$_2$	[62]

Table 1 (Continued)

Compound	Ref.
$[\{Fe(\eta^5\text{-}C_9H_7)(CO)_2\}_2\mu\text{-}\{Ph_2As(CH_2)_2AsPh_2\}][BF_4]_2$	[62]
$[Fe(\eta^5\text{-}C_9H_7)(Et_2C_2B_4H_4)Ni(Et_2MeC_3B_2Et_2)Co(\eta^5\text{-}C_5H_5)]$	[22]
Ruthenium mononuclear η^5 *half-sandwich complexes*	
$[Ru(\eta^5\text{-}C_9H_7)LL'X]$	
$[Ru(\eta^5\text{-}C_9H_7)I(CO)_2]$	[71]
$[Ru(\eta^5\text{-}C_9H_7)(EMe_3)(CO)_2]$ (E = Si, Ge)	[72]
$[Ru(\eta^5\text{-}C_9H_7)I(CO)(PR_3)]$ (R = Ph, CH_2Ph[c])	[71]
$[Ru(\eta^5\text{-}C_9H_7)I(CO)(PR_3)]$ (R = ^{i}Pr, Cy[c])	[a]
$[Ru(\eta^5\text{-}C_9H_7)I(CO)(PMePh_2)]$	[71]
$[Ru(\eta^5\text{-}C_9H_7)I(CO)\{P(OR)_3\}]$ (R = Me, Et, ^{i}Pr, C_6H_4Me-2)	[71]
$[Ru\ (\eta^5\text{-}C_9H_4Me_3)Br(CO)(PR_3)]$ (R = Ph, ^{i}Pr, Cy)	[a]
$[Ru(\eta^5\text{-}C_9H_4Me_3)I(CO)(PR_3)]$ (R = Ph, ^{i}Pr, Cy)	[a]
$[Ru\ (\eta^5\text{-}C_9Me_7)Br(CO)(PR_3)]$ (R = Ph, ^{i}Pr, Cy)	[a]
$[Ru(\eta^5\text{-}C_9Me_7)I(CO)(PR_3)]$ (R = Ph, ^{i}Pr, Cy)	[a]
$[Ru(\eta^5\text{-}C_9H_4Me_3)H(CO)(PR_3)]$ (R = Ph, ^{i}Pr)	[75]
$[Ru(\eta^5\text{-}C_9H_4Me_3)(Me)(CO)(PPh_3)]$	[a]
$[Ru(\eta^5\text{-}C_9H_4Me_3)(C{\equiv}CPh)(CO)(PPh_3)]$	[73]
$[Ru(\eta^5\text{-}C_9H_7)(\eta^3\text{-}C_3H_5)(CO)]$	[60,74]
$[Ru(\eta^5\text{-}C_9H_7)(C{\equiv}CCPh_2OMe)(CO)(P^iPr_3)]$	[a]
$[Ru(\eta^5\text{-}C_9H_4Me_3)(C{\equiv}CCPh_2OMe)(CO)(PPh_3)]$	[73]
$[Ru(\eta^5\text{-}C_9H_7)(C{\equiv}CCPh_2C{\equiv}CPh)(CO)(P^iPr_3)]$	[a]
$[Ru(\eta^5\text{-}C_9H_4Me_3)(C{\equiv}CCPh_2C{\equiv}CH)(CO)(PPh_3)]$	[73]
$[Ru(\eta^5\text{-}C_9H_7)(C{\equiv}CCPh_2R)(CO)(P^iPr_3)]$ (R = C_3H_7N, $C_8H_{10}N$)	[a]
$[Ru(\eta^5\text{-}C_9H_4Me_3)(C{\equiv}CCPh_2R)(CO)(PPh_3)]$ (R = C_3H_7N, $C_8H_{10}N$)	[a]
$[Ru(\eta^5\text{-}C_9H_4Me_3)\{(E)\text{-}C(CO_2Me){=}CH(CO_2Me)\}(CO)(PR_3)]$ (R = Ph, ^{i}Pr)	[75]
$[Ru(\eta^5\text{-}C_9H_7)Cl(COD)]$	[76]
$[Ru(\eta^5\text{-}C_9H_7)X(PPh_3)_2]$ (X = Cl, I)	[77]
$[Ru(\eta^5\text{-}C_9H_7)Cl(PPh_3)(L)]$ (L = $PMePh_2$, PMe_2Ph, PMe_3)	[78]
$[Ru(\eta^5\text{-}C_9H_7)Cl(PPh_3)\{\kappa^1\text{-}(P)\text{-}Ph_2PCH_2C(O)^tBu\}]$	[79]
$[Ru(\eta^5\text{-}C_9H_7)(PPh_3)\{\kappa^2\text{-}(P,O)\text{-}Ph_2PCHC(O)^tBu\}]$	[79]
$[Ru(\eta^5\text{-}C_9H_7)Cl(L)_2]$ ($L_2 = (PMePh_2)_2$, $(PMe_2Ph)_2$, dppm)	[78]
$[Ru(\eta^5\text{-}C_9H_7)Cl\{\kappa^2\text{-}(P,P)\text{-}dppe\}]$	[77]
$[Ru(\eta^5\text{-}C_9H_7)Cl\{(S,S)\text{-}\kappa^2\text{-}(P,P)\text{-}Ph_2PCH(Me)CH(Me)PPh_2\}]$[c]	[76]
$[Ru(\eta^5\text{-}C_9H_7)Cl\{(R,R)\text{-}\kappa^2\text{-}(P,P)\text{-}Ph_2P\overline{CH(CH_2)_3C}HPPh_2\}]$	[76]
$[Ru(\eta^5\text{-}C_9H_4Me_3)Br\{\kappa^2\text{-}(P,P)\text{-}dppm\}]$	[a]
$[Ru(\eta^5\text{-}C_9H_7)H(PPh_3)_2]$[c]	[77]
$[Ru(\eta^5\text{-}C_9H_7)H(PMe_2Ph)_2]$	[75]
$[Ru(\eta^5\text{-}C_9H_7)H(PPh_3)(PMe_2R)]$ (R = Me, Ph)	[75]
$[Ru(\eta^5\text{-}C_9H_7)H\{Ph_2P(CH_2)_nPPh_2\}]$ (n = 1, 2)	[75]
$[Ru(\eta^5\text{-}C_9H_7)(Me)(PPh_3)_2]$	[77]
$[Ru(\eta^5\text{-}C_9H_7)(CN)(PPh_3)_2]$	[80]
$[Ru(\eta^5\text{-}C_9H_7)(C{\equiv}CPh)(PPh_3)_2]$	[77]
$[Ru(\eta^5\text{-}C_9H_7)(C{\equiv}CPh)\{Ph_2P(CH_2)_nPPh_2\}]$ (n = 1, 2[c], 3,4)	[81,82]
$[Ru(\eta^5\text{-}C_9H_7)(C{\equiv}CR)(PPh_3)_2]$ (R = ^{t}Bu, ^{n}Pr, H)	[82]
$[Ru(\eta^5\text{-}C_9H_7)(C{\equiv}CR)\{\kappa^2\text{-}(P,P)\text{-}dppe\}]$ (R = ^{t}Bu, ^{n}Pr, H)	[82]
$[Ru(\eta^5\text{-}C_9H_7)(C{\equiv}CH)(PPh_3)(PMe_3)]$	[83]
$[Ru(\eta^5\text{-}C_9H_7)(C{\equiv}CR)(PPh_3)_2]$ (R = ^{n}Bu, Bz, Cy)	[81]
$[Ru(\eta^5\text{-}C_9H_7)\{C{\equiv}C\overline{C{=}CH(CH_2)_nC}H_2\}(PPh_3)_2]$ (n = 2,3,4)	[84]
$[Ru(\eta^5\text{-}C_9H_7)\{C{\equiv}C\overline{C{=}CH(CH_2)_nC}H_2\}\{\kappa^2\text{-}(P,P)\text{-}dppe\}]$ (n = 2,3,4)	[84]

Table 1 (Continued)

Compound	Ref.
$[Ru(\eta^5\text{-}C_9H_7)\{C\equiv CC(Ph)_2C\equiv CR\}(PPh_3)_2]$ (R = Ph, ^{n}Pr)	[85]
$[Ru(\eta^5\text{-}C_9H_7)\{C\equiv CC(Ph)_2C\equiv CH\}(PPh_3)_2]$[c]	[86]
$[Ru(\eta^5\text{-}C_9H_7)\{C\equiv CC(R)Ph_2\}(PPh_3)_2]$ (R = Me, ^{n}Bu)	[86]
$[Ru(\eta^5\text{-}C_9H_7)\{C\equiv CC(R)Ph_2\}(dppe)]$ (R = Me, ^{n}Bu)	[86]
$[Ru(\eta^5\text{-}C_9H_7)\{C\equiv CCH(OMe)Ph\}(PPh_3)_2]$	[87]
$[Ru(\eta^5\text{-}C_9H_7)\{C\equiv CC(Ph)_2OMe\}(PPh_3)_2]$	[85]
$[Ru(\eta^5\text{-}C_9H_7)\{C\equiv CC(Ph)_2OMe\}\{Ph_2P(CH_2)_nPPh_2\}]$ (n = 1,2)	[85]
$[Ru(\eta^5\text{-}C_9H_7)\{C\equiv CC(OMe)Ph_2\}(PPh_3)\{\kappa\text{-}P\text{-}Ph_2PCH_2C(O)^tBu\}]$	[79]
$[Ru(\eta^5\text{-}C_9H_7)\{C\equiv CCH=CH(C\equiv CPh)\}(PPh_3)_2]$	[88]
$[Ru(\eta^5\text{-}C_9H_7)\{C\equiv CCPh_2(C_{10}H_9O)\}(PPh_3)_2]$	[88]
$[Ru(\eta^5\text{-}C_9H_7)\{C\equiv CCPh_2(C_{10}H_{11}O)\}(PPh_3)_2]$	[88]
$[Ru(\eta^5\text{-}C_9H_7)\{C\equiv CCH=CH(C_{16}H_{15}O)\}(PPh_3)_2]$	[88]
$[Ru(\eta^5\text{-}C_9H_7)(C\equiv CC_6H_4NO_2)(PPh_3)_2]$	[80]
$[Ru(\eta^5\text{-}C_9H_7)(C\equiv CCH=CHC_5H_4N)(PPh_3)_2]$	[80]
$[Ru(\eta^5\text{-}C_9H_7)\{C\equiv CCH=C(C_6H_4NO_2)_2\}(PPh_3)_2]$[c]	[80]
$[Ru(\eta^5\text{-}C_9H_7)(C\equiv CCH=CHC_6H_4A)(PPh_3)_2]$ (A = NO_2, CN)	[80]
$[Ru(\eta^5\text{-}C_9H_7)(C\equiv CCH=CHCH=CHC_6H_4NO_2)(PPh_3)_2]$	[80]
$[Ru(\eta^5\text{-}C_9H_7)\{C\equiv CC(Ph)=CH_2\}(PPh_3)_2]$	[87]
$[Ru(\eta^5\text{-}C_9H_7)\{C\equiv CC(Ph)=CH_2\}\{\kappa^2\text{-}(P,P)\text{-}Ph_2P(CH_2)_nPPh_2\}]$ (n = 1,2)	[87]
$[Ru(\eta^5\text{-}C_9H_7)(C\equiv CCPh=CR_2)(PPh_3)_2]$ (R_2 = Ph_2, C_6H_{10})	[89]
$[Ru(\eta^5\text{-}C_9H_7)(C\equiv CCPh=CHMe)(PPh_3)_2]$	[89]
$[Ru(\eta^5\text{-}C_9H_7)(C\equiv CCPh=C=NPh)(PPh_3)_2]$	[89]
$[Ru(\eta^5\text{-}C_9H_7)\{C\equiv CCPh_2CH_2C(O)R\}(PPh_3)_2]$ (R = Ph, ^{i}Pr, CH=CHPh)	[b]
$[Ru(\eta^5\text{-}C_9H_7)(C\equiv CCPh_2C_{10}H_{13}O)(PPh_3)_2]$[c]	[b]
$[Ru(\eta^5\text{-}C_9H_7)(C\equiv CCPh_2C_{10}H_{15}O)(PPh_3)_2]$	[b]
$[Ru(\eta^5\text{-}C_9H_7)\{C\equiv CCPhHCH_2C(O)R\}(PPh_3)_2]$ (R = Ph, ^{i}Pr)	[b]
$[Ru(\eta^5\text{-}C_9H_7)(C\equiv CI)(PPh_3)_2]$	[83]
$[Ru(\eta^5\text{-}C_9H_7)(C\equiv CI)\{\kappa^2\text{-}(P,P)\text{-}dppe\}]$	[83]
$[Ru(\eta^5\text{-}C_9H_7)\{C\equiv CC[S(C_6H_4Me\text{-}2)]Ph_2\}(PPh_3)_2]$	[86]
$[Ru(\eta^5\text{-}C_9H_7)\{C[S(C_6H_4Me\text{-}2)]=C=CPh_2\}\{\kappa^2\text{-}(P,P)\text{-}dppm\}]$	[86]
$[Ru(\eta^5\text{-}C_9H_7)(C\equiv CSnPh_3)(PPh_3)(PR_3)]$ (R = Ph, Me)	[83]
$[Ru(\eta^5\text{-}C_9H_7)(C\equiv CSnPh_3)(\kappa\text{-}P\text{-}dppe)]$	[83]
$[\overline{Ru(\eta^5\text{-}C_9H_7)(PPh_3)\{\kappa^2\text{-}(C,P)\text{-}C(=C=CPh_2)CHC(O)^tBu\}P}Ph_2]$[c]	[79]
$[Ru(\eta^5\text{-}C_9H_7)\{(E)\text{-}C(CO_2Me)=CH(R)\}(PPh_3)(PMe_3)]$ (R = H, CO_2Me)	[75]
$[Ru(\eta^5\text{-}C_9H_7)\{(E)\text{-}C(CO_2Me)=CH(R)\}(PMe_2Ph)_2]$ (R = H, CO_2Me)	[75]
$[Ru(\eta^5\text{-}C_9H_7)\{(E)\text{-}C(CO_2Me)=CH(CO_2Me)\}(PPh_3)(PMe_2Ph)]$	[75]
$[Ru(\eta^5\text{-}C_9H_7)\{(E)\text{-}C(CO_2Me)=CH(R)\}\{\kappa^2\text{-}(P,P)\text{-}dppm\}]$ (R = H, CO_2Me)	[75]
$[Ru(\eta^5\text{-}C_9H_7)\{(E)\text{-}C(CO_2Me)=CH(R)\}\{\kappa^2\text{-}(P,P)\text{-}dppe\}]$ (R = H, CO_2Me)	[75]
$[Ru(\eta^5\text{-}C_9H_7)\{(E)\text{-}CH=CHPh\}\{\kappa^2\text{-}(P,P)\text{-}dppm\}]$	[75]
$[Ru(\eta^5\text{-}C_9H_7)\{(E)\text{-}CH=CHCR=CH_2\}\{\kappa^2\text{-}(P,P)\text{-}dppm\}]$ (R = H, Me)	[90]
$[Ru(\eta^5\text{-}C_9H_7)\{(E)\text{-}CH=CH\overline{C=CHCH_2(CH_2)_nC}H_2\}\{\kappa^2\text{-}(P,P)\text{-}dppm\}]$ (n = 1,2,3)	[90]
$[Ru(\eta^5\text{-}C_9H_7)\{(E)\text{-}CH=CHCH_2OH\}\{\kappa^2\text{-}(P,P)\text{-}dppm\}]$	[90]
$[\overline{Ru(\eta^5\text{-}C_9H_7)\{Ph_2PCHC}(=C=CPh_2)PPh_2\}]$	[86]
$[Ru(\eta^5\text{-}C_9H_7)(SR)(PPh_3)_2]$ (R = Et, ^{i}Pr, CH_2Ph, C_6H_4Me-4)	[91]
$[Ru(\eta^5\text{-}C_9H_7)(SnCl_3)(PPh_3)_2]$	[77]
$[Ru(\eta^5\text{-}C_9H_7)LL'L'']^+$	
$[Ru(\eta^5\text{-}C_9H_4Me_3)(MeCN)(CO)(PPh_3)][BF_4]$	[a]
$[Ru(\eta^5\text{-}C_9H_7)\{C\equiv CC(Ph)_2(PMe_3)\}(CO)(P^iPr_3)][BF_4]$	[a]

Table 1 (Continued)

Compound	Ref.
[Ru(η^5-C$_9$H$_4$Me$_3$){C≡CC(Ph)$_2$(PMe$_3$)}(CO)(PR$_3$)][BF$_4$] (R = Ph, ^{i}Pr)	[a]
[Ru(η^5-C$_9$H$_4$Me$_3$){C≡CCPh(H)(PPh$_3$)}(CO)(PPh$_3$)][BF$_4$]	[a]
[Ru(η^5-C$_9$H$_4$Me$_3$){C(O)CH=CPh$_2$}(CO)(PPh$_3$)][BF$_4$]	[a]
[Ru(η^5-C$_9$H$_7$){CH=C(R)(PPh$_3$)}(CO)(P^{i}Pr$_3$)][BF$_4$] (R = Ph, (CH$_2$)$_2$Me, C$_8$H$_{13}$)	[a]
[Ru(η^5-C$_9$H$_4$Me$_3$){CH=CR(PPh$_3$)}(CO)(PPh$_3$)][BF$_4$] (R = Ph, (CH$_2$)$_2$Me, C$_8$H$_{13}$)	[a]
[Ru(η^5-C$_9$H$_4$Me$_3$){CH=CPh(PPh$_3$)}(CO)(PR$_3$)][BF$_4$] (R = Ph, ^{i}Pr)	[a]
[Ru(η^5-C$_9$H$_4$Me$_3$){C(PMe$_3$)C=CPh$_2$}(CO)(PPh$_3$)][BF$_4$]	[a]
[Ru(η^5-C$_9$H$_4$Me$_3$){=C(OMe)CH=CPh$_2$}(CO)(PR$_3$)][BF$_4$] (R = Ph, Cy, ^{i}Pr)	[a]
[Ru(η^5-C$_9$H$_4$Me$_3$){=C(OEt)CH=CPh$_2$}(CO)(PR$_3$)][BF$_4$] (R = Ph[c], ^{i}Pr)	[a]
[Ru(η^5-C$_9$H$_4$Me$_3$){=C(CH$_2$)$_3$O}(CO)(PPh$_3$)][BF$_4$]	[a]
[Ru(η^5-C$_9$H$_7$)(=C=C=CPh$_2$)(CO)(P^{i}Pr$_3$)][BF$_4$]	[a]
[Ru(η^5-C$_9$H$_4$Me$_3$)(=C=C=CPh$_2$)(CO)(PR$_3$)][BF$_4$] (R = Ph[c], ^{i}Pr, Cy)	[73]
[Ru(η^5-C$_9$H$_4$Me$_3$){=C(OR)CH=CPh$_2$}(CO)(PPh$_3$)][BF$_4$] (R = Me, Et)	[73]
[Ru(η^5-C$_9$H$_7$)(CO)(PPh$_3$)$_2$][ClO$_4$][c]	[77]
[Ru(η^5-C$_9$H$_7$)(CO){(*S*,*S*)-κ^2-(*P*,*P*)-Ph$_2$PCH(Me)CH(Me)PPh$_2$}]Cl	[76]
[Ru(η^5-C$_9$H$_7$)(CO){(*R*,*R*)-κ^2-(*P*,*P*)-Ph$_2$P$\overline{\mathrm{CH(CH_2)_3C}}$HPPh$_2$}]Cl	[76]
[Ru(η^5-C$_9$H$_7$)(PPh$_3$){-κ^2-(*P*,*P*)-dppm}]Cl	[78]
[Ru(η^5-C$_9$H$_7$)(PMe$_3$)$_3$]Cl	[78]
[Ru(η^5-C$_9$H$_7$){(*R*,*R*)-κ^2-(*P*,*P*)-Ph$_2$P$\overline{\mathrm{CH(CH_2)_3C}}$HPPh$_2$}(PMe$_2$Ph)]Cl	[76]
[Ru(η^5-C$_9$H$_7$){(*S*,*S*)-κ^2-(*P*,*P*)-Ph$_2$PCH(CH$_3$)CH(CH$_3$)PPh$_2$}(PMe$_2$Ph)]Cl	[76]
[Ru(η^5-C$_9$H$_7$)(H)$_2$(PPh$_3$)$_2$][BF$_4$][c]	[a]
[Ru(η^5-C$_9$H$_7$){(*S*,*S*)-κ^2-(*P*,*P*)-Ph$_2$PCH(Me)CH(Me)PPh$_2$}(MeCN)]Cl	[76]
[Ru(η^5-C$_9$H$_7$){(*S*,*S*)-κ^2-(*P*,*P*)-Ph$_2$PCH(Me)CH(Me)PPh$_2$}(κ-*P*-dppe)][PF$_6$]	[76]
[Ru(η^5-C$_9$H$_7$)(PPh$_3$){κ^2-(*P*,*O*)-Ph$_2$PCH$_2$C(O)R}][PF$_6$] (R = Ph, ^{t}Bu)	[79]
[Ru(η^5-C$_9$H$_7$)(PPh$_3$){κ^2-(*P*,*O*)-Ph$_2$PCH(Me)C(O)^{t}Bu}][PF$_6$][c]	[79]
[Ru(η^5-C$_9$H$_7$)(η^2-C$_2$H$_4$)(PPh$_3$)$_2$][ClO$_4$]	[77]
[Ru(η^5-C$_9$H$_7$)(RCN)(PPh$_3$)$_2$][ClO$_4$] (R = Me, C$_6$H$_4$Cl-2, CH$_2$=CH)	[77]
[Ru(η^5-C$_9$H$_7$){R(CN)$_2$}(PPh$_3$)$_2$][ClO$_4$] (R = C$_6$H$_4$-1,2, C$_2$H$_4$)	[77]
[Ru(η^5-C$_9$H$_7$)(N$_2$H$_4$)(PPh$_3$)$_2$][ClO$_4$]	[77]
[Ru(η^5-C$_9$H$_7$)(^{t}BuNC)(PPh$_3$)$_2$][ClO$_4$]	[77]
[Ru(η^5-C$_9$H$_7$)(chel)(PPh$_3$)][ClO$_4$] (chel = nbd, tfb, en, pn, Hbim, bipy, phen)	[77]
[Ru(η^5-C$_9$H$_7$)(C=CH$_2$)(PPh$_3$)(PMe$_3$)][PF$_6$]	[83]
[Ru(η^5-C$_9$H$_7$){=C=C(H)Ph}(PPh$_3$)$_2$][X] (X = PF$_6$[c], ClO$_4$)	[77,82]
[Ru(η^5-C$_9$H$_7$){=C=C(H)CPh$_2$R}(PPh$_3$)$_2$][BF$_4$] (R = Me, ^{t}Bu)	[86]
[Ru(η^5-C$_9$H$_7$){=C=C(H)Ph}{(*S*,*S*)-κ^2-(*P*,*P*)-Ph$_2$PCH(Me)CH(Me)PPh$_2$}][PF$_6$]	[76]
[Ru(η^5-C$_9$H$_7$){=C=C(H)R}(PPh$_3$)$_2$][PF$_6$] (R = ^{t}Bu, ^{n}Pr, H)	[82]
[Ru(η^5-C$_9$H$_7$){=C=C(H)Ph}{κ^2-(*P*,*P*)-dppm}][PF$_6$]	[82]
[Ru(η^5-C$_9$H$_7$){=C=C(H)R}{κ^2-(*P*,*P*)-dppe}][BF$_4$] (R = Ph, ^{t}Bu, ^{n}Pr, H)	[82]
[Ru(η^5-C$_9$H$_7$){=C=C(H)C$_6$H$_4$NO$_2$}(PPh$_3$)$_2$][PF$_6$]	[80]
[Ru(η^5-C$_9$H$_7$){=C=C(H)CPh$_2$CH$_2$C(O)R}(PPh$_3$)$_2$][BF$_4$] (R = Ph, ^{i}Pr, CH=CHPh)	[b]
[Ru(η^5-C$_9$H$_7$){=C=C(H)C(H)PhCH$_2$C(O)R}(PPh$_3$)$_2$][BF$_4$] (R = Ph, ^{i}Pr)	[b]
[Ru(η^5-C$_9$H$_7$){=C=C(Me)R}(PPh$_3$)$_2$][CF$_3$SO$_3$] (R = Ph, ^{t}Bu, ^{n}Pr, Me[c])	[82]
[Ru(η^5-C$_9$H$_7$)(=C=CMe$_2$)(PPh$_3$)(PMe$_3$)][CF$_3$SO$_3$]	[83]
[Ru(η^5-C$_9$H$_7$){=C=C(Me)Ph}{κ^2-(*P*,*P*)-dppm}][CF$_3$SO$_3$]	[82]
[Ru(η^5-C$_9$H$_7$){=C=C(Me)R}{κ^2-(*P*,*P*)-dppe}][CF$_3$SO$_3$] (R = Ph, ^{t}Bu, ^{n}Pr, Me)	[82]
[Ru(η^5-C$_9$H$_7$){=C(OR)Me}(PPh$_3$)$_2$][PF$_6$] (R = Me, Et)	[82]
[Ru(η^5-C$_9$H$_7$){=C(OR)Me}{κ^2-(*P*,*P*)-dppm}][PF$_6$] (R = Me, Et)	[82]
[Ruη^5-C$_9$H$_7$){=C(OR)Me}{κ^2-(*P*,*P*)-dppe}][PF$_6$] (R = Me, Et)	[82]
[Ru(η^5-C$_9$H$_7$){=C=CH(CH$_2$OH)}(PPh$_3$)$_2$][PF$_6$]	[87]
[Ru(η^5-C$_9$H$_7$){=C(OMe)(CH=CHR)}{κ^2-(*P*,*P*)-dppm}][PF$_6$] (R = H, Ph)	[87]

Table 1 (Continued)

Compound	Ref.
$[Ru(\eta^5-C_9H_7)\{=C(OMe)(CH=CHPh)\}\{\kappa^2-(P,P)-dppe\}][PF_6]$	[87]
$[Ru(\eta^5-C_9H_7)\{=C(OMe)Bz\}\{\kappa^2-(P,P)-dppm\}][PF_6]$	[82]
$[Ru(\eta^5-C_9H_7)\{=C(NH_2)Me\}\{\kappa^2-(P,P)-dppm\}][PF_6]$	[82]
$[Ru(\eta^5-C_9H_7)\{=C=C(H)\overline{C=CH(CH_2)_3C}H_2\}(PPh_3)_2][PF_6]$	[92]
$[Ru(\eta^5-C_9H_7)(=C=C(Me)C=CH(CH_2)_3CH_2\}(PPh_3)_2][CF_3SO_3]^c$	[84,92]
$[Ru(\eta^5-C_9H_7)\{=C=C(H)CHPhOMe\}(PPh_3)_2][PF_6]$	[87]
$[Ru(\eta^5-C_9H_7)\{=C=C(H)CH_2OH\}(PPh_3)_2][PF_6]$	[87]
$[Ru(\eta^5-C_9H_7)\{=C=C(H)\overline{C=CH(CH_2)_nC}H_2\}(PPh_3)_2][PF_6]$ ($n = 2, 4, 5$)	[84]
$[Ru(\eta^5-C_9H_7)\{=C=C(H)\overline{C=CH(CH_2)_nC}H_2\}\{\kappa^2-(P,P)-dppe\}][PF_6]$ ($n = 2, 3, 4$)	[84]
$[Ru(\eta^5-C_9H_7)\{=C=C=C(H)Ph\}(PPh_3)_2][PF_6]$	[89]
$[Ru(\eta^5-C_9H_7)\{=C=C=C(Me)Ph\}(PPh_3)_2][PF_6]$	[87]
$[Ru(\eta^5-C_9H_7)(=C=C=Ph_2)(PPh_3)_2][PF_6]^c$	[85,87]
$[Ru(\eta^5-C_9H_7)(=C=C=Ph_2)\{Ph_2P(CH_2)_nPPh_2\}][PF_6]$ ($n = 1, 2$)	[85]
$[Ru(\eta^5-C_9H_4Me_3)(=C=C=CPh_2)\{\kappa^2-(P,P)-dppm\}][BF_4]$	[73]
$[Ru(\eta^5-C_9H_7)(=C=C=Ph_2)(PPh_3)\{\kappa-P-Ph_2PCH_2C(O)^tBu\}][PF_6]$	[79]
$[Ru(\eta^5-C_9H_7)(=C=C=CC_{12}H_8)(PPh_3)_2][PF_6]$	[87]
$[Ru(\eta^5-C_9H_7)(=C=C=CC_{12}H_8)\{\kappa^2-(P,P)-Ph_2P(CH_2)_nPPh_2\}][PF_6]$ ($n = 1, 2$)	[87]
$[Ru(\eta^5-C_9H_7)(=C=C=CC_{13}H_{20})(PPh_3)_2][PF_6]^c$	[92]
$[Ru(\eta^5-C_9H_7)\{C\equiv CC(Ph)_2(PMe_3)\}(PPh_3)_2][PF_6]$	[85]
$[Ru(\eta^5-C_9H_7)\{C\equiv CC(Ph)_2(PMe_2Ph)\}(PPh_3)_2][PF_6]$	[86]
$[Ru(\eta^5-C_9H_7)\{C\equiv CC(Ph)_2(PMe_3)\}\{\kappa^2-(P,P)-Ph_2P(CH_2)_nPPh_2\}][PF_6]$ ($n = 1, 2$)	[86]
$[Ru(\eta^5-C_9H_7)\{C(PMe_3)=C=C(Ph)_2\}\{\kappa^2-(P,P)-dppm\}][PF_6]$	[85]
$[Ru(\eta^5-C_9H_7)\{C(PMe_2Ph)=C=C(Ph)_2\}\{\kappa^2-(P,P)-dppm\}][PF_6]$	[86]
$[Ru(\eta^5-C_9H_7)\{C\equiv CCH_2(PPh_3)\}(PPh_3)_2][PF_6]$	[80]
$[Ru(\eta^5-C_9H_7)\{C\equiv CCH(Ph)(PMe_3)\}(PPh_3)_2][PF_6]$	[89]
$[Ru(\eta^5-C_9H_7)\{C\equiv CCH(Ph)(L)\}(PPh_3)_2][PF_6]$ ($L = PPh_3, PMe_2Ph, PPh_2Me$)	[86]
$[Ru(\eta^5-C_9H_7)\{=C=C(H)CPh_2(C\equiv CR)\}(PPh_3)_2][BF_4]$ ($R = H, Ph, {}^nPr$)	[86]
$[Ru(\eta^5-C_9H_7)\{=C=C(H)CPh_2(C_{10}H_9O)\}(PPh_3)_2][BF_4]$	[88]
$[Ru(\eta^5-C_9H_7)\{=C=C(H)CPh_2(C_{10}H_{11}O)\}(PPh_3)_2][BF_4]$	[88]
$[Ru(\eta^5-C_9H_7)\{C(H)=C(PPh_3)(R)\}(PPh_3)_2][PF_6]$ ($R = C_6H_9{}^c, C_7H_{11}$)	[84]
$[Ru(\eta^5-C_9H_7)(=CHCH=CRMe)\{\kappa^2-(P,P)-dppm\}][BF_4]$ ($R = H, Me$)	[90]
$[Ru(\eta^5-C_9H_7)\{=CHCH=\overline{CCH_2(CH_2)_nC}H_2\}\{\kappa^2-(P,P)-dppm\}][BF_4]$ ($n = 2, 3, 4$)	[90]
$[Ru(\eta^5-C_9H_7)(=CHCH=CRPh)\{\kappa^2-(P,P)-dppm\}][BF_4]$ ($R = H, Ph$)	[90]
Ruthenium di and polynuclear complexes	
$[Ru(\eta^5-C_9H_7)(CO)_2]_2$	[93]
$[\{Ru(CO)_2\}_2\{\eta^5:\eta^5-MeCH(C_9H_6)_2\}]^c$	[94]
$[\{Ru(\eta^5-C_9H_7)(\mu-SEt)(CO)]_2{}^c$	[91]
$[Ru(\eta^5-C_9H_7)\{C\equiv CAu(PPh_3)\}(PPh_3)(PR_3)]$ ($R = Ph, Me$)	[83]
$[Ru(\eta^5-C_9H_7)(\{C\equiv CAu(PPh_3)\}\{\kappa^2-(P,P)-dppe\}]$	[83]
$[Ru(\eta^5-C_9H_7)\{C\equiv NM(CO)_5\}(PPh_3)_2]$ ($M = Cr, W$)	[80]
$[Ru(\eta^5-C_9H_7)\{C\equiv CCH=CHC_6H_4CNM(CO)_5\}(PPh_3)_2]$ ($M = Cr, W$)	[80]
$[Ru(\eta^5-C_9H_7)\{C\equiv CCPh_2CH_2C(OMe)=M(CO)_5\}(PPh_3)_2]$ ($M = Cr, Mo, W^c$)	[89]
$[Ru(\eta^5-C_9H_7)\{C\equiv CCH=CHC_5H_4NM(CO)_5\}(PPh_3)_2]$ ($M = Cr, W$)	[80]
$[\{Ru_2(\eta^5-C_9H_7)_2(\mu-SEt)(CO)_4][PF_6]^c$	[91]
$[Ru(\eta^5-C_9H_7)\{=C=C(H)CPh_2CH_2C(OMe)=M(CO)_5\}(PPh_3)_2][BF_4]$ ($M = Cr, Mo, W$)	[89]
$[Ru(\eta^5-C_9H_7)\{C\equiv NRu(NH_3)_5\}(PPh_3)_2][CF_3SO_3]_3$	[80]
$[Ru(\eta^5-C_9H_7)\{C\equiv CCH=CHC_6H_4CNRu(NH_3)_5\}(PPh_3)_2][CF_3SO_3]_3$	[80]

Table 1 (Continued)

Compound	Ref.
$[\{Ru(\eta^5\text{-}C_9H_7)(\mu\text{-}SEt)]_3$	[91]
$[\{Ru_3(\eta^5{:}\eta^5\text{-}C_9H_6C_9H_6)(CO)_8]$[c]	[95]
$[Ru(\eta^5\text{-}C_9H_7)\{C{\equiv}CCPh_2(\mu^2\text{-}\eta^2\text{-}C{\equiv}CH)Co_2(CO)_6\}(PPh_3)_2]$	[88]
$[Ru(\eta^5\text{-}C_9H_7)\{C{\equiv}CCH{=}CH(\mu^2\text{-}\eta^2\text{-}C{\equiv}CH)Co_2(CO)_6\}(PPh_3)_2]$	[88]
$[\{Ru_3(\eta^5\text{-}C_9H_7)_3(\mu\text{-}SEt)_3(\mu\text{-}CO)(CO)]$[c]	[91]
$[\{Ru_3(\eta^5\text{-}C_9H_7)_3(\mu\text{-}SEt)_2(\mu\text{-}SEtMe)][A]$ (A = I[c], PF_6)	[91]
$[Ru(\eta^5\text{-}C_9H_7)\{{=}C{=}C(H)CPh_2(\mu^2\text{-}\eta^2\text{-}C{\equiv}CH)Co_2(CO)_6\}(PPh_3)_2][BF_4]$	[88]
$[Ru(\eta^5\text{-}C_9H_7)\{{=}C{=}C(H)CH{=}CH(\mu^2\text{-}\eta^2\text{-}C{\equiv}CH)Co_2(CO)_6\}(PPh_3)_2][BF_4]$	[88]
$[Ru(\eta^5\text{-}C_9H_7)\{{=}C{=}C(C_{10}H_7Co_4(CO)_9\}(PPh_3)_2]$[c]	[88]
$[\{Ru(\eta^5\text{-}C_9H_7)(\mu\text{-}SEt)Cl]_n$	[91]
Osmium mononuclear η^5 half-sandwich complexes	
$[Os(\eta^5\text{-}C_9H_7)LL'X]$	
$[Os(\eta^5\text{-}C_9H_7)Cl(PPh_3)_2]$	[96]
$[Os(\eta^5\text{-}C_9H_7)X(PPh_3)_2]$ (X = Br, I)	[a]
$[Os(\eta^5\text{-}C_9H_7)Br(PPh_3)(L)]]$ (L = PMe_3, PMe_2Ph)	[a]
$[Os(\eta^5\text{-}C_9H_7)H(PPh_3)_2]$	[a]
$[Os(\eta^5\text{-}C_9H_7)(C{\equiv}CR)(PPh_3)_2]$ (R = H, ^{t}Bu)	[96]
$[Os(\eta^5\text{-}C_9H_7)\{C{\equiv}C\overline{CH(CH_2)_nC}H_2\}(PPh_3)_2]$ (n = 2, 3, 4)	[96]
$[Os(\eta^5\text{-}C_9H_7)(C_6H_5)_2(N)]$[c]	[97]
$[Os(\eta^5\text{-}C_9H_7)LL'L'']^+$	
$[Os(\eta^5\text{-}C_9H_7)(H)_2(PPh_3)_2][BF_4]$	[a]
$[Os(\eta^5\text{-}C_9H_7)(MeCN)(PPh_3)_2][PF_6]$	[a]
$[Os(\eta^5\text{-}C_9H_7)\{{=}C{=}C(H)R\}(PPh_3)_2][PF_6]$ (R = H, ^{t}Bu)	[96]
$[Os(\eta^5\text{-}C_9H_7)\{{=}C{=}C(H)\overline{C{=}CH(CH_2)_nC}H_2\})(PPh_3)_2][PF_6]$ (n = 2, 3, 4)	[96]
$[Os(\eta^5\text{-}C_9H_7)\{{=}C{=}C(H)(CH_2)_4OH\}(PPh_3)_2][PF_6]$	[96]
$[Os(\eta^5\text{-}C_9H_7)\{{=}C{=}C(Me)^tBu\}(PPh_3)_2][CF_3SO_3]$	[96]
$[Os(\eta^5\text{-}C_9H_7)\{{=}\overline{CO(CH_2)_nC}H_2\}(PPh_3)_2][PF_6]$ (n = 2, 3)	[96]
$[Os(\eta^5\text{-}C_9H_7)({=}C{=}C{=}CPh_2)(PPh_3)_2][PF_6]$[c]	[87]
$[Os(\eta^5\text{-}C_9H_7)({=}C{=}C{=}CC_{12}H_8)(PPh_3)_2][PF_6]$	[87]
Other coordination modes	
$[Fe(\eta^1\text{-}C_9H_7)(\eta^5\text{-}C_5H_5)(CO)_2]$	[98,99]
$[PPN][Fe(\eta^3\text{-}C_9H_7)(CO)_3)]$[c]	[100]
$[Ru_3(\mu\text{-}\eta^1{:}\eta^5\text{-}C_9H_6)_3(CO)_6]$[c]	[95]
$[Ru_3(\mu\text{-}\eta^1{:}\eta^5\text{-}C_9H_6)(CO)_{10}]$	[95]
$[Ru_4(\mu_3\text{-}\eta^2{:}\eta^5{:}\eta^2\text{-}C_9H_7)(\eta^5\text{-}C_9H_9)(CO)_7(\mu\text{-}CO)_2]$[c]	[93]
$[Os_4H\ (\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^5\text{-}C_9H_5Et_2)(CO)_9]$[c]	[101]
$[Ru(\eta^5\text{-}C_9H_7)(\mu\text{-}\ \eta^5{:}\eta^6\text{-}C_9H_7)Ru(\eta^5\text{-}C_5R_5)][PF_6]$ (R = H, Me)	[21]
$[Ru(\eta^5\text{-}C_5H_5)(\mu\text{-}\ \eta^5{:}\eta^6\text{-}C_9H_7)Ru(\eta^5\text{-}C_5R_5)][PF_6]$ (R = H, Me[c])	[21]
$[Ru(\eta^5\text{-}C_5Me_5)(\mu\text{-}\ \eta^5{:}\eta^6\text{-}C_9H_7)Ru(\eta^5\text{-}C_5R_5)][PF_6]$ (R = H, Me)	[21]
$[Ru(\eta^5\text{-}C_5H_5)(\mu\text{-}\ \eta^6{:}\eta^5\text{-}C_9H_7)Ru(\mu\text{-}\ \eta^5{:}\eta^6\text{-}C_9H_7)Ru\ (\eta^5\text{-}C_5R_5)][PF_6]_2$ (R = H, Me)	[21]
$[Ru(\eta^5\text{-}C_5Me_5)(\mu\text{-}\ \eta^6{:}\eta^5\text{-}C_9H_7)Ru(\mu\text{-}\ \eta^5{:}\eta^6\text{-}C_9H_7)Ru\ (\eta^5\text{-}C_5Me_5)][PF_6]_2$	[21]
$[Ru(\eta^6\text{-}C_9H_7)(\eta^5\text{-}C_5Me_5)]$	[21]
$Na[Ru(\eta^6\text{-}C_9H_7)(\eta^5\text{-}C_5Me_5)(O_3SCF_3)]$	[102]

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[a] J. Gimeno, unpublished results.

[b] J. Gimeno, in press.

[c] X-Ray data.

As also occurs for cyclopentadienyl complexes the bonding mode η^5-C_9H_7 (**A**) is by far the most common (Table 1) and only a few examples of the rest have been reported to date. In particular the bonding mode **B** has only been described in the complex [Ru(η^6-C_9H_7)(η^5-C_5Me_5)][3]. Although the formation of the η^3-C_9H_7 (**C**) and η^1-C_9H_7 (**D**) bonding types is well documented for other transition metals [103][4] (also known for cyclopentadienyl rings) [104] only the trihapto and monohapto indenyl complexes [PPN][Fe(η^3-C_9H_7)(CO)$_3$] [100], [Fe(η^1-C_9H_7)(η^5-C_5H_5)(CO)$_2$] [98,105] have been isolated for Group 8 metals. An X-ray crystal structure of the former has also been reported[5]. Mixed bonding types **E**(μ-η^6:η^5), **F** (μ-η^1:η^5) and **G**(μ-η^5:η^2:η^2) are also known. Type **E** has been found in a series of triple and tetra-decker complexes of the type [(η^5-C_5H_5)Ru(μ-η^6:η^5-C_9H_7)Ru(η^5-C_5Me_5)][PF$_6$] (crystallographically characterized) and [(η^5-C_5R_5)Ru(μ-η^6:η^5-C_9H_7)Ru(μ-η^6:η^5-C_9H_7)Ru(η^5-C_5R_5)][PF$_6$]$_2$ [21]. Types **F** and **G** are shown by the cluster complexes [Ru$_3$(μ-η^1:η^5-C_9H_6)(CO)$_{10}$], [Ru$_3$(μ-η^1:η^5-C_9H_6)$_3$(CO)$_6$] [95] and [Ru$_4$(μ_3-η^2:η^5:η^2-C_9H_7)(η^5-C_9H_9)(CO)$_7$(μ-CO)$_2$] [93]. The electronic saturation (eighteen electrons) around the metal atoms allow the stabilization of these unusual bonding types.

The most significant structural feature of η^5-indenyl complexes is the general distortion from η^5- toward η^3-coordination shown by the indenyl ligand. Although this distorted structure is similar to that shown by η^5-cyclopentadienyl complexes [106], the ability of the indenyl ligand to stabilize the allyl-ene intermediate by aromatization of the benzene ring enables a more pronounced distortion in the indenyl complexes.

Different parameters can be used to describe the slip–fold distortion in the indenyl complexes [5d, 106]. For the comparison of solid state structures the distortion parameters used by Taylor and Marder have been chosen (see Chart II): (i) the slip parameter (Δ) defined as the difference in the average bond lengths of the metal to the ring junction carbons, C(3a), C(7a) and of the metal to adjacent carbon atoms of the five membered ring, C(1), C(3): $\Delta = \text{avg. d[Ru–C(3a),C(7a)]} - \text{avg. d[Ru–C(1),C(3)]}$; (ii) the hinge angle (HA) defined as the angle between the planes defined by [C(1), C(2), C(3)] and [C(1), C(3), C(3a),C(7a)]; (iii) the fold angle (FA) defined as the angle between the planes defined by [C(1), C(2), C(3)] and [C(3a), C(4), C(5), C(6), C(7),C(7a)]. The hinge angle and the fold angle represent the bending of the indenyl ligand at C(1), C(3) and C(3a), C(7a), respectively.

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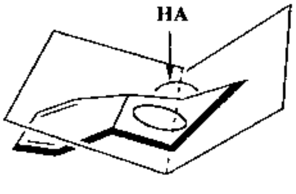
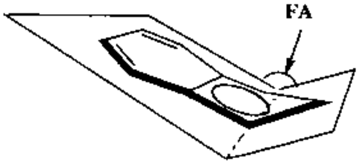
[3] This coordination mode was proposed on the basis of NMR spectroscopic data: see Ref. [21].

[4] [W(η^5-C_9H_7)(η^3-C_9H_7)(CO)$_2$] was the first structurally characterized η^3-C_9H_7 metal complex. For a typical η^1-C_9H_7 complex: see Ref. [103c]

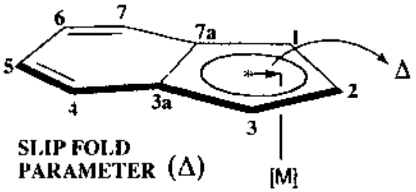
[5] The analogous ruthenium [Ru(η^3-C_9H_7)(CO)$_3$]$^-$ complex has been proposed to be formed in solution (characterized by reduction of [Ru(η^3-C_9H_7)(CO)$_2$]$_2$ with Na/Hg in THF solution under 1 atm of CO. Spectroscopic evidence for the formation of [Fe(η^3-C_9H_7)H(CO)$_3$] at low temperatures is reported in Ref. [36].



HINGE ANGLE (HA)



FOLD ANGLE (FA)



In general, indenyl complexes considered to be η^5 show values of HA and Δ less than 10° and 0.25 Å, respectively [106]. In contrast, complexes considered to be η^3 show HA values of ca. 20°–30° while those of Δ are between 0.69 and 0.80 Å [107]. Thus, an almost perfect η^5-coordination is reported for the complex $[Fe(\eta^5\text{-}C_9H_7)_2]$ ($\Delta = 0.043(4)$ Å), while $[PPN][Fe(\eta^3\text{-}C_9H_7)(CO)_3]$ ($\Delta = 0.689(7)$ Å) is considered as true η^3 complex [100a]. Analogous η^3-indenyl complexes show similar values: $[Ir(\eta^3\text{-}C_9H_7)(PMe_2Ph)_3]$ ($\Delta = 0.79(1)$ Å) [108], $[W(\eta^3\text{-}C_9H_7)(\eta^5\text{-}C_9H_7)(CO)_2]$ ($\Delta = 0.72(2)$ Å) [103a] and $[Mo(\eta^3\text{-}C_9H_7)(\eta^5\text{-}C_5H_5)(CO)_2]$ [9i].

Tables 2 and 3 show the structural distortions reported in the literature for the indenyl ligand and the distances between the metal atom and the centroid of the five membered ring (C*). This distance lies in the range 1.71–1.79 Å for the iron complexes and in the range 1.82–1.99 Å for the ruthenium and osmium complexes.

Most complexes show a small or moderate distortion towards an η^3 binding with slip distortion parameter, Δ, between ca. 0–0.22 Å and HA less than 13°. The more pronounced distortion is observed (Table 3) for the nitride complex $[Os(\eta^5\text{-}C_9H_7)(Ph)_2(N)]$ ($\Delta = 0.40$ Å, HA = 13.5°, FA = 14.3°); at least two other indenyl complexes $[Ni(\eta^5\text{-}C_9H_7)_2]$ ($\Delta = 0.418$ Å, HA = 13.9°, FA = 13.1°) [5d] and $[W(\eta^5\text{-}C_9H_7)_2(CO)_2]$ ($\Delta = 0.498$ Å) [109] also show a similar distortion. To the best of our knowledge the complex $[PPN][Fe(\eta^3\text{-}C_9H_7)(CO)_3]$ is the only Group 8 metal complex that presents a true η^3-coordination mode for the indenyl ligand.

It is interesting to compare these distortions with those found in cyclopentadienyl complexes. In general, the HA and Δ values are less than 5° and 0.15 Å, respectively, for η^5-complexes [106]. The few structurally characterized η^3-complexes have HA values close to 20° and Δ values around 0.6 Å [110].

An additional distortion parameter is also necessary for the sandwich complexes (see Table 2). The rotation angle (RA) has been defined as the angle formed by the intersection of the two lines determined by the centroids of the five- and six-membered rings [23,111]. A rotation angle of 0° would indicate a completely eclipsed geometry, whereas an angle of 180° corresponds to the fully staggered arrangement

Table 2
Comparison of solid state and solution ^{13}C-NMR structural data for η^5-indenyl sandwich complexes

Compound	M–C*[a]	δ (C-3a,7a)[b]	$\Delta\delta$ (C-3a,7a)[c]	Δ (Å)[d]	HA (°)[e]	FA (°)[f]	RA (°)[g]	Ref.
$[Fe(\eta^5\text{-}C_9H_7)_2]$	1.71	87.0	-43.7	Avg. 0.043(4)[h]	Avg. 2.2[h]	Avg. 0.8[h]	6.0, 13.0[i]	[5c,d]
$[Fe(\eta^5\text{-}C_9H_5Me_2)_2][PF_6]$	1.716	–	–	0.074(4)	4.4	–	–	[15]
$[Fe(\eta^5\text{-}C_9Me_7)_2]$	–	85.5	-38.3	0.030(4)	2.5	4.4	151.3	[5d]
$[Fe\{\eta^5\text{-}C_9Me_6)_2SiMe_2\}]$	–	–	–	Avg. 0.049(8)[h]	–	–	138.2	[18]
$[Fe(\eta^5\text{-}C_9Me_7)_2][TCNQ]\cdot CH_2Cl_2$	–	–	–	0.072	3.45	1.45	85.0	[23]
$[Fe(\eta^5{:}\eta^5\text{-}C_9H_6C_5H_4)]_2$	–	–	–	Avg. 0.05(14)[h]	–	–	–	[24]
$[Ru(\eta^5\text{-}C_9H_7)_2]$	1.8216	89.9	-40.8	0.030(14)	ca. 0	ca. 0	0.196	[6b] [j]
$[Ru(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_5Me_5)]$	1.840	92.48	-38.22	0.041(6)	ca. planar	ca. planar	2.0	[28,21]
$[Ru(\eta^5\text{-}C_9H_7)(Me_3tacn)][PF_6]$	–	92.9	-37.8	0.095(6)	ca. planar	ca. planar	–	[30]

[a] C* = centroid of C(1), C(2), C(3), C(3a), C(7a).

[b] δ in ppm.

[c] $\Delta\delta$(C-3a,7a) = δ(C-3a,7a(η–indenyl complex)) − δ(C-3a,7a(η–sodium indenyl)); δ(C-3a,7a(η–sodium indenyl)) = 130.7 ppm.

[d] Δ = avg. d[Ru–C(3a), C(7a)] − avg. d[Ru–C(1), C(3)].

[e] HA = hinge angle = angle between the planes defined by [C(1), C(2), C(3)] and [C(1), C(3), C(3a), C(7a)].

[f] FA = fold angle = angle between the planes defined by [C(1), C(2), C(3)] and [C(3a), C(4), C(5), C(6) C(7), C(7a)].

[g] RA = rotation angle = angle formed by the intersection of the two lines determined by the centroids of the five- and six-membered rings.

[h] Average value for two independent molecules in the unit cell.

[i] RA values for two independent molecules in the unit cell.

[j] ^{13}C-NMR: G. Stringer, Ph.D. Thesis, Oxford University, 1988.

Table 3
Comparison of solid state and solution ^{13}C-NMR structural data for indenyl complexes[a]

	M–C*[b]	δ C-3a,7a[c]	Δδ (C-3a,7a)[d]	Δ (Å)[e]	HA (°)[f]	FA (°)[g]	CA (°)[h]	Ref.
Iron mononuclear complexes								
[Fe(η^5-C_9H_7)($C_8H_4ClN_2$)$(CO)_2$]	–	104.64	−26.06	0.0805	–	–	–	[47]
[Fe(η^5-C_9H_7)($SiMe_3$)$(CO)_2$]	1.753	105.4	−25.3	0.096	–	6.7	–	[51]
[Fe(η^5-C_9H_7)(Si_2Me_5)$(CO)_2$]	1.747	105.8	−24.9	–	–	3.9	–	[51]
[Fe(η^5-C_9H_7){SiMe($SiMe_3$)$_2$}$(CO)_2$]	1.744	105.4	−25.3	–	–	3.2	–	[51]
[Fe(η^5-C_9H_7)(CO_2SnPPh_3)(CO)(PPh_3)]	–	–	–	0.136	–	–	–	[54]
[Fe(η^5-C_9H_7)($COCHMe_2$)(CO)(PPh_3)]	1.797	107.93	−22.77	0.122	ca. planar	6.3(2)	–	[40]
[Fe(η^5-C_9H_7)($SiMe_3$)(CO)(PPh_3)]	1.774	105.5	−25.2	–	–	8.5	–	[51]
[Fe(η^5-C_9H_7)(Si_2Me_5)(CO)(PPh_3)]	1.785	–	–	–	–	11.1	–	[51]
[Fe(η^5-C_9H_7){SiMe($SiMe_3$)$_2$}(CO)(PPh_3)]	1.779	–	–	0.13	–	8.9	–	[51]
[Fe(η^5-C_9H_7)(CO){κ^2-(*P*,*P*)-dppm}][BF_4]	–	103.62	−27.08	0.093(8)	ca. planar	ca. planar	–	[62]
[Fe(η^5-C_9H_7)$(CO)_3$][PF_6]	–	–	–	0.080(8)	ca. planar	ca. planar	–	[61]
Iron di and polinuclear complexes								
[Fe_2{(η^5-C_9H_6)$_2$$SiMe_2$}(CO)}$_2$($\mu$-CO)$_2$]	–	–	–	0.068	–	–	–	[64]
[Fe_2{(η^5-C_9H_6)$_2$)$Me_2SiSiMe_2$}(CO)}$_2$(μ-CO)$_2$]	1.784	–	–	0.077(3)	--	–	–	[65]
[Fe_2{μ-η^5:η^1-κ^2-(*C*,*Si*)-$C_9H_6SiMe_2$}$_2$$(CO)_4$]	1.740	–	–	0.078(5)	–	–	–	[65]
[PPN][Fe(η^5-C_5H_5)(COMe)(μ-CO)$_2$-Fe(η^5-C_9H_7)CO)]	–	107.8^{i}	−22.9	–	–	5.2	–	[41]
		105.4^{j}	−25.3					
[Fe(η^5-C_9H_7)(CO)(μ-CO)$_2$Co$(CO)_3$]	1.76	–	–	0.103(15)	ca. planar	ca. planar	–	[67]
[Fe(η^5-C_9H_7)$(CO)_2$(μ-η^1:η^6-Ph)Cr$(CO)_3$]	1.748	105.51	−25.19	0.102(5)	–	–	–	[69]
[Fe(η^5-C_9H_7)($Et_2C_2B_4H_4$)Ni(η^5-C_5Me_5)]	–	–	–	0.121(4)	–	–	–	[22]
Ruthenium mononuclear complexes								
[Ru(η^5-C_9H_7)I(CO){P(CH_2Ph)$_3$}]	1.8953	–	–	0.10	3.32	5.59	–	[71]
[Ru(η^5-$C_9H_4Me_3$)Br(CO)(PPh_3)]	1.924(5)	–	–	0.129(8)	6.5(4)	8.9(4)	3.1(5)^{j}	p
[Ru(η^5-C_9H_7)H$(PPh_3)_2$]	1.945(3)	–	–	0.154(3)	5.1(3)	8.4(3)	14.93(7)^{k}	p
[Ru(η^5-C_9H_7)Cl{(*S*,*S*)Ph_2PCH(Me)CH(Me)-PPh_2}]	–	110.05	−20.65	0.171(7)	–	7.6	–	[76]
[Ru(η^5-C_9H_7)(C≡CPh){κ^2-(*P*,*P*)-dppe}]	–	–	–	0.092(8)	–	–	–	[81]
[Ru(η^5-C_9H_7){C≡CC(C≡CH)Ph)$_2$}$(PPh_3)_2$]	1.942(2)	109.47	−21.23	0.168(2	6.0(2)	11.8(2)	18.1(1)^{l}	[86]
[Ru(η^5-C_9H_7)(C≡C$CPh_2C_{10}H_{13}O$)$(PPh_3)_2$]	1.956(1)	110.67	−20.03	0.14(1)	7.0(1)	5.5(8)	61.3(4)^{l}	q

Table 3 (continued)

	M–C*[b]	δ C-3a,7a[c]	$\Delta\delta$ (C-3a,7a)[d]	Δ (Å)[e]	HA (°)[f]	FA (°)[g]	CA (°)[h]	Ref.
$[Ru(\eta^5\text{-}C_9H_7)\{C{\equiv}CCH{=}C(C_6H_4\text{-}NO_2)_2\}(PPh_3)_2]\cdot 2C_4H_4O$	1.94(1)	110.07	−20.63	0.15(1)	2.6(8)	4.3(5)	15.0(6)[l]	[q]
$[Ru(\eta^5\text{-}C_9H_7)\{C{\equiv}C(CH{=}CH)_2(C_6H_4\text{-}NO_2)\}(PPh_3)_2]\cdot C_4H_4O/C_5H_{12}$	1.95(2)	109.79	–20.91	0.22(2)	3.0(2)	6.0(1)	19.0(1)[l]	[q]
$[Ru(\eta^5\text{-}C_9H_7)(PPh_3)\{\kappa^2\text{-}(C,P)C({=}C{=}CPh_2)\text{-}CHC(O)^tBu\}PPh_2]\cdot CH_2Cl_2$	1.935(8)	106.0	−24.7	0.125(8)	4.6(6)	7.4(6)	–	[79]
$[Ru(\eta^5\text{-}C_9H_7)(CO)(PPh_3)_2][ClO_4]\cdot 1/2CH_2Cl_2$	1.945(3)	–	–	0.102(5)	3.77	5.19	–	[77]
$[Ru(\eta^5\text{-}C_9H_7)H_2(PPh_3)_2][BF_4]\cdot CH_2Cl_2$	1.928(2)	–	–	0.102(3)	4.8(2)	8.6(2)	–	[p]
$[Ru(\eta^5\text{-}C_9H_7)(PPh_3)\{\kappa^2(P,O)\text{-}Ph_2PCH(Me)\text{-}C(O)^tBu\}][PF_6]$	1.892(6)	–	–	0.135(7)	6.0(5)	6.7(5)	–	[79]
$[Ru(\eta^5\text{-}C_9H_7)({=}C{=}CMe_2)(PPh_3)_2][CF_3SO_3]\cdot 1/2\ CH_2Cl_2$	1.97(9)	–	–	0.197(7	8.1(6)	13.1(6)	22.2(4)[l]	[82]
$[Ru(\eta^5\text{-}C_9H_7)\{{=}C{=}C(Me)C{=}CH(CH_2)_3CH_2\}\text{-}(PPh_3)_2][CF_3SO_3]$	1.970(9)	116.95	−13.75	0.198(5)	7.5(4)	12.2(4)	20.0(3)[l]	[84]
$[Ru(\eta^5\text{-}C_9H_7)\{{=}C{=}C(H)Ph\}(PPh_3)_2][PF_6]$	1.964(6)	114.37	−16.33	0.175(6)	6.6(5)	11.9(5)	15.4(3)[l]	[82][p]
$[Ru(\eta^5\text{-}C_9H_7)\{{=}C(O)(CH_2)_4CH_2\}(PPh_3)_2][PF_6]$	1.99(9)	116.0	−14.7	0.22(5)	6(1)	11(1)	16.6(6)[l]	[p]
$[Ru(\eta^5\text{-}C_9H_7)({=}C{=}C{=}CPh_2)(PPh_3)_2][PF_6]\cdot CH_2Cl_2$	1.951(5)	112.40	−18.3	0.121(5)	6.2(4)	8.1(3)	9.6(3)[m]	[87]
$[Ru(\eta^5\text{-}C_9H_7)\{{=}C{=}C{=}C(C_{13}H_{20})\}(PPh_3)_2][PF_6]$	1.942(5)	111.49	−19.21	0.0820(4)	5.3(5)	5.1(5)	12.2(6)[m]	[92]
$[Ru(\eta^5\text{-}C_9H_7)\{C(H){=}C(PPh_3)C_6H_9\}(PPh_3)_2][PF_6]$	1.981(5)	114.13	−16.56	0.217(5)	8.4(4)	14.8(4)	17.5(2)[l]	[84]
$[Ru(\eta^5\text{-}C_9H_4Me_3)({=}C{=}C{=}CPh_2)(CO)(PPh_3)][BF_4]$	1.93(1)	–	–	0.08(1)	3.0(1)	8.9(9)	79.6(5)[m]	[73]
$[Ru(\eta^5\text{-}C_9H_4Me_3)\{C(H){=}CPh(PPh_3)\}(CO)(PPh_3)][BF_4]$	1.953(5)	–	–	0.078(7)	6.0(4)	11.3(7)	24.6(3)[l]	[p]
$[Ru(\eta^5C_9H_4Me_3)\{{=}C(OEt)CH{=}CPh_2\}(CO)(PPh_3)][BF_4]$	1.963(7)	–	–	0.123(7)	8.3(4)	15.1(4)	14.7(3)[l]	[p]
Ruthenium di and polynuclear complexes								
$[\{Ru(CO)_2\}_2\{\eta^5{:}\eta^5\text{-}MeCH(C_9H_6)_2\}$	–	110.12	−20.58	0.096(10)	ca. planar	ca. planar	–	[94]
$[Ru(\eta^5\text{-}C_9H_7)(\mu\text{-}\ SEt)(CO)]_2$	–	–	–	Avg. 0.133(8)	–	–	–	[91]
$[Ru(\eta^5\text{-}C_9H_7)(C{\equiv}CC\{CH_2C(OMe){=}W(CO)_5\}Ph_2)(PPh_3)_2]\cdot C_6O_{14}$	1.942(8)	110.71	−19.99	0.1320(6)	4.4(7)	7.7(7)	59.3(6)[l]	[89]
$[Ru_2(\eta^5\text{-}C_9H_7)_2(\mu\text{-}SEt)(CO)_4][PF_6]$	–	–	–	Avg. 0.127(10)	–	–	–	[91]
$[Ru_3(\eta^5\text{-}C_9H_7)_3(\mu\text{-}SEt)_3(\mu\text{-}CO)(CO)]$	–	–	–	Avg. 0.130(6)[n]	–	–	–	[91]
$[Ru_3(\eta^5{:}\eta^5\text{-}C_9H_6C_9H_6)(CO)_8]$	1.934 avg.	–	–	Avg. 0.115	ca. planar	ca. planar	–	[95]
$[Ru_3(\eta^5\text{-}C_9H_7)_3(\mu\text{-}SEt)_2(\mu\text{-}SEtMe)]\text{-}I\cdot CH_2Cl_2$	–	–	–	Avg. 0.159	Avg. 4.85	Avg. 7.5	–	[91]
$[Ru(\eta^5\text{-}C_9H_7)\{{=}C{=}C(C_{10}H_7Co_4(CO)_9\}(PPh_3)_2]$	1.924	116.29	−14.41	0.205	12.6	10.7	–	[88]

Table 3 (continued)

	M–C*[b]	δ C-3a,7a[c]	Δδ (C-3a,7a)[d]	Δ (Å)[e]	HA (°)[f]	FA (°)[g]	CA (°)[h]	Ref.
Osmium mononuclear complexes								
$[Os(\eta^5-C_9H_7)(Ph)_2(N)]$	–	–	–	0.40	13.5	14.3	–	[97]
$[Os(\eta^5-C_9H_7)(PPh_3)_2(=C=C=CPh_2)][PF_6]\ CH_2Cl_2$	1.950(5)	110.12	−20.58	0.095(4)	5.3(3)	7.9(3)	9.4(2)[m]	[87]
Other coordination modes								
$[PPN][Fe(\eta^3-C_9H_7)(CO)_3)]$	–	157.3	+26.6	0.689(7)	–	22	–	[100]
$[Ru_3(\eta^1:\eta^5-C_9H_6)_3(CO)_6]$	–	–	–	Avg. 0.05[j] Avg. 0.037(4)[i]	ca. planar	ca. planar	–	[95]
$[Ru(\eta^5-C_5H_5)(\mu-\ \eta^5:\eta^6-C_9H_7)Ru(\eta^5-C_5Me_5)][PF_6]\cdot MeNO_2$	–	65.24	–[o]	0.043(8)	4.7	–	–	[21]
$[Ru_4(\eta^2:\eta^5:\eta^2-C_9H_7)(\eta^5-C_9H_9)(CO)_7-(\mu-CO)_2]$	–	–	–	–	ca. planar	8.3	–	[93]
$[Os_4(\mu^3-\eta^2:\eta^2:\eta^5-C_9H_5Et_2)H(CO)_9]$	–	–	–	0.005	5.2	1.3	–	[101]

[a] The data for η^5-indenyl sandwich complexes are collected in Table 2.

[b] C* = centroid of C(1), C(2), C(3), C(3a), C(7a).

[c] δ in ppm.

[d] Δδ(C-3a,7a) = δ(C-3a,7a(η–indenyl complex)) − δ(C-3a,7a(η–sodium indenyl)); δ(C-3a,7a(η–sodium indenyl)) = 130.7 ppm.

[e] Δ = avg. d[Ru–C(3a), C(7a)] − avg. d[Ru–C(1), C(3)].

[f] HA = hinge angle = angle between the planes defined by [C(1), C(2), C(3)] and [C(1), C(3), C(3a), C(7a)].

[g] FA = fold angle = angle between the planes defined by [C(1), C(2), C(3)] and [C(3a), C(4), C(5), C(6) C(7), C(7a)].

[h] CA = conformational angle = angle between the planes defined by C**, C*, Ru and C*, Ru, C_α, C** = centroid of C(4), C(5), C(6), C(7) C(3a),C(7a).

[i] Two isomers.

[j] CA = 0° for benzo ring and CO mutually *trans*.

[k] CA = 0° for benzo ring and H mutually *trans*.

[l] CA = 0° for benzo ring and unsaturated organic ligand mutually *trans*.

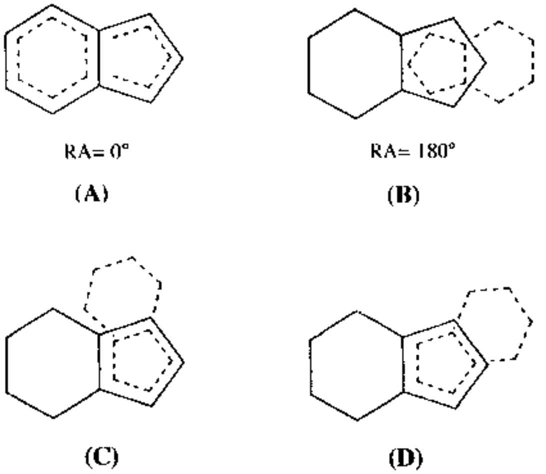
[m] CA = 0° for benzo ring and allenylidene ligand mutually *cis*.

[n] Average value for two independent molecules in the unit cell.

[o] The correlations between hapticity of indenyl ligand and ^{13}C-NMR shifts have been made only for the complexes with terminal indenyl ligand and application of such correlations to bridging indenyl ligand seems to be incorrect [21].

[p] J. Gimeno, unpublished results.

[q] J. Gimeno, in press.



of the two rings (see Chart III, A and B). Other eclipsed conformations (Chart III, C and D) have also been found.

The two indenyl ligands are eclipsed in the complex $[Ru(\eta^5\text{-}C_9H_7)_2]$ (RA = 0.196) (See Table 2). Similar conformation is found in the triple-decker complex $[Ru(\eta^5\text{-}C_5H_5)(\mu\text{-}\eta^5\text{:}\ \eta^6\text{-}C_9H_7)Ru(\eta^5\text{-}C_5Me_5)][PF_6]$ in which ciclopentadienyl and indenyl ligands are coordinated to the same ruthenium atom through the five membered rings[6].

The sandwich complex $[Fe(\eta^5\text{-}C_9H_7)_2]$ also shows [5d] a small RA value and for $[Fe(\eta^5\text{-}C_9Me_7)_2]$ a nearly eclipsed conformation (Chart III, D) is found [5d]. Staggered structures are also found for $[Fe(\eta^5\text{-}C_9H_5Me_2)_2][PF_6]$ [15] and $[Fe(\eta^5\text{-}C_9Me_7)_2][TCNQ]$ [23].

Marder et al. have related the slip–fold distortion to the σ-donor/π-acceptor nature of the ligands [112]. According to these authors a good σ-donor ligand should stabilize η^3-coordination by its ability to donate electron density to metal; conversely, a good π-acceptor ligand would remove electron density from the metal center and favor η^5-coordination of the indenyl ligand. Steric factors have generally not been considered of importance.

The slip–fold distortion of the coordinated indenyl ligand persists in solution [113]. Baker and Tulip have reported [113a], in agreement with Kohler analysis [113b], that the hapticity of the indenyl ligand can be evaluated spectroscopically by comparing the ^{13}C-NMR chemical shifts of the ring-junction carbon atoms (C(3a), C(7a)) in the metal complex with those of the sodium indenyl: larger distortions result in larger downfield shifts. The parameter $\Delta\delta(\text{C–3a,7a}) = \delta(\text{C–3a,7a } (\eta\text{-indenyl complex})) - \delta(\text{C–3a,7a (sodium indenyl)}$ has been proposed as an indication of the indenyl distortion, having values in the range -20 to -40 ppm for planar η^5-indenyl, -10 to -20 ppm for a partially slipped η^5-indenyl and $+5$ to $+30$ ppm for η^3-indenyl ligands.

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[6] Coordination of two bridgehead atoms C(3a) and C(7a) of the indenyl ligand by two metal atoms leads to considerable decrease of the π-character of the bond between these atoms and to a longer C(3a)–C(7a) distance as compared with that for the same ligand when coordinated by only one metal atom: see Ref. [21]

The C(3a) and C(7a) shifts together with the $\Delta\delta$ values for those complexes wherein ^{13}C-NMR data are available are given in Tables 2 and 3. A good correlation of the degree of slip–fold distortion in solution and in the solid state can be observed.

The hindrance of indenyl rotation observed in several rhodium complexes is attributed to slip–fold distortion of indenyl away from η^5-mode [113a,114]. Steric interactions raising from the size of ancillary ligands can also hinder the rotation of the indenyl ligand around the metal [115][7].

It has been found in some cases that although there is a relatively free rotation of the indenyl ligand, a specific conformation is favored in solution. Thus, NMR experiments carried out on the complexes $[M(\eta^5\text{-}C_9H_7)I(CO)L]$ (M = Fe, Ru; L = phosphine or phosphite) show that the phosphine or phosphite ligands orientate themselves in a preferred conformation in which they are close to indenyl arene ring [55,71]. Unusual effects of preferred geometries are the large ring-current shifts produced by the six membered ring when for a preferred conformation the benzo ring is predominently located in a position over a proton in another ligand in the complex. For example, this has been observed in the complexes $[Mo(\eta^5\text{-}C_9H_7)(\eta^3\text{-}C_4H_7)(CO)_2]$ and $[Ir(\eta^5\text{-}C_9H_7)H(PPh_3)_2][BF_4]$ [46,53,106,116].

Faller and Crabtree [106] have suggested that in most of η^5-indenyl complexes, the preferred conformation of the indenyl ligand relative to the other ligands is such that the ligands with the greatest *trans* influence are placed *trans* to the six-membered ring of the indenyl group. The driving force for adopting this conformation must be the greater degree of recovery of resonance energy in the benzo ring when the ligand of greater *trans* influence is *trans* to the C(3a)–C(7a) bond (most likely in order to decrease ene-to-metal interaction, and to favour greater aromatization of the benzo ring). This is the case for complex $[Os(\eta^5\text{-}C_9H_7)(Ph)_2(N)]$ in which the ligand *trans* to benzo ring is the nitride [97] but not for the complex $[Fe(\eta^5\text{-}C_9H_7)(COCHMe_2)(CO)(PPh_3)]^+$ in which the acyl group $COCHMe_2$, instead of the CO ligand, is *trans* to the benzo ring[8] [40,117]. Our group has previously reported that the orientation of the benzo ring of the indenyl ligand in vinylidene, alkynyl, alkenyl, and allenylidene ruthenium(II) complexes is clearly dependent on the nature of these unsaturated ligands [82,84,86]. For example, the vinylidene ligand of complexes $[Ru(\eta^5\text{-}C_9H_7)({=}C{=}CR^1R^2)(PPh_3)_2]^+$ is oriented *trans* to the benzo ring (CA = 0°, for benzo ring and vinylidene group mutually *trans*), whilst the allenylidene ligand of complexes $[Ru\ (\eta^5\text{-}C_9H_7)\{{=}C{=}C{=}CR_2\}(PPh_3)_2]^+$ places *cis* to the

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[7] Extended Hückel calculations on $[Ru(\eta^5\text{-}C_9H_7)({=}C{=}CH_2)(PH_3)_2]^+$ and $[Ru(\eta^5\text{-}C_9H_7)({=}C{=}C{=}CH_2)(PH_3)_2]^+$ as models of the vinylidene and allenylidene complexes, respectively, have a determined low barrier (7.9 and 5.9 kcal mol^{-1}, respectively) for the rotation of indenyl ligand. However, space-filling representation of the complexes $[Ru(\eta^5\text{-}C_9H_7)({=}C{=}CMe_2)(PPh_3)_2]^+$ and $[Ru(\eta^5\text{-}C_9H_7)({=}C{=}C{=}CPh_2)(PPh_3)_2]^+$ indicates that the potential rotation of the indenyl ligand around the ruthenium atom is hindered by the phenyl rings of the triphenylphosphine ligands.

[8] The general trend in the conformations of indenyl complexes outlined by Faller and Crabtree is not followed by some indenyl complexes of metals of other groups, for instance (a) $[Ir(\eta^5\text{-}C_9H_7)Ph)(Me)(Pme_3)]$: see Ref. [9g] and (b) $[Ir(\eta^5\text{-}C_9H_7)H_2(P^iPr_3)]$. In some cases steric reasons are invoked by the authors.

benzo ring (CA = 0°, for benzo ring and allenylidene group mutually *cis*). (CA values are compiled in Tables 2 and 3). The EHMO calculations [82,87,115] performed on $[Ru(\eta^5\text{-}C_9H_7)({=}C{=}CH_2)(PH_3)_2]^+$ and $[Ru(\eta^5\text{-}C_9H_7)({=}C{=}C{=}CH_2)(PH_3)_2]^+$ are in accordance with experimental results. The nature of the unsaturated carbene ligand seems to determine both the preferred conformation and the $\eta^5-\eta^3$ distortion of the indenyl ligand. The lesser distortion of the indenyl ligand found in the allenylidene versus vinylidene complexes may arise from the stronger π-acceptor electron capacity of allenylidene group, as has been found by EHMO calculations. The carbonyl ligand and the benzo ring of the indenyl group are mutually *trans* in complexes $[Ru(\eta^5\text{-}C_9H_4Me_3)Br(CO)(PPh_3)]$ and $[Ru(\eta^5C_9H_4Me_3)({=}C{=}C{=}CPh_2)(CO)(PPh_3)]$-$[BF_4]$ whilst the benzo ring is trans to the unsaturated organic ligand in complexes $[Ru(\eta^5\text{-}C_9H_4Me_3)\{{=}C(OEt)CH{=}CPh_2\}(CO)(PPh_3)][BF_4]$ and $[Ru(\eta^5\text{-}C_9H_4Me_3)$-$\{CH{=}CPh(PPh_3)\}(CO)(PPh_3)][BF_4]$ [118].

Theoretical calculations have been used to analyze the haptotropic rearrangement η^5/η^6 of indenyl ligand in the complex $[Fe(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_5H_5)]$ showing than the η^5-indenyl complex is significantly more stable than the η^6 indenyl derivative [119a]. Experimental evidence for haptotropic shifts in indenyl complexes is scarce [22,119b,c]. Recently, it has been reported that a solution of the zwitterionic species $Na[Ru(\eta^6\text{-}C_9H_7)(\eta^5\text{-}C_5H_5)(O_3SCF_3)]$ is quite stable at room temperature showing a reluctance for the η^6-to-η^5 haptotropic rearrangement [102].

Combined photoelectron spectra and extended Hückel molecular orbital calculations performed for the d^6 indenyl complexes [17,27], $[Fe(\eta^5\text{-}C_9H_7)_2]$, $[Ru(\eta^5\text{-}C_9H_7)_2]$, $[Ru(\eta5\text{-}C_9H_7)(\eta^5\text{-}C_5Me_5)]$ and $[Fe(\eta^5\text{-}C_9Me_7)_2]$ have also been reported.

3. Synthetic methods

3.1. Reaction of $M[C_9H_7]$ (M = Li, Na, K, SiR_3, SnR_3) with metal halides or metal complexes

Several sources of the indenyl salt have been reported depending on the reagent used for the extrusion of the acid hydrogen of indene (Li or NaR/THF, KOH/MeOH). This approach was employed for the synthesis of the first sandwich type derivative $[Fe(\eta^5\text{-}C_9H_7)_2]$ which was obtained either by the treatment of $FeCl_2$ with NaC_9H_7 [19] or $FeCl_3$ with LiC_9H_7 [11]. The analogous derivatives $[Ru(\eta^5\text{-}C_9H_7)_2]$ [21,25] $[Fe(\eta^5\text{-}C_9H_{7-x}Me_x)_2]$ ($x = 1, 2$) [14,15,18] and mixed sandwich complexes $[M(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_5R_5)]$ (R = H, Me) [14,19,28] were similarly synthesized. Half-sandwich complexes have also been prepared by this method (Eqs. (1) and (2)) [77,96].

$$[RuCl_2(PPh_3)_3]_x + C_9H_8 + KOH/MeOH \rightarrow [Ru(\eta^5\text{-}C_9H_7)Cl(PPh_3)_2] \quad (1)$$

$$[OsCl_2(PPh_3)_3] + LiC_9H_7 \rightarrow [Os(\eta^5\text{-}C_9H_7)Cl(PPh_3)_2] \quad (2)$$

The osmium sandwich complex $[Os(\eta^5\text{-}C_9H_7)_2]$ was prepared from the reduction of the Os(IV) complex $[NBu_4]_2[OsCl_6]$ with zinc in the presence of indene [32]. Complexes containing labile ligands have been used as starting materials for the synthesis of half-sandwich complexes [76] (Eq. (3)) and sandwich type multi-decker derivatives (Eq. (4)) [21].

$$[\mathrm{RuH(COD)(NH_2NMe_2)_3}][\mathrm{BPh_4}] \xrightarrow[\text{(2) CHCl}_3]{\text{(1) KH/C}_9\text{H}_8} [\mathrm{Ru}(\eta^5\text{-}\mathrm{C_9H_7})\mathrm{Cl(COD)}] \quad (3)$$

$$[\mathrm{Ru}(\eta^5\text{-}\mathrm{C_5H_5})(\eta^5\text{-}\mathrm{C_9H_7})] + [\mathrm{Ru}(\eta^5\text{-}\mathrm{C_5H_5})(\mathrm{MeCN})_3][\mathrm{PF_6}] \rightarrow$$
$$[\mathrm{Ru}(\eta^5\text{-}\mathrm{C_5H_5})(\mu\text{-}\eta^5{:}\eta^6\text{-}\mathrm{C_9H_7})\mathrm{Ru}(\eta^5\text{-}\mathrm{C_5H_5})][\mathrm{PF_6}] + 3\mathrm{MeCN} \quad (4)$$

An alternative to the indenyl salts are the tin [74] or silicon [30] derivatives $\mathrm{Me_3SiC_9H_7}$ and $\mathrm{Me_3SnC_9H_7}$ (Eqs. (4) and (5))

$$[\mathrm{RuCl_3(Me_3tacn)}] + \mathrm{Me_3SiC_9H_7} + \mathrm{Ag^+} \rightarrow [\mathrm{Ru}(\eta^5\text{-}\mathrm{C_9H_7})(\mathrm{Me_3tacn})]^+$$
$$+ 3\mathrm{AgCl}\ (\mathrm{Me_3tacn} = \text{1,4,7-trimethyl-1,4,7-triazacyclononane})$$

$$[\mathrm{RuBr}(\eta^3\text{-}\mathrm{C_3H_5})(\mathrm{CO})_3] + \mathrm{Me_3SnC_9H_7} \rightarrow$$
$$[\mathrm{Ru}(\eta^5\text{-}\mathrm{C_9H_7})(\eta^3\text{-}\mathrm{C_3H_5})(\mathrm{CO})] + \mathrm{Me_3SnBr} \quad (5)$$

3.2. Reaction of metal carbonyl complexes with indene

This procedure allows the entry to the most useful indenyl carbonyl precursors $[\mathrm{M}(\eta^5\text{-}\mathrm{C_9H_7})(\mathrm{CO})_2]_2$ and $[\mathrm{M}(\eta^5\text{-}\mathrm{C_9H_4Me_3})(\mathrm{CO})_2]_2$ (M = Fe, Ru) (Eqs. (6) and (7)). The commercially available carbonyl complexes $[\mathrm{Fe(CO)_5}]$ and $[\mathrm{Ru_3(CO)_{12}}]$ are used as starting materials. The thermal reactions with indene or methyl substituted indene derivatives give in good yields the dimers [2,63,93,118]:

$$\begin{matrix}[\mathrm{Fe(CO)_5}]\\ \text{or}\\ [\mathrm{Ru_3(CO)_{12}}]\end{matrix} + \mathrm{C_9H_8} \rightarrow [\mathrm{M}(\eta^5\text{-}\mathrm{C_9H_7})(\mathrm{CO})_2]_2 + \mathrm{CO} + \mathrm{H_2} \quad (\mathrm{M} = \mathrm{Fe},\ \mathrm{Ru}) \quad (6)$$

$$[\mathrm{Ru_3(CO)_{12}}] + \mathrm{C_9H_5Me_3} \rightarrow [\mathrm{Ru}(\eta^5\text{-}\mathrm{C_9H_4Me_3})(\mathrm{CO_2})_2] + \mathrm{CO} + \mathrm{H_2} \quad (7)$$

Complexes of the type $[\mathrm{Ru}(\eta^5\text{-}\mathrm{C_9H_7})(\mathrm{EMe_3})(\mathrm{CO})_2]$ (E = Si, Ge) have been similarly prepared by the reaction of $[\mathrm{Ru(EMe_3)(CO)_4}]_2$ with $\mathrm{C_9H_8}$ [72].

The fate and the yields of these thermal processes depend upon the reaction conditions. Thus, by heating under reflux a solution of $[\mathrm{Ru_3(CO)_{12}}]$ and indene in methylcyclohexane the reaction leads to the formation of the cluster complex $[\mathrm{Ru_4}(\mu_3\text{-}\eta^2{:}\eta^5{:}\eta^2\text{-}\mathrm{C_9H_7})(\eta^5\text{-}\mathrm{C_9H_9})(\mathrm{CO})_7(\mu\text{-}\mathrm{CO})_2]$ [93] in low yield while $[\mathrm{Os_3(CO)_{12}}]$ with 1,3-diethylindene in refluxing nonane for 8 h. gives the tetranuclear complex $[\mathrm{Os_4H}(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^5\text{-}\mathrm{C_9H_5Et_2})(\mathrm{CO})_9]$ [101].

4. Redox processes

4.1. Reduction of $[M(\eta^5\text{-}C_9H_7)(CO)_2]_2$

Anionic carbonylates $[\mathrm{M}(\eta^5\text{-}\mathrm{C_9H_7})(\mathrm{CO})_2]^-$ are easily prepared by reduction of the corresponding dimers $[\mathrm{M}(\eta^5\text{-}\mathrm{C_9H_7})(\mathrm{CO})_2]_2$ using the classical treatment with 1%

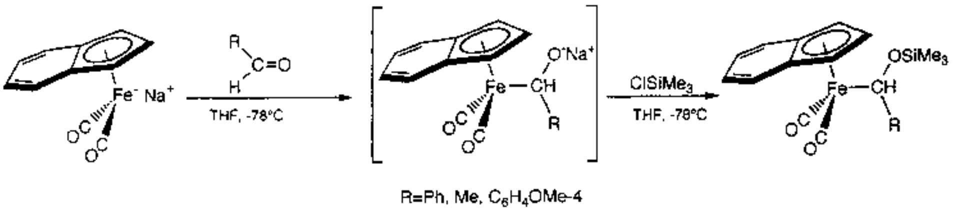
Na (or K)/Hg in THF solution in an inert atmosphere (M = Fe [37], Ru [100]). Although these sodium or potassium salts are not isolated they can be used in situ for further transformations. The analogous lithium salts Li $[Fe(\eta^5\text{-}C_9H_6\text{–}R)(CO)_2]$ (R = Si_xMe_y) can be also generated from base-induced additions of the silyl group to the indenyl ligand (vide infra) [39].

4.1.1. *Reactivity of anionic complexes* $[M(\eta^5\text{-}C_9H_7)(CO)_2]^-$ *(M = Fe, Ru)*

A THF solution of the iron carbonylate complex $M'[Fe(\eta^5\text{-}C_9H_7)(CO)]_2^1$ (M′ = Li, Na) irreversibly incorporates CO (1 atm) affording the stable complex $[Fe(\eta^3\text{-}C_9H_7)(CO)_3]^-$ isolated as its PPN^+ salt. An X-ray crystal structure determination confirms the unusual η^3-indenyl coordination [100]. The complex has proven to be a good precursor for insertion reactions (vide infra) and also reacts with Ph_3SnCl to give $[Fe(\eta^5\text{-}C_9H_7)(SnPh_3)(CO)_2]$. Furthermore, the reaction of a solution of the sodium salt complex in THF-d_8 with glacial acetic acid at − 40°C has been studied by ^{1}H-NMR [36]. Along with proton resonances of the indenyl ring, assigned to the presence of the hydride complex $[Fe(\eta^5\text{-}C_9H_7)H(CO)_2]$, the spectrum also shows resonances which can be compared to those of $[V(\eta^3\text{-}C_9H_7)H(CO)_3]^-$ supporting the formation of the hydride species $[Fe(\eta^3\text{-}C_9H_7)H(CO)_3]$.

The relatively strong nucleophilicity of the iron carbonylate species allows a wide series of nucleophilic substitutions in alkyl and aryl halides leading to the formation of σ-M–C bonds. Thus, the treatment of a solution of $[Fe(\eta^5\text{-}C_9H_7)(CO)_2]^-$ with RI (R = Me [37], ^{i}Pr [40], Et, C_3H_7 [43], C_3H_5, $CH_2C(CH_3){=}CH_2$ [46]) gives the corresponding alkyl iron(II) indenyl complexes $[Fe(\eta^5\text{-}C_9H_7)R(CO)_2]$. The methyl and isopropyl derivatives were isolated as air sensitive oils. Related complexes (R = CH_2COMe, $CH_2N(C_8H_4O_2)$ [43], CH_2Ph [42], (R = 3-chloroquinoxaline) [47], $[Fe(\eta^5\text{-}C_9H_6R)(Me)(CO)_2]$ (R = Me, ^{t}Bu) [38] and the unstable π-allyl complexes $[M(\eta^5\text{-}C_9H_7)(\eta^3\text{-}C_3H_5)(CO)]$ (M = Fe, Ru) [60] are similarly obtained. Moreover, the ^{13}C-labelled (95–99%) acetyl complex $[Fe\{^{13}C(O)Me\}(\eta^5\text{-}C_9H_7)(CO)_2]$ has been prepared by acylation with $Me^{13}COCl$ [120].

Unstable α-alkoxyalkylcomplexes $[Fe(CH_2OR)(\eta^5\text{-}C_9H_7)(CO)_2]$ (R = Me; Et) have been spectroscopically characterized and isolated as unstable solids [49]. In contrast, the analogous α-siloxyalkyl complexes $[Fe(\eta^5\text{-}C_9H_7)\{CH(OSiMe_3)R\}(CO)_2]$ are stable and can be synthesized in moderate yields through the nucleophilic addition of $M'[Fe(\eta^5\text{-}C_9H_7)(CO)_2]$ (M′ = Na, K) to aldehydes RCHO (R = Ph, C_6H_4OMe-4, Me) followed by the treatment with Me_3SiCl [50] (Scheme 1).



Scheme 1.

By using a similar synthetic approach Pannell et al. have described the reactions with silyl and silylmethylchlorides which afford a wide series of silyl and oligosilyl complexes of the following types: (a) $[Fe(\eta^5\text{-}C_9H_7)E(CO)_2]$ ($E = SiMe_3$, Si_2Me_5, Si_3Me_7, Si_4Me_9, $c\text{-}Si_6Me_{11}$) [39,51]; (b) triphenyl(dimethyl)disilane isomers $[Fe(\eta^5\text{-}C_9H_7)(Si_2Me_2Ph_3)(CO)_2]$ [52]; (c) monosilyl complexes $[Fe(\eta^5\text{-}C_9H_7)(SiMe_n\text{-}Ph_{3-n})(CO)_2]$ ($n = 0–2$) obtained from complexes of type (b) via elimination of silylene fragments by UV irradiation; (d) di- or tri-silylmethyl complexes $[Fe(\eta^5\text{-}C_9H_7)E(CO)_2]$ ($E = CH_2Si_2Me_5$, $CH_2Si_3Me_7$) [44,45] and related iron–tin derivatives $[Fe(\eta^5\text{-}C_9H_6R)(SnPh_3)(CO)_2]$ ($R = SiMe_3$, Si_2Me_5, Si_3Me_7, Si_4Me_9, $c\text{-}Si_6Me_{11}$) [39] $[Fe(\eta^5\text{-}C_9H_7)(SnR_3)(CO)_2]$ (R = Me, Ph) which are synthesized analogously using triphenyl or trimethyltinchloride, are also known [53].

The potential synthetic utility of the iron carbonylate complex is evidenced in the reaction with η^6-phenylfluoride chromium complex $[Cr(\eta^6\text{-}C_6H_4F)(CO)_3]$ which leads through the nucleophilic substitution of fluoride to the complex $[Fe(\eta^5\text{-}C_9H_7)(CO)_2(\mu\text{-}\eta^1\text{:}\eta^6\text{-}Ph)Cr(CO)_3]$ [69].

4.2. Oxidative addition and other oxidation processes

The dimers $[M(\eta^5\text{-}C_9H_7)(CO)_2]_2$ undergo typical oxidative addition processes with bromine and iodine via cleavage of the metal–metal bond to give the halide metal(II) derivatives $[M(\eta^5\text{-}C_9H_7)X(CO)_2]$ in good yields (M = Fe; X = Br [33]; X = I [2,34]; M = Ru, X = I [71]). Similarly the treatment of $[Ru(\eta^5\text{-}C_9Me_3R_4)(CO)_2]_2$ with bromine and iodine gives $[Ru(\eta^5\text{-}C_9Me_3R_4)X(CO)_2]$ (X = Br, I; R = H; X = Br; R = Me) [118]. Formal oxidative additions of tin (II) halides to the iron dimer lead to the formation of a series of complexes containing Fe–Sn bonds such as $[Fe(\eta^5\text{-}C_9H_7)(SnX_3)(CO)_2]$ (X = Cl, Br, I), and $[\{Fe(\eta^5\text{-}C_9H_7)(CO)_2\}_n(SnX_{4-n})]$ ($n = 2$, 3) [34].

The dimer $[Fe(\eta^5\text{-}C_9H_7)(CO)_2]_2$ can be oxidized with chemical oxidants such as $[Fe(\eta^5\text{-}C_5H_5)_2]^+$ and $[Ph_3C]^+$ in CH_2Cl_2, acetone or THF. The oxidations are very rapid in contrast to the long reaction times required for the analogous $\eta^5\text{-}C_5H_5$ and $\eta^5\text{-}C_5Me_5$ complexes. Although the attempts to isolate the solvent complexes $[Fe(\eta^5\text{-}C_9H_7)S(CO)_2]^+$ were unsuccessful, the reactions led to the formation of the $[Fe(\eta^5\text{-}C_9H_7)(CO)_3]^+$ even in the absence of CO (yields 55–60% with $[Ph_3C][BF_4]$ in CH_2Cl_2) [33]. An X-ray crystal structure was later reported [61]. In the presence of nucleophiles this tricarbonyl derivative undergoes typical rapid ligand CO substitution (vide infra). The reduction of $[Fe(\eta^5\text{-}C_9H_7)(CO)_3]^+$ with $NaBH_4$ and $Na[BH_3CN]$ in acetone have been studied by IR and ^{1}H-NMR at variable temperatures. Spectroscopic evidence of the formation of the complex $[Fe(\eta^3\text{-}C_9H_7)H(CO)_3]$ from the reaction with $Na[BH_3CN]$ at −40°C was reported. At −10°C this complex loses CO to form $[Fe(\eta^5\text{-}C_9H_7)H(CO)_2]$ which at room temperature is rapidly transformed into the dimer $[Fe(\eta^5\text{-}C_9H_7)(CO)_2]_2$ [36]. In contrast the reaction with sodium borohydride at −80°C leads to the transient formation of the formyl complex $[Fe(\eta^5\text{-}C_9H_7)(CHO)(CO)_2]$ (via nucleophilic addition to the carbonyl group) which is only stable below −55°C. On raising the temperature the spectroscopic data indicate the formation of the hydride species $[Fe(\eta^5\text{-}C_9H_7)H(CO)_2]$ which remains in solution up to −10°C [35].

Sandwich methyl substituted indenyl iron(II) derivatives can be also oxidized to form stable iron(III) cationic paramagnetic complexes of the types: (i) $[Fe(\eta^5\text{-}C_9H_5Me_2\text{-}1,3)_2]^+$ obtained from the treatment of $[Fe(\eta^5\text{-}C_9H_5Me_2\text{-}1,3)_2]$ with HCl or $AgPF_6$. The structure of the hexafluorophosphate salt has been determined by X-ray diffraction [15]. (ii) $[Fe(\eta^5\text{-}C_9Me_7)_2][PF_6]$ synthesized from the reaction of $[Fe(\eta^5\text{-}C_9Me_7)_2]$ with $[Fe(\eta^5\text{-}C_5H_5)_2][PF_6]$. EPR and magnetic susceptibility experiments were reported [17].

4.3. Electrochemical and charge-transfer processes

Information on electrochemical potentials of redox couples determined by cyclic voltammetry (CV) have been reported for a wide number of indenyl derivatives. Oxidation potential data of complexes of the type $[Ru(\eta^5\text{-}C_9H_7)XLL']$ are known [78]. Comparison of these data with those of the corresponding cyclopentadienyl derivatives indicates a sequence of oxidation potentials such as $\eta^5\text{-}C_5Me_5 \leq \eta^5\text{-}C_9H_7 < \eta^5\text{-}C_5H_5$. This is in accord with photoelectron spectroscopy studies [9e] and infrared data [40] which show that the indenyl ligand is a stronger electron donor than the cyclopentadienyl ring (i.e. 0.43, 0.45, 0.56 V for $[Ru(\eta^5\text{-}C_5Me_5)Cl(PPh_3)_2]$, $[Ru(\eta^5\text{-}C_9H_7)Cl(PPh_3)_2]$ and $[Ru(\eta^5\text{-}C_5H_5)Cl(PPh_3)_2]$, respectively).

Several reports on electrochemical behaviour (CV) of other indenyl iron, ruthenium and osmium complexes are known, including: (a) $[Fe(\eta^5\text{-}C_9H_7)(CO)_2(\mu\text{-}\eta^1{:}\eta^6\text{-}Ph)Cr(CO)_3]$ [69]; (b) carborane complexes such as $[Fe(\eta^5\text{-}C_9H_7)(Et_2C_2B_4H_4)]^-$ and $[Fe(\eta^5\text{-}C_9H_7)(Et_2C_2B_4H_4)]$ [22]; and (c) sandwich complexes of the types: (i) $[Fe(\eta^5\text{-}C_9H_7)L]$ ($L = \eta^5\text{-}C_9H_7$, $\eta^5\text{-}C_5H_5$) and $[Fe(\eta^5\text{-}C_9H_5RR')_2]$ ($R = H$, $R' = Me$; $R = R' = Me$) [14]; it is shown that the ease of oxidation follows the sequence $[Fe(\eta^5\text{-}C_9H_7)_2] > [Fe(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_5H_5)] > [Fe(\eta^5\text{-}C_5H_5)_2]$ and $[Fe(\eta^5\text{-}C_9H_5Me_2\text{-}1,3)_2] > [Fe(\eta^5\text{-}C_9H_6Me\text{-}1)_2] > [Fe(\eta^5\text{-}C_9H_7)_2]$; (ii) $[M(\eta^5\text{-}C_9H_7)L]$ ($M = Ru$; $L = \eta^5\text{-}C_9H_7$, $\eta^5\text{-}C_5H_5$, $\eta^5\text{-}C_5Me_5$ ($M = Os$, $L = \eta^5\text{-}C_9H_7$) [32]; (iii) $[Ru(\eta^5\text{-}C_9H_7)(\eta^6\text{-}C_6H_6)]^+$ [29]; (iv) $[Fe(\eta^5\text{-}C_9Me_7)_2]$ [17].

A detailed electrochemical study of $[Fe(\eta^5\text{-}C_9H_7)(CO)_3]^+$ by cyclic voltammetry has been reported [61]. It is shown that the reduction at 23°C under CO is characterized by two reversible one-electron couples corresponding to the formation of the relatively stable complex $[Fe(\eta^5\text{-}C_9H_7)(CO)_3]$ which undergoes a reversible second reduction to form $[Fe(\eta^5\text{-}C_9H_7)(CO)_3]^-$. In contrast, the cyclopentadienyl complex $[Fe(\eta^5\text{-}C_5H_5)(CO)_3]$ undergoes a rapid dissociation of CO to give the 17-electron species. This is in accord with the kinetic studies carried out in the substitution reactions of the indenyl complexes which show a slower rate (inverse indenyl effect: vide infra). The electrochemical behaviour of $[Fe(\eta^5\text{-}C_9H_7)(CO)_3]^+$ in the presence of nucleophiles L confirms that the CO substitution to give complexes $[Fe(\eta^5\text{-}C_9H_7)(CO)_2L]^+$ (vide infra) proceeds through an ETC mechanism in which the 19-electron species $[Fe(\eta^5\text{-}C_9H_7)(CO)_3]$ undergoes a dissociative substitution.

Chiral iron(II) complex $(R_{Fe}S_C)$-$[Fe(\eta^5\text{-}C_9H_7)(Me)(CO)L]$ ($L = (S)\text{-}(+)\text{-}P(Ph)_2N(Me)CH(Me)Ph$) undergoes electrocatalytic epimerization both via oxidation and reduction [58]. Thus, by using sodium amalgam as a reducing agent an epimerization occurs at $-35°C$ in THF. This transformation is the result of the electron transfer to give a 19-electron anion which loses the phosphine. The resulting 17 electron species changes the configuration before the coordination of the dissociated phosphine and transfer of the electron back to the catalyst completing the catalytic cycle. $[Fe(\eta^5\text{-}C_5H_5)_2]^+$ only induces an incomplete epimerization at $+20°C$ after 30 min. The cyclovoltammogram of the complex is in agreement with this chemical behaviour.

Addition of a solution of $[Fe(\eta^5\text{-}C_9Me_7)_2]$ to solutions containing polycyano acceptor molecules A (A = TCNE (tetracyanoethylene), TCNQ (7,7,8,8-tetracyano-*p*-quinodimethane), DDQ(2,3-dichloro-5,6-dicyanobenzoquinone)) results in the formation of 1:1 charge transfer salts $[Fe(\eta^5\text{-}C_9Me_7)_2]^+[A]^-$ [23]. The structure of the complex $[Fe(\eta^5\text{-}C_9Me_7)_2][TCNQ]$ has been determined by X-ray diffraction. Solid state magnetic susceptibilities and EPR spectra are also reported.

5. Ligand exchange reactions in $[M(\eta^5\text{-}C_9H_7)XL_2]$ (M = Fe, Ru, Os; X = Cl, Br)

5.1. Exchange of halides

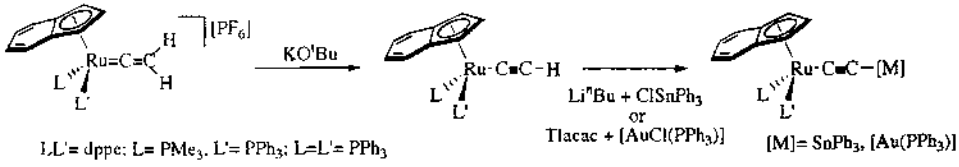
5.1.1. Neutral derivatives

Most of the precursor complexes for the exchange reactions of X by other anionic nucleophiles are the chloride derivatives. The metathesis for other halides or pseudo halides takes place in polar solvents. The synthesis of the complexes $[Ru(\eta^5\text{-}C_9H_7)I(PPh_3)_2]$ [77], $[Ru(\eta^5\text{-}C_9H_7)(CN)(PPh_3)_2]$ [80] illustrate this synthetic approach. The exchange reactions for alkoxides provide the best synthesis of the hydride derivatives. In typical examples [75,77] the treatment of $[Ru(\eta^5\text{-}C_9H_7)ClL_2]$ ($L = PPh_3$; L_2 = dppm) with NaOMe in refluxing methanol gives $[Ru(\eta^5\text{-}C_9H_7)HL_2]$ likely through the initial formation of the methoxide complex which undergoes a rapid β-hydrogen elimination to give the hydride complex and the simultaneous formation of formaldehyde.

Nucleophilic substitutions by anionic metalates such as $[Co(CO)_4]^-$ and $[Re(CO)_5]^-$ lead to the formation of metal–metal bonds in the complexes $[Fe(\eta^5\text{-}C_9H_7)(CO)(\mu\text{-}CO)_2Co(CO)_3]$ [66,67] and $[Fe(\eta^5\text{-}C_9H_7)(CO)_2Re(CO)_5]$ [68].

Although most of the complexes containing σ-M–C bonds have been synthesized from the reaction of metalate anions with alkyl and benzyl halides (vide supra) a series of alkynyl complexes namely $[Ru(\eta^5\text{-}C_9H_7)(C{\equiv}CR)L_2]$ (R = Ph; $L = PPh_3$) [77] (R = ^{t}Bu, ^{n}Pr; $L = PPh_3$, L_2 = dppm, dppe) [82] (R = Ph; L_2 = dppp, dppb; R = ^{n}Bu, Cy, *p*-Tol; $L = PPh_3$) [81] have been prepared from the reaction of different indenyl halide complexes with lithium or potassium alkynyl salts (generally generated in situ from a mixture in THF or methanol of the terminal alkyne and Li^{n}Bu or KOH, respectively).

An alternative route for the synthesis of alkynyl complexes (i.e. $[Ru(\eta^5\text{-}C_9H_4Me_3)(C{\equiv}CPh)(CO)(PPh_3)]$ [73], $[Ru(\eta^5\text{-}C_9H_7)(C{\equiv}CR)(PPh_3)_2]$ [80,82,92], $[Os(\eta^5\text{-}C_9H_7)(C{\equiv}CR)(PPh_3)_2]$ [96]) is based on the deprotonation of the corresponding cationic vinylidene derivatives which may be generated in situ from the reaction



Scheme 2.

of the halide complex with the terminal alkyne in the presence of a halide abstractor (vide infra and Scheme 9). This synthetic procedure is especially useful for the preparation of the acetylide complexes [Ru(η^5-C_9H_7)(C≡CH)L_2] which are formed from the deprotonation of [Ru(η^5-C_9H_7)(=C=CH_2)L_2]$^+$ (L_2 = dppe; L_2 = PMe_3, PPh_3; L = $2PPh_3$) [82]. The acetylide complexes are used as precursors of bimetallic species containing the ethynediyl group as bridging ligand of the types [Ru(η^5-C_9H_7)(C≡C–M)L_2] (M = $SnPh_3$, $AuPPh_3$) (Scheme 2) [83].

An analogous iron–molybdenum bimetallic species [Fe(η^5-C_9H_7){C≡C(thiop)-C≡C–Mo (η^5-C_5H_5)$(CO)_3$}$(CO)_2$] (thiop = 2,5-substituted thiophene) containing a bis-acetylide bridging system has been also isolated [70].

It was found that the treatment of the alkynyl complex, [Ru(η^5-C_9H_7)(C≡CPh)$(PPh_3)_2$], with NO in the presence of $NaClO_4$ affords [Ru(η^5-C_9H_7)(CO)$(PPh_3)_2$][ClO_4] and benzonitrile. The reaction was rationalized as a formal metathesis reaction of the acetylide group which proceeds through the cycloaddition of NO to the triple C≡C bond followed by the opening of the cycle to give the carbonyl complex and the nitrile [81].

5.1.2. Cationic derivatives

A large series of cationic complexes of general formula [Ru(η^5-C_9H_7)$(PPh_3)_2$L′]$^+$ and [Ru(η^5-C_9H_7)(PPh_3)(L–L)]$^+$ have been described. They are generally obtained through the abstraction of the halide group from the precursor complexes [M(η^5-C_9H_7)XL_2] in the presence of the entering ligand [77,79]. These include complexes with typical two-electron L′ (L′ = CO, CNR, C_2H_4, N-donor ligands and four-electron chelate ligands (L–L = diolefins, bidentate N-donor ligands) [77] and P–O ketophosphines $Ph_2PCH(R)C(O)R'$ [79]. The complex [Ru(η^5-C_9H_7)(PPh_3)-{κ^2(*P*,*O*)-$Ph_2PCH(Me)C(^tBu)$=O}][PF_6] has been obtained diastereoselectively and identified by X-ray crystallography as the enantiomeric pair $S_{Ru,}R_C/R_{Ru},S_C$ [79]. Complexes of the type [Ru(η^5-C_9H_7)L′(L–L)]$^+$ (L′ = CO, PMe_2Ph; L–L = (*R*,*R*) or (*S*,*S*)-$Ph_2PCH(Me)CH(Me)PPh_2$ [76]) have been also described. Direct substitution of iodide occurs in the thermal reactions of [M(η^5-C_9H_7)I$(CO)_2$] (M = Fe, Ru) with phosphines, in the presence of [Fe(η^5-C_5H_5)$(CO)_2$]$_2$ as catalyst, to give the cationic species [M(η^5-C_9H_7)$(CO)_2$L]I (M = Fe; L = PMe_2Ph, $PMePh_2$, PPh_3, $P(CH_2Ph)_3$, $P(OMe)_2Ph$). M = Ru; L = $P(OC_6H_4Me\text{-}2)_3$) which were isolated as insoluble salts [55,71].

5.2. Carbonyl substitutions

5.2.1. Neutral derivatives

Seminal work on the reactivity of indenyl Group 8 metal complexes was concerned with carbonyl substitution reactions in complexes $[Fe(\eta^5\text{-}C_9H_7)I(CO)_2]$ by $P(OR)_3$ which yield monocarbonyl complexes $[Fe(\eta^5\text{-}C_9H_7)I(CO)\{P(OR)_3\}]$ (R = Et, Ph) [2]. Kinetic studies show that the reactions proceed through a S_N1 mechanism (vide infra). Some years later analogous phosphite (R = Me, ^{i}Pr, $C_6H_4Me\text{-}2$) and phosphine complexes $[Fe(\eta^5\text{-}C_9H_7)I(CO)L]$ (L = PPh_3, $P(CH_2Ph)_3$, $P(OMe)_2Ph$, $P(OMe)Ph_2$, PMe_2Ph, $PMePh_2$) were prepared and spectroscopically characterized [55]. They have been obtained by the thermal reaction of $[Fe(\eta^5\text{-}C_9H_7)I(CO)_2]$ with the ligands L. For L = phosphines, intermediate insoluble salts $[Fe(\eta^5\text{-}C_9H_7)(CO)_2L]I$ were isolated (vide supra) which undergo, by heating in the presence of $Me_3NO.2H_2O$, an exchange of CO by the iodide anion to give the neutral complexes. Similar ruthenium monocarbonyl complexes $[Ru(\eta^5\text{-}C_9H_7)I(CO)L]$ (L = $PMePh_2$, PPh_3, $P(CH_2Ph)_3$; L = $P(OR)_3$ R = Me, Et, ^{i}Pr, $C_6H_4Me\text{-}2$) [71], $[Ru(\eta^5\text{-}C_9H_7)I(CO)(PCy_3)]$, $[Ru(\eta^5\text{-}C_9H_4Me_3)I(CO)(PR_3)]$ (R = Ph, ^{i}Pr) and all substituted complexes $[Ru(\eta^5\text{-}C_9H_4Me_3)I\{\kappa^2\text{-}(P,P)\text{-dppm}\}]$ [124] and $[Ru(\eta^5\text{-}C_9H_7)Cl(L\text{–}L)]$ (L–L = (*R*,*R*)-$Ph_2P\overline{CH(CH_2)_3C}HPPh_2$ or (*S*,*S*)-$Ph_2PCH(Me)CH(Me)PPh_2$) [76] (prepared from $[Ru(\eta^5\text{-}C_9H_7)Cl(COD)]$), are also known. The photochemical reactions of $[Fe(\eta^5\text{-}C_9H_7)(Me)(CO)_2]$ in the presence of PPh_3 proceed with the evolution of CO leading to the formation of the monocarbonyl derivative $[Fe(\eta^5\text{-}C_9H_7)(Me)(CO)(PPh_3)]$. Analogous reactions with the optically active phosphines L = (*S*)-(+)-$P(Ph)_2N(Me)\text{–}CH(Me)Ph$ proceed via substitution of one of the two enantiotopic CO groups to give a diastereoisomeric 50:50 mixture of $R_{Fe}S_C$ and $S_{Fe}S_C$-$[Fe(\eta^5\text{-}C_9H_7)(Me)(CO)L]$. The absolute configuration of the isomer $R_{Fe}S_C$ has been determined by X-ray crystallography [58]. Kinetic studies on the epimerization processes were also carried out (vide infra). Analogous complexes $[Fe(\eta^5\text{-}C_9H_6R)(Me)(CO)L]$ (R = Me-1, ^{t}Bu-1) are obtained as a mixture of four diastereoisomers some of which can be separated by liquid chromatography [38]. π-Olefin complexes $[Fe(\eta^5\text{-}C_9H_7)(SnR_3)(CO)(olefin)]$ (R = Me, Ph; olefi*n* = C_2H_4, C_3H_6) are obtained via irradiation of the dicarbonyl complexes $[Fe(\eta^5\text{-}C_9H_7)(SnR_3)(CO)_2]$ in the presence of the free olefin [53].

5.2.2. Cationic derivatives

The best route for the synthesis of cationic complexes of the type $[Fe(\eta^5\text{-}C_9H_7)(CO)_2L]^+$ and $[Fe(\eta^5\text{-}C_9H_7)(CO)(L\text{–}L)]^+$ in good yields starts from the tricarbonyl complex $[Fe(\eta^5\text{-}C_9H_7)(CO)_3]^+$, which can be generated from the dimer $[Fe(\eta^5\text{-}C_9H_7)(CO)_2]_2$ by oxidation with $[Ph_3C][BF_4]$ [33,61,62]. This complex readily loses one CO group at room temperature on reaction with a large range of two and four electron ligands (P-donors, N-donors). The presence of traces of NEt_3 (ca. 1 mol%) has been claimed to induce an immediate and quantitative conversion [61]. Surprisingly, these contributions do not report the reactions with olefins. These complexes $[Fe(\eta^5\text{-}C_9H_7)(CO)_2(olefin)]^+$ (olefin = C_2H_4, C_3H_6, $^iC_4H_8$) had been described previously [46] and synthesized by the treatment of the corresponding alkyl derivatives with trityl tetrafluoroborate (C_2H_4) or HBF_4 (C_3H_6).

5.3. Phosphine exchange

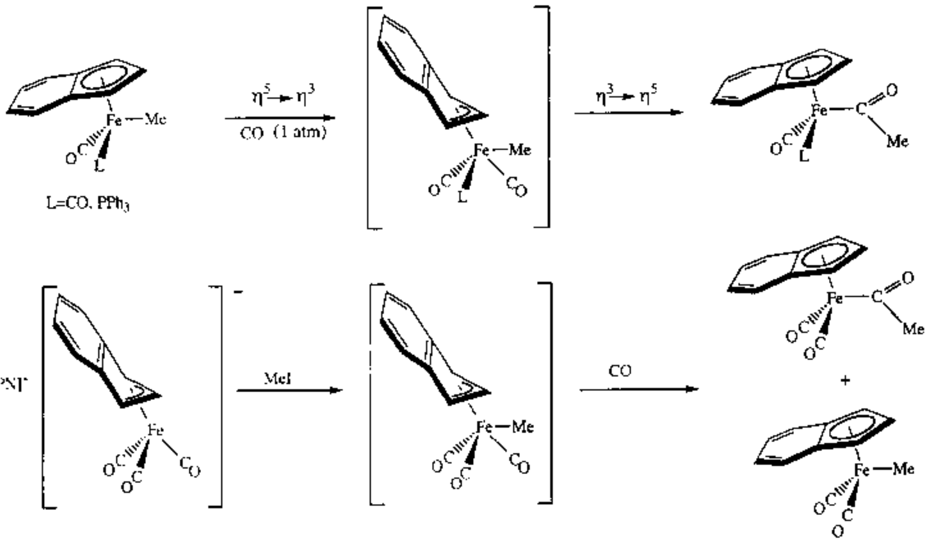
The complex [Ru(η^5-C_9H_7)Cl(PPh_3)$_2$] reacts in toluene or tetrahydrofuran with monodentate (L = $PMePh_2$, PMe_2Ph, PMe_3) or bidentate (L–L = dppm, dppe,) phosphines to give monosubstituted [Ru(η^5-C_9H_7)Cl(PPh_3)L], bisubstituted [Ru(η^5-C_9H_7)Cl(L)$_2$] or chelated complexes [Ru(η^5-C_9H_7)Cl(L–L)] [78]. The reaction with β-ketophosphines $Ph_2PCH(R')C(=O)R$ (R = ^{t}Bu. R′ = H, Me; R = Ph. R′ = H) affords the complexes [Ru(η^5-C_9H_7)Cl(PPh_3)(κ-(*P*)-ketophosphine)] [79]. Although the cyclopentadienyl complex [Ru(η^5-C_5H_5)Cl(PPh_3)$_2$] also undergoes a ready dissociation of triphenylphosphine ligands, a higher temperature or longer reaction time is required. In refluxing toluene PMe_3 and dppm give ionic products [Ru(η^5-C_9H_7)(PMe_3)$_3$]Cl and [Ru(η^5-C_9H_7)(PPh_3){κ^2-(*P*,*P*)-dppm}]Cl. The kinetics of PPh_3 substitution has been studied (vide infra).

6. Insertion reactions

6.1. Migratory insertions

Following the pioneering kinetic studies on the reaction of [Mo(η^5-C_9H_7)(Me)(CO)$_3$] with PPh_3 to give [Mo(η^5-C_9H_7)(COMe)(CO)$_2$(PPh_3)] [1a] a series of analogous migratory insertion reactions with the alkyl complexes [Fe(η^5-C_9H_7)R(CO)$_2$] was studied. First examples were reported in 1973 by Wojcicki [42] who described the reaction of the complex [Fe(η^5-C_9H_7)(CH_2Ph)(CO)$_2$] with SO_2 leading to the formation of the sulphinate complex [Fe(η^5-C_9H_7){κ-(*S*)-S(O)$_2$CH$_2$Ph}(CO)$_2$]. Since the reaction proceeds at a rate comparable to that of the cyclopentadienyl complex, ruling out the formation of the η^3-indenyl complex, an electrophilic attack of SO_2 on the α-carbon is proposed rather than a nucleophilic addition to the metal.

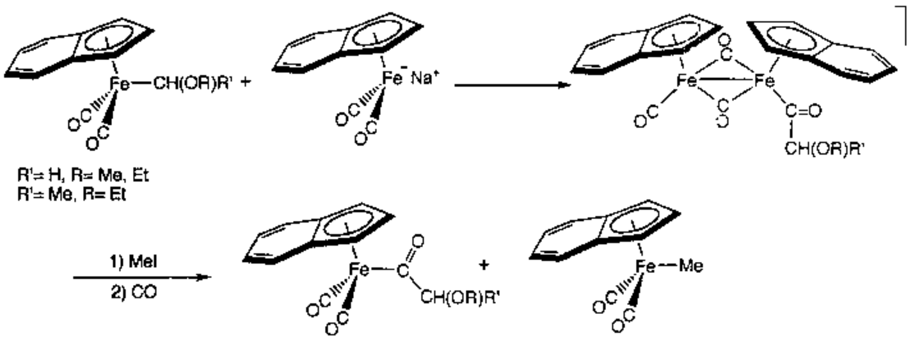
Some years later Cutler and co-workers, in the context of the studies on carbonylation reactions of methyl cyclopentadienyl complexes [Fe(η^5-C_5H_5)(Me)(CO)(L)] (L = CO, PPh_3), found that the incorporation of the indenyl ligand in place of cyclopentadienyl gives rise to a notorious ease in the formation of the corresponding acetyl complexes. In particular, [Fe(η^5-C_9H_7)(Me)(CO)(PPh_3)] was found to react in very mild reaction conditions (CO atmospheric pressure; room temperature) to give [Fe(η^5-C_9H_7)(COMe)(CO)(PPh_3)] (Scheme 3) [37,56]. Analogous complexes [Fe(η^5-C_9H_7)(COR)(CO)(PPh_3)] (R = Et, ^{n}Pr) are obtained in good yields by treatment of [Fe(η^5-C_9H_7)R(CO)$_2$] with PPh_3 in acetonitrile at reflux [43]. Deprotonation and alkylation of these acyl complexes generate 2-methylbutanoyl derivatives [Fe(η^5-C_9H_7){COCH(Me)Et)}(CO)$_2$] with high stereoselectivities. The role of the indenyl ring favoring the carbonylation was attributed to its ability to undergo a $\eta^5 \rightarrow \eta^3$ slippage promoting the associative reaction to give [Fe(η^3-C_9H_7)(Me)(CO)$_3$] as the intermediate in the subsequent methyl migration. Actually, it was found that this complex, generated from methylation of the anionic complex [PPN][Fe(η^3-C_9H_7)(CO)$_3$], reacts with CO to give the acyl derivative [Fe(η^5-C_9H_7)(COMe)(CO)$_2$] along with [Fe(η^5-C_9H_7)(Me)(CO)$_2$] [100a].



Scheme 3.

More recently Bassetti et al. have reported detailed studies on the synthesis of a series of acyl complexes [Fe(η^5-C_9H_7)(COR)(CO)L] (R = ^{i}Pr, Me), in the context of mechanistic and kinetic studies (vide infra) concerning the role of the indenyl effect in these migratory insertion reactions. The acyl complexes are readily obtained from the dicarbonyl complexes [Fe(η^5-C_9H_7)R$(CO)_2$] through the alkyl migration induced by phosphines (L = PR'_3, R′ = alkyl, aryl groups; L = Ph_2PCH_2-(aza-15 crown-5)) [40,59]. In general, these reactions show faster rates as compared to those of the analogous cyclopentadienyl complexes. An X-ray crystal structure of the complex [Fe(η^5-C_9H_7)($COCHMe_2$)(CO)(PPh_3)] is also reported. Analogous acyl complexes [Fe(η^5-C_9H_7)(COR)(CO)(L)] (R = Me, Et, ^{i}Pr, CH_2Ph) containing the chiral phosphine L = (*S*)-(+)-P$(Ph)_2$N(Me)CH(Me)Ph have been prepared. The pair of diastereomers *RS* and *SS* were separated by preparative liquid chromatography. The optically pure complexes are configurationally stable at room temperature. At higher temperatures they equilibrate with [Fe(η^5-C_9H_7)R$(CO)_2$] and epimerize with respect to the iron configuration [58b].

Stable binuclear anionic acetyl complexes [Fe(η^5-C_9H_7)(COMe)(μ-$CO)_2$Fe(η^5-C_9H_7)(CO)]$^-$ can be isolated as PPN$^+$ salts (PPN=Ph_3=N=PPh_3) from the reaction of metalate anions [Fe(η^5-C_9H_7)$(CO)_2$]$^-$ with [Fe(η^5-C_9H_7)(Me)$(CO)_2$]. The analogous complex [Fe_2(η^5-C_5H_5)(η^5-C_9H_7)(COMe)$(CO)_3$]$^-$ was also synthesized and isolated as a mixture of two isomers; one of them [Fe(η^5-C_9H_7)(CO)(μ-$CO)_2$Fe(η^5-C_5H_5)(COMe)]$^-$ was selectively crystallized and its structure was determined by X-ray diffraction [41]. Analogous alkoxymethyl complexes [Fe(η^5-C_9H_7)(CO)(μ-$CO)_2$Fe(η^5-C_9H_7)($COCH_2OR$)]$^-$ (R = Me, Et) have been also prepared [49]. The binuclear complexes react with MeI and CO (1 atm) to give the mononuclear derivatives [Fe(η^5-C_9H_7)($COCH_2OR$)$(CO)_2$] (Scheme 4). The synthe-



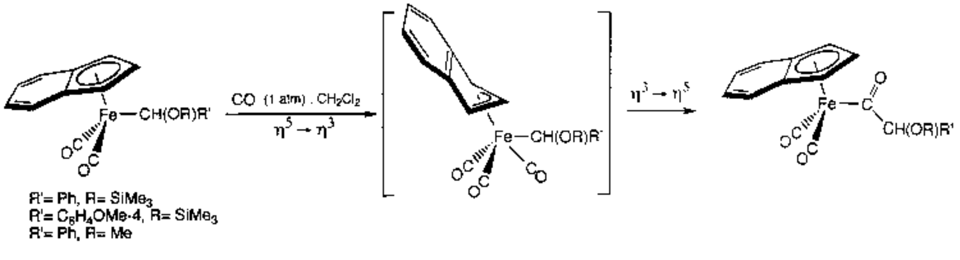
Scheme 4.

sis is also achieved in a one pot operation through the sequential treatment of the parent complexes with the metalate anion followed by CO/Me. In contrast direct carbonylation of the parent complexes does not occur up to 100 atm of CO.

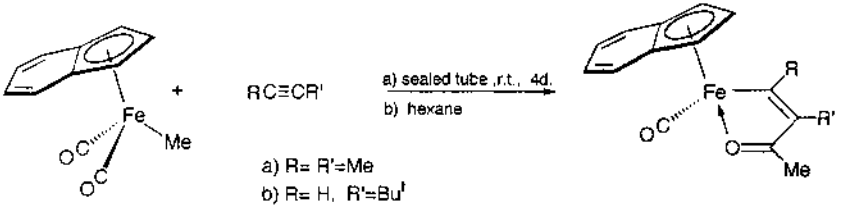
However, a direct method of carbonylation of α-alkoxyalkyl iron complexes under mild reaction conditions (1 atm, 6–16 h) which avoids the use of the anionic complex $[Fe(\eta^5\text{-}C_9H_7)(CO)_2]^-$ has also been reported (Scheme 5) [48]. The processes are surprisingly very simple and only 1 atm of CO at ambient temperature is required. In contrast the complexes $[Fe(\eta^5\text{-}C_9H_7)(CH_2Ph)(CO)_2]$ and $[Fe(\eta^5\text{-}C_9H_7)\{CH(OSiMe_3)Me\}(CO)_2]$ were found to be inert. It is interesting to note that the carbonylation of the related complex $[Mn\{CH(OSiMe_3)Ph\}(CO)_5]$ requires 2000 psi of CO gas at 25°C in THF (25% yield). It is suggested that the ease of carbonylation of the iron complexes is facilitated by the η^5 to η^3 indenyl slippage. This proposal is assessed by the unreactivity of the cyclopentadienyl complex $[Fe(\eta^5\text{-}C_5H_5)\{CH(OSiMe_3)Ph\}(CO)_2]$ under the same reaction conditions. It is apparent that these reactions are dependent on the combined effects of an indenyl ligand, a phenyl group and an α-siloxy/alkoxy substituent.

6.2. Insertion into the M–X bonds

Insertion reactions into M–C bonds of indenyl Group 8 metal complexes are very scarce. The only examples have been described for the methyl complex $[Fe(\eta^5\text{-}$



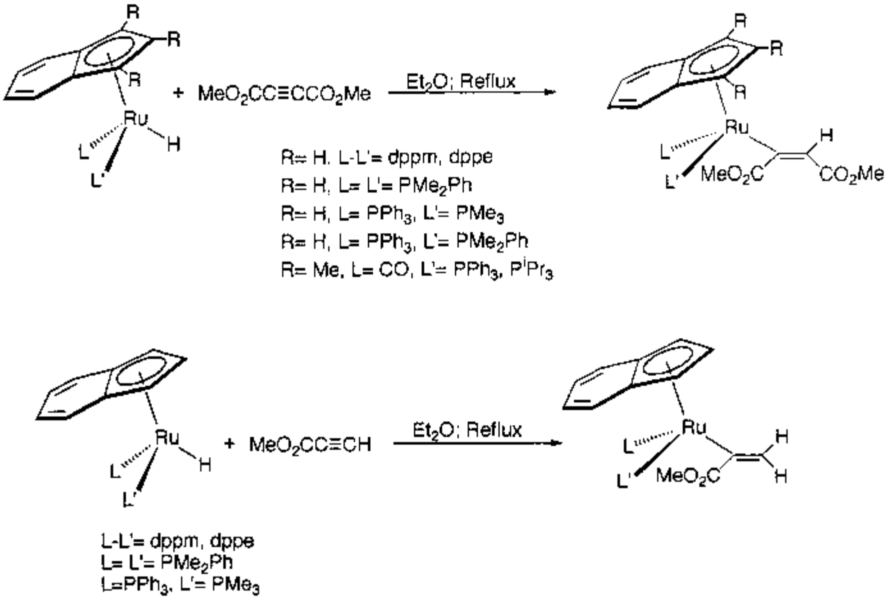
Scheme 5.



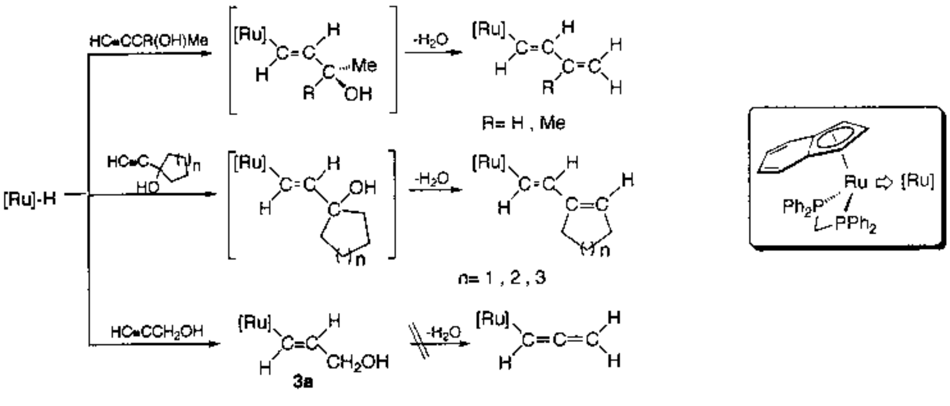
Scheme 6.

$C_9H_7)Me(CO)_2]$ which was found to react with 2-butyne and 3,3-dimethylbut-1-yne to give the corresponding vinyl ketone complexes (Scheme 6) [57]. The proposed mechanism is based on the initial formation of the acyl complex followed by the π-coordination of the alkyne to give the vinylketone complex after migration of the acyl group onto the coordinated alkyne. ^{1}H-NMR data support the regiochemistry of the coupling reaction.

Indenyl ruthenium hydride complexes of the type $[Ru(\eta^5\text{-}C_9H_7)XLL']$ react with phenylacetylide and activated alkynes leading to regio and stereoselective insertion products (Scheme 7) [75]. The reactions are strongly dependent on the ancillary ligands since only those complexes containing the less sterically demanding systems are reactive. Thus, $[Ru(\eta^5\text{-}C_9H_7)X\{\kappa^2\text{-}(P,P)dppm\}]$, X = H, D) react with phenylacetylene to give the products of the 1,2 insertion (*syn* addition) into the Ru–X bond $[Ru(\eta^5\text{-}C_9H_7)X\{(E)\text{-}CH{=}CXPh\}\{\kappa^2\text{-}(P,P)dppm\}]$. In contrast the cyclopenta-



Scheme 7.



Scheme 8.

dienyl complex [Ru(η^5-C_5H_5)H{κ^2-(*P*,*P*)dppm}] and the related indenyl complexes [Ru(η^5-C_9H_7)HLL′] (L,L′ = dppe; L,L′ = monodentate phosphines) do not react even under forcing conditions. A series of alkenylderivatives [Ru(η^5-C_9H_7){(*E*)-C(CO_2Me)=CH(CO_2Me)}LL′], [Ru(η^5-$C_9H_4Me_3$){(*E*)-C(CO_2Me)=CH(CO_2Me)}-(CO)(PR_3)] and [Ru(η^5-C_9H_7){(*E*)-C(CO_2Me)=CH_2}LL′] are obtained as the insertion products of the reactions with electron-withdrawing terminal alkynes dimethylacetylenedicarboxylate and methylpropiolate. A kinetic study for the reaction between [Ru(η^5-C_5H_5)H{κ^2-(*P*,*P*)dppm}] and phenylacetylene which shows an associative mechanism has also been carried out (vide infra).

The hydride complex [Ru(η^5-C_9H_7)H(κ^2-(*P*,*P*)dppm)] also reacts with propargylic alcohols HC≡CCR(OH)Me and cyclic alkynols to give in a regio and stereoselective manner vinylalkenyl complexes [Ru(η^5-C_9H_7){(*E*)-CH=CHCR=CH_2}(κ^2-(*P*,*P*)-dppm)] (Scheme 8). The reactions proceed through the regio and stereoselective insertion of the alcohols in the Ru–H bonds leading to transient hydroxyvinyl complexes which undergo a rapid dehydration process to give the final products. The hydroxyalkenyl complex [Ru(η^5-C_9H_7){(*E*)-CH=CHCH_2OH}{κ^2-(*P*,*P*)dppm}] is sufficiently stable towards the dehydration and can be isolated.

Formal insertion into the Ru–Cl bond has also been described in the formation of [Ru(η^5-C_9H_7)($SnCl_3$)(PPh_3)$_2$] from the reaction of [Ru(η^5-C_9H_7)Cl(PPh_3)$_2$] and $SnCl_2$ [77].

7. Carbene complexes

7.1. Vinylidene complexes

7.1.1. Synthesis

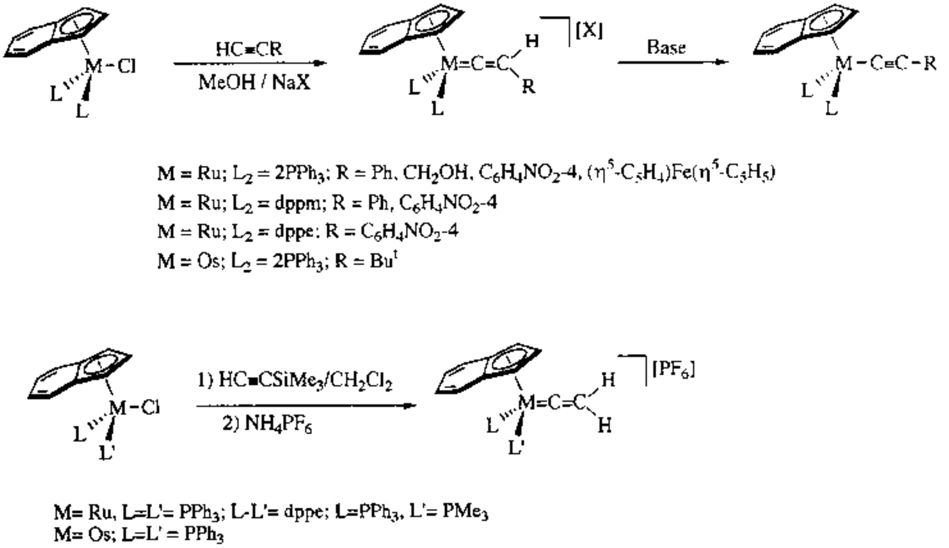
Only indenyl vinylidene ruthenium(II) and osmium (II) complexes [M(η^5-C_9H_7){=C=C(H)R}L_2][X] are known. They have been prepared in high yields by the classical methods:

1. Direct activation of terminal alkynes HC≡CR by an halide complex via the generation of unstable η^2-alkyne intermediates which tautomerize to the thermodinamically more stable vinylidene isomers (Scheme 9). The unsubstituted vinylidene complexes $[M(\eta^5\text{-}C_9H_7)(=C=CH_2)L_2][PF_6]$ have been prepared from $HC\equiv CSiMe_3$ and NH_4PF_6 which enables the cleavage of the C–Si bond [77,80,82,87,96,122,123]. These vinylidene derivatives can be readily deprotonated with mild bases to generate neutral σ-alkynyl complexes $[M(\eta^5\text{-}C_9H_7)(C\equiv CR)L_2]$ and $[M(\eta^5\text{-}C_9H_7)(C\equiv CH)L_2]$ in high yields (Scheme 9) [82,84,96].
2. The regioselective addition of electrophiles (HBF_4 or $MeOSO_2CF_3$) to the nucleophilic C_β atom of neutral σ-alkynyl derivatives (Scheme 10) [77,82,96].

Furthermore, dimethylvinylidene complexes $[Ru(\eta^5\text{-}C_9H_7)(=C=CMe_2)LL'][CF_3SO_3]$ can be regioselectively prepared by treatment of lithioalkynyl species $[Ru(C\equiv CLi)(\eta^5\text{-}C_9H_7)LL']$ (generated in situ) with an excess of $MeOSO_2CF_3$ (Scheme 10) [83]. A large series of vinylidene complexes have been also prepared through protonation of alkynyl functionalized complexes which are synthesized from nucleophilic additions to allenylidene complexes (vide infra).

7.1.2. Reactivity

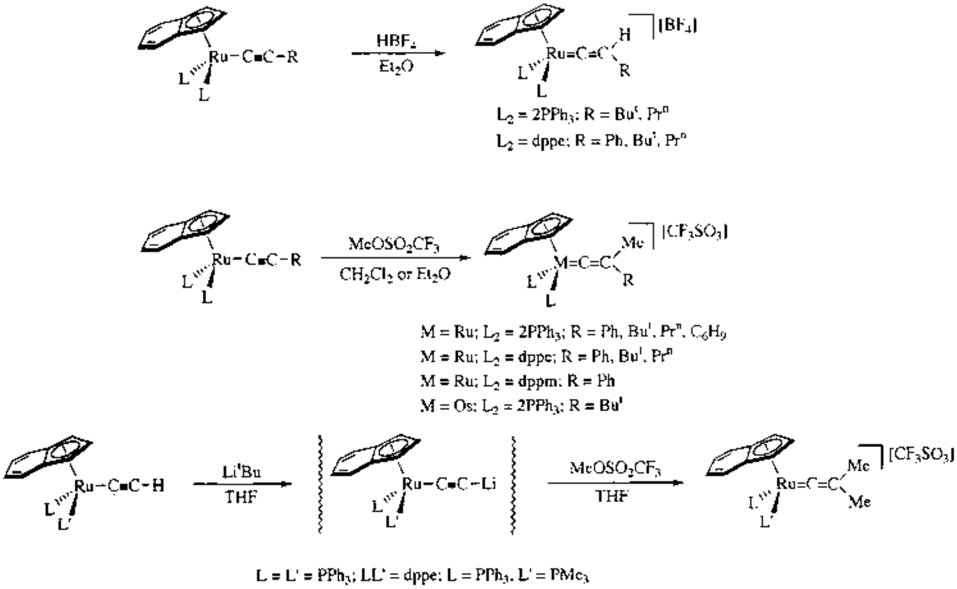
7.1.2.1. Nucleophilic additions of alcohols. The most significant reactions of cationic transition-metal vinylidene complexes are nucleophilic attacks of alcohols at the electrophilic C_α atom to afford Fischer type alkoxycarbene derivatives [124,125]. In accordance with this, the unsubstituted indenyl vinylidene ruthenium(II) complexes $[Ru(\eta^5\text{-}C_9H_7)(=C=CH_2)L_2][PF_6]$ react with methanol or ethanol to yield the Fischer



$M = Ru$; $L_2 = 2PPh_3$; $R = Ph, CH_2OH, C_6H_4NO_2\text{-}4, (\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)$
$M = Ru$; $L_2 = dppm$; $R = Ph, C_6H_4NO_2\text{-}4$
$M = Ru$; $L_2 = dppe$; $R = C_6H_4NO_2\text{-}4$
$M = Os$; $L_2 = 2PPh_3$; $R = Bu^t$

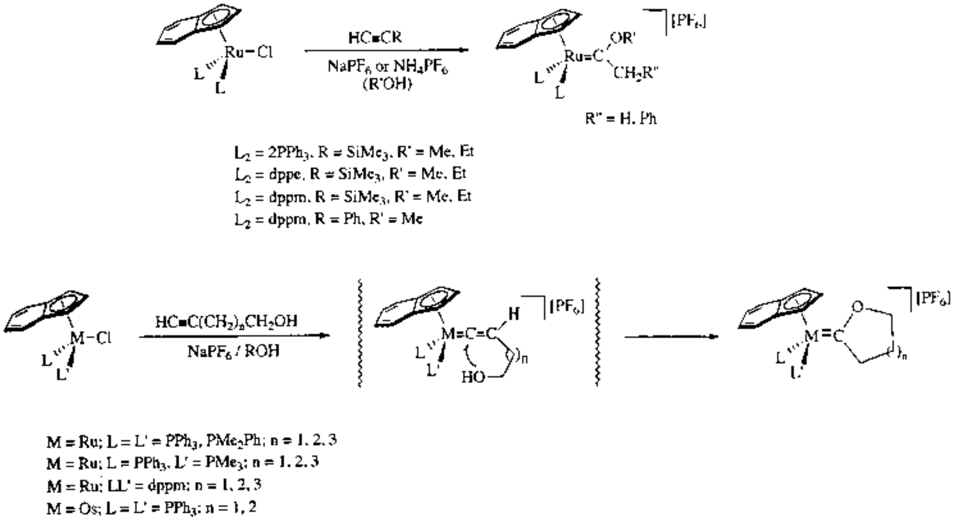
$M= Ru$, $L=L'= PPh_3$; $L\text{-}L'= dppe$; $L=PPh_3$, $L'= PMe_3$
$M= Os$; $L=L' = PPh_3$

Scheme 9.



Scheme 10.

type carbene derivatives [Ru(η^5-C_9H_7){=C(OR)Me}L_2][PF_6] (Scheme 11) [82]. These carbene species can be also prepared, via one-pot synthesis, by treatment of [Ru(η^5-C_9H_7)ClL_2] (L_2 = 2PPh_3, dppe, dppm) with HC≡CSiMe_3 and NH_4PF_6 in the corresponding alcohol. In contrast, the unsubstituted vinylidene [Os(η^5-



Scheme 11.

$C_9H_7)(=C=CH_2)(PPh_3)_2][PF_6]$ is unreactive towards alcohols exhibiting the typical inertness of osmium derivatives [96].

The influence of the substituents on the ability of the vinylidene moiety to undergo nucleophilic additions to the C_α atom is clearly shown by the behaviour of monosubstituted vinylidene complexes $[Ru(\eta^5\text{-}C_9H_7)\{=C=C(H)R\}L_2][PF_6]$ ($L_2 =$ $2PPh_3$, dppe) which are unreactive towards methanol or ethanol (used as solvents in their synthesis) [77,80,82,87,122,123].

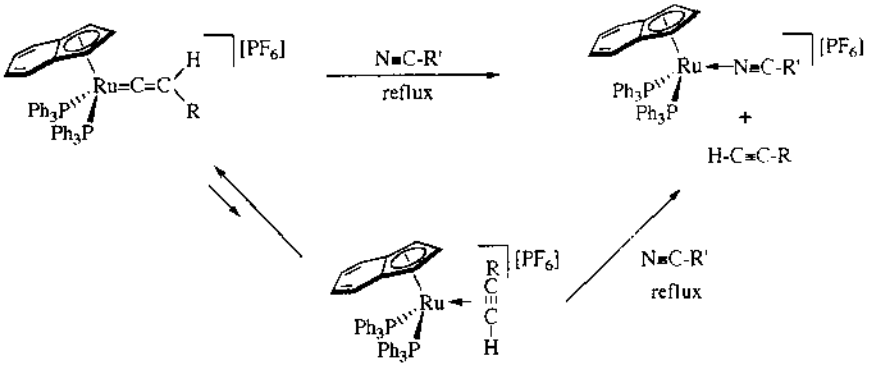
In contrast, the analogous complex $[Ru(\eta^5\text{-}C_9H_7)\{=C=C(H)Ph\}\{\kappa^2\text{-}(P,P)\text{dppm}\}][PF_6]$, containing the small-bite chelating dppm ligand, reacts with methanol to give $[Ru(\eta^5\text{-}C_9H_7)\{=C(OMe)CH_2Ph\}\{\kappa^2\text{-}(P,P)\text{dppm}\}][PF_6]$ [82], showing the steric influence of the auxiliary phosphine ligands. The related aminocarbene complex $[Ru(\eta^5\text{-}C_9H_7)\{=C(NH_2)Me\}\{\kappa^2\text{-}(P,P)\text{dppm}\}][PF_6]$ has also been prepared [82].

The reactions of alkynols $HC{\equiv}C(CH_2)_nCH_2OH$=with $[M(\eta^5\text{-}C_9H_7)ClLL']$ ($M =$ Ru, Os) affords in a one-pot synthesis cyclic carbene complexes (Scheme 11). Recently, the analogous cyclic carbene derivative $[Ru(\eta^5\text{-}C_9H_4Me_3)\{=\overline{CH_2CH_2CH_2O}\}(CO)(PPh_3)][BF_4]$ has also been obtained in our laboratory [121]. The reactions proceed via initial formation of vinylidene derivatives $[M(\eta^5\text{-}C_9H_7)\{=C=C(H)(CH_2)_nOH\}(PPh_3)_2][PF_6]$, followed by an intramolecular attack of the terminal alcohol group at the α-carbon of the vinylidene chain [82,96]. However, the treatment of $[Os(\eta^5\text{-}C_9H_7)Cl(PPh_3)_2]$ with $HC{\equiv}C(CH_2)_4OH$ gives instead the vinylidene complex $[Os(\eta^5\text{-}C_9H_7)\{=C=CH(CH_2)_4OH\}(PPh_3)_2][PF_6]$ which is stable towards the cyclization [96].

It should be noted that the related iron(II) ethoxycarbene complex $[Fe(\eta^5\text{-}C_9H_7)\{=C(OEt)Me\}(CO)_2][PF_6]$, obtained by alkylation of the acetyl compound $[Fe(\eta^5\text{-}C_9H_7)(COMe)(CO)_2]$ with triethyloxonium hexafluorophosphate, is the unique stable indenyl iron carbene derivative described in the literature [49]. In addition, transient $[Fe(\eta^5\text{-}C_9H_7)\ \{=C(H)R\}(CO)_2][CF_3SO_3]$ ($R =$ Ph, Me, $C_6H_4\text{-}OMe\text{-}4$) species have been used as carbene transfer agents in the cyclopropanation of olefins [50].

7.1.2.2. η^1-Vinylidene to η^2-alkyne tautomerizations. The treatment of monosubstituted vinylidene derivatives $[Ru(\eta^5\text{-}C_9H_7)\{=C=C(H)R\}(PPh_3)_2][PF_6]$ with nitriles at high temperature results in the generation of cationic nitrile complexes $[Ru(\eta^5\text{-}C_9H_7)(N\equiv CR')(PPh_3)_2][PF_6]$ through the elimination of the corresponding terminal alkyne (Scheme 12) [123].

Under these reaction conditions, the formation of complexes $[Ru(\eta^5\text{-}C_9H_7)(N\equiv CR')(PPh_3)_2][PF_6]$ can be explained taking into account that the vinylidene complexes are in equilibrium with the η^2-alkyne tautomers $[Ru(\eta^5\text{-}C_9H_7)(\eta^2\text{-}HC{\equiv}CR)(PPh_3)_2][PF_6]$. The rapid substitution in the transient π-alkyne species of the labile coordinated alkyne by the more basic nitrile ligands favors the displacement of the equilibrium to afford complexes $[Ru(\eta^5\text{-}C_9H_7)(N\equiv CR')(PPh_3)_2][PF_6]$ and the free alkyne. Ab initio molecular orbital (MO) calculations on the model $[Ru(\eta^5\text{-}C_9H_7)(=C=CH_2)(PH_3)_2]^+$ are in accord with this behaviour showing that the tautomerization process proceeds through the classic



$R = Ph, C_6H_4NO_2$-4, $(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)$

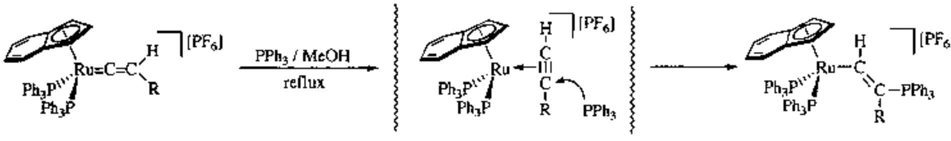
R' = Me, Et, Ph

Scheme 12.

1,2-[H] shift mechanism with a calculated energy barrier of 18.9 kcal mol^{-1} [123]. This relatively low value can be readily overcome in the reaction conditions allowing the formation of the kinetically labile π-alkyne complex.

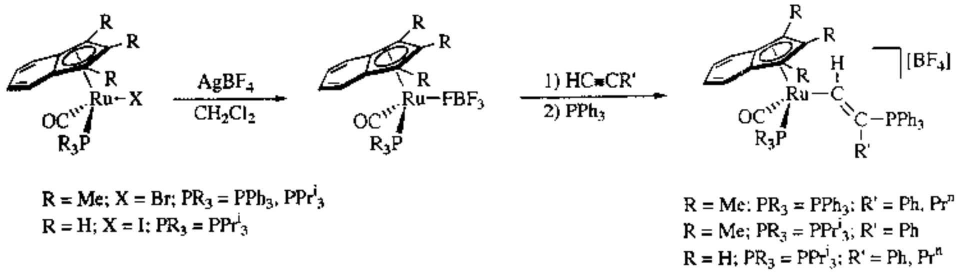
The existence of this equilibrium is clearly confirmed in the reaction of $[Ru(\eta^5\text{-}C_9H_7)\{=C=C(H)R\}(PPh_3)_2][PF_6]$ with triphenylphosphine in refluxing methanol to yield the alkenyl-phosphonio derivatives $[Ru(\eta^5\text{-}C_9H_7)\{(E)\text{-}C(H)=C(PPh_3)R\}\text{-}(PPh_3)_2][PF_6]$ (Scheme 13). These complexes are formed via the nucleophilic addition of PPh_3 to the coordinated π-alkyne on the intermediate $[Ru(\eta^5\text{-}C_9H_7)(\eta^2\text{-}HC\equiv CR)(PPh_3)_2][PF_6]$ species [84,123].

Theoretical calculations seem to indicate that the less the electron density at the ruthenium atom the more the tendency of η^1-vinylidene ligands to rearrange to η^2-alkyne ligands [126]. In agreement with this, the more electrophilic ruthenium(II) complexes $[Ru(\eta^5\text{-}C_9H_4Me_3)X(CO)(PR_3)]$ react with $AgBF_4$ and terminal alkynes $HC\equiv CR'$ in dichloromethane at room temperature, to yield equilibrium mixtures containing the corresponding vinylidene and π-bonded alkyne complexes [73,118,121]. The addition of triphenylphosphine to these reaction mixtures (Scheme 14) favors the displacement of the vinylidene-π-alkyne equilibrium and the alkenyl-phosphonio derivatives $[Ru(\eta^5\text{-}C_9H_4R_3)\{(E)\text{-}C(H)=C(PPh_3)R'\}(CO)\text{-}(PR''_3)][BF_4]$ are formed in high yields [118].



$R = Ph, C_6H_9, C_7H_{11}$

Scheme 13.



Scheme 14.

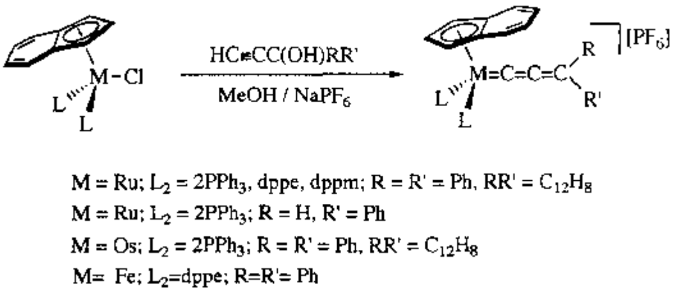
7.2. Allenylidene complexes

7.2.1. Synthesis

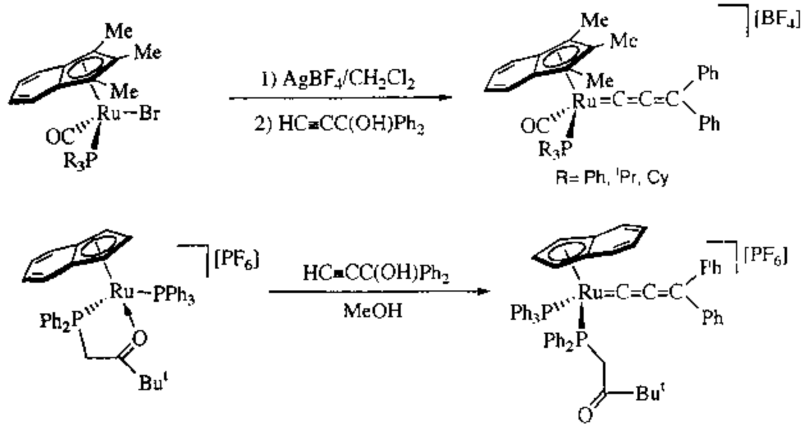
A large series of allenylidene complexes have been described. They are prepared through the dehydration of propargyl alcohols by a variety of η^5-indenyl ruthenium(II) and osmium(II) phosphine complexes (Scheme 15). Thus, the treatment of $[M(\eta^5\text{-}C_9H_7)ClL_2]$ (M = Ru, $L_2 = 2PPh_3$, dppe, dppm; M = Os, $L_2 = 2PPh_3$) with $HC{\equiv}CC(OH)RR'$ (R = R' = Ph; RR' = $C_{12}H_8$; R = H, R' = Ph), in the presence of $NaPF_6$, yields the cationic allenylidene derivatives $[M(\eta^5\text{-}C_9H_7)({=}C{=}C{=}CRR')L_2][PF_6]$ in high yields [87]. Furthermore, the first allenylidene iron(II) complex $[Fe(\eta^5\text{-}C_9H_7)({=}C{=}C{=}CPh_2)(dppe)]^+$ has been recently prepared in our laboratory [121].

In a similar way, the diphenylallenylidene derivatives $[Ru(\eta^5\text{-}C_9H_4Me_3)({=}C{=}C{=}CPh_2)LL'][BF_4]$ (L = CO, L' = PPh_3, P^iPr_3, PCy_3; LL' = dppm) [73,121] and $[Ru(\eta^5\text{-}C_9H_7)({=}C{=}C{=}CPh_2)(PPh_3)\{\kappa\text{-}P\text{-}Ph_2PCH_2C({=}O)^tBu\}][PF_6]$ (Scheme 16) [79] have also been prepared.

We have also reported the synthesis of an unprecedented allenylidene complex, namely $[Ru(\eta^5\text{-}C_9H_7)\{{=}C{=}C{=}C(C_{13}H_{20})\}(PPh_3)_2][PF_6]$, which contains the 4-spirocyclohexanebicyclo[3.3.1]non-2-en-9-ylidene moiety ($C_{13}H_{20}$). This complex is the result of the coupling between the vinylvinylidene derivative $[Ru(\eta^5\text{-}C_9H_7)\{{=}C{=}C(H)R\}(PPh_3)_2][PF_6]$ (R = 1-cyclohexenyl) and 1-ethynyl-1-cyclohexanol. (Scheme 17) [92,127].



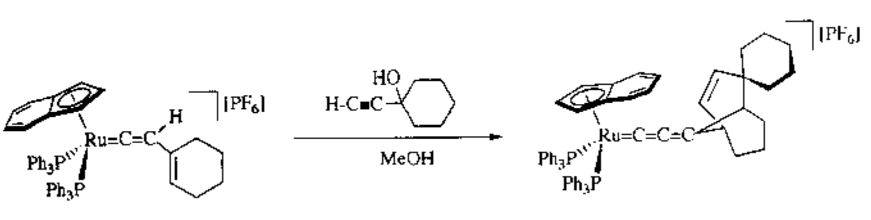
Scheme 15.



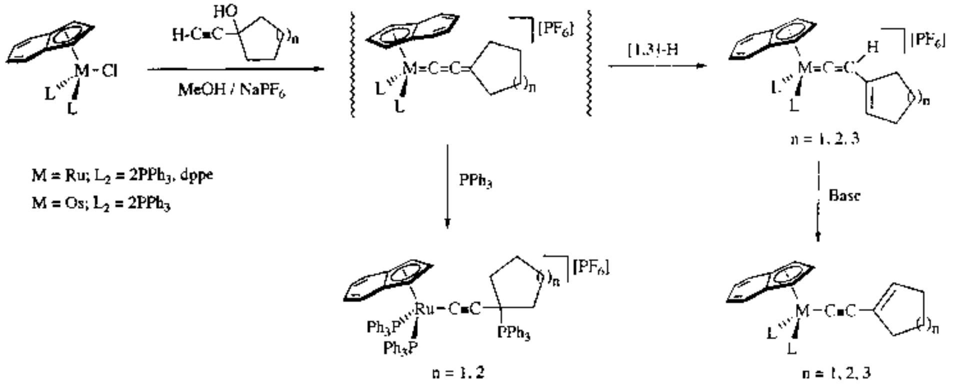
Scheme 16.

In contrast, under similar reaction conditions the activation of 1-ethynyl-1-cycloalkynols by [M(η^5-C_9H_7)ClL$_2$] yields regioselectively vinylvinylidene derivatives [M(η^5-C_9H_7){=C=C(H)R}L$_2$][PF$_6$] (R = 1-cycloalkenyl). These complexes are formed via the initial formation of unstable allenylidene species which rapidly undergo a tautomerization process, through a formal [1,3]-H shift, to the thermodynamically more stable vinylvinylidene tautomers (Scheme 18). The easy deprotonation of these vinylvinylidene complexes affords the neutral σ-enynyl derivatives [M(η^5-C_9H_7)(C≡CR)L$_2$] (R = 1-cycloalkenyl) in high yields [84,96]. The reactions of [Ru(η^5-C_9H_7)Cl(PPh$_3$)$_2$] with 1-ethynyl-1-cyclopentanol or 1-ethynyl-1-cyclohexanol in the presence of triphenylphosphine confirm the formation of the transient allenylidene intermediates. These processes lead to stable alkynyl-phosphonio derivatives which are formed through the nucleophilic addition of the phosphine to the electrophilic C_γ atom of the cumulene chain.

However, the reaction of [Ru(η^5-C_9H_7)ClL$_2$] with HC≡CCMe(OH)Ph and NaPF$_6$ proceeds in a different way since a mixture of vinylvinylidene complexes [Ru(η^5-C_9H_7){=C=C(H)C(Ph)=CH$_2$}L$_2$][PF$_6$] and disubstituted allenylidene complexes [Ru(η^5-C_9H_7){=C=C=C(Me)Ph}L$_2$][PF$_6$] is obtained (Scheme 19) [87]. The outcome of the aforementioned reactions giving either allenylidene or vinylvinylidene complexes shows the two possible pathways in the activation of 1-alkyn-3-ols by transition-metal complexes [124].



Scheme 17.



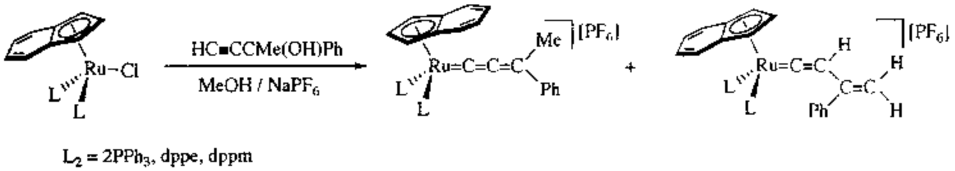
Scheme 18.

7.2.2. *Reactivity*

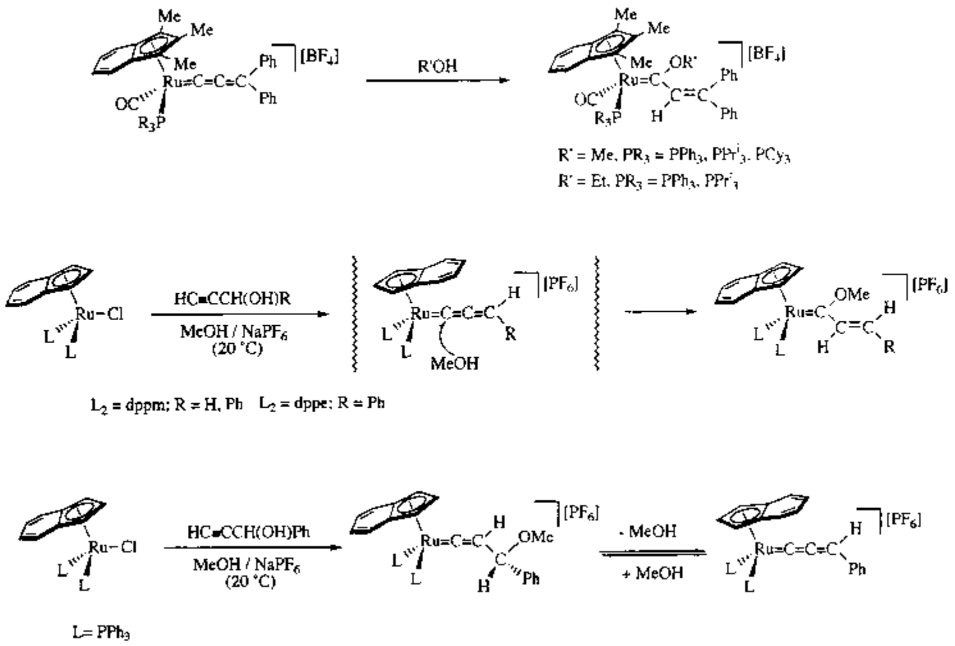
Although the reactivity of transition-metal allenylidene complexes has been only sparsely investigated there is ample experimental evidence [124,128–132] to conclude that C_α and C_γ atoms of the unsaturated chain are electrophilic centers and that C_β is nucleophilic. Theoretical calculations (EHMO) have also been performed on the model $[Ru(\eta^5\text{-}C_9H_7)(=C=C=CH_2)(PH_3)_2]^+$ which show rather small differences in the electrophilicity of C_α and C_γ atoms (LUMO is centered on ca. 25% and C_γ 33%) [115]. However, the preferred *cis* orientation of the benzo ring of the indenyl ligand with respect to the allenylidene chain (see Section 2) and the presence of bulky ancillary ligands on the ruthenium atom protect sterically the electrophilic C_α atom of the cumulene chain.

The general studies on the reactivity of indenyl–ruthenium(II) allenylidene derivatives towards nucleophiles have demonstrated that the regioselectivity of the nucleophilic additions can be controlled by the appropriate selection both of the substituents on the hydrocarbon unsaturated chain and of the ancillary ligands on the ruthenium atom.

7.2.2.1. Additions of neutral nucleophiles. The reactivity of indenyl–ruthenium(II) and osmium(II) allenylidene complexes towards alcohols shows that the ability of the unsaturated chain to undergo nucleophilic additions is mainly dependent on the electronic and steric nature of the ancillary ligands. Thus, while the disubstituted



Scheme 19.



Scheme 20.

allenylidene derivatives $[M(\eta^5\text{-}C_9H_7)(=C=C=CR_2)L_2][PF_6]$ (M = Ru, Os) (L_2 = 2PPh_3, dppe, dppm; R_2 = 2Ph, $C_{12}H_8$) are unreactive towards alcohols (see Scheme 15) [87], the diphenylallenylidene complexes $[Ru(\eta^5\text{-}C_9H_4Me_3)(=C=C=CPh_2)(CO)(PR_3)][BF_4]$ containing the less sterically demanding and more π-accepting CO/PR_3 combination, react with methanol or ethanol at room temperature to yield the corresponding α,β-unsaturated-alkoxycarbene derivatives $[Ru(\eta^5\text{-}C_9H_4Me_3)\{=C(OR')C(H)=CPh_2\}(CO)(PR_3)][BF_4]$ (Scheme 20) [73,121].

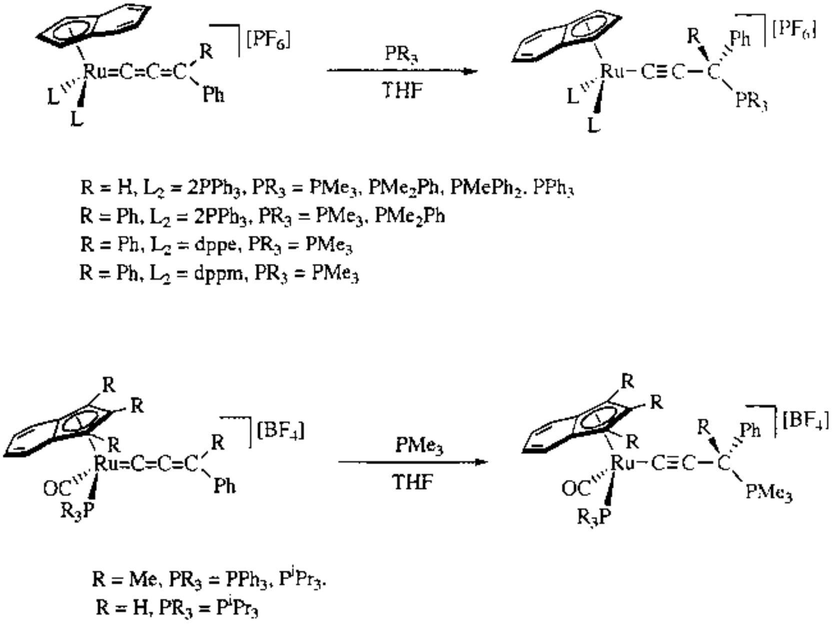
The influence of the allenylidene substituents in the stability of these metal–cumulene systems is also evident since the α,β-unsaturated-methoxycarbene complexes $[Ru(\eta^5\text{-}C_9H_7)\{=C(OMe)C(H)=CH(R)\}L_2][PF_6]$ are easily obtained by treatment of $[Ru(\eta^5\text{-}C_9H_7)ClL_2]$ with HC≡CC(OH)HR and $NaPF_6$ in methanol at room temperature (Scheme 20) [87]. In contrast, $[Ru(\eta^5\text{-}C_9H_7)\{=C=C=C(H)Ph\}(PPh_3)_2][PF_6]$ reacts with methanol in a different way since the vinylidene derivative $[Ru(\eta^5\text{-}C_9H_7)\{=C=C(H)C(H)Ph(OMe)\}(PPh_3)_2][PF_6]$ is formed (Scheme 20). This fact indicates that the bis(triphenylphosphine)ruthenium auxiliary is able to protect sterically the C_α atom of the allenylidene chain and only the attack at the C_γ atom is observed.

The allenylidene complexes $[Ru(\eta^5\text{-}C_9H_7)\{=C=C=C(R)Ph\}(PPh_3)_2][PF_6]$ also undergo regioselective nucleophilic additions of phosphines at the C_γ atom yielding cationic alkynyl-phosphonio derivatives in high yields (Scheme 21) [85,86,121]. The related alkynyl-phosphonio complexes $[Ru(\eta^5\text{-}C_9H_7)\{C\equiv CCH_2(PPh_3)\}(PPh_3)_2][PF_6]$

and [Ru(η^5-$C_9H_4Me_3$){C≡CC(H)Ph(PPh_3)}(CO)(PPh_3)][BF_4] have also been prepared [121,122].

Complexes [Ru(η^5-C_9H_7){C≡CCPh$_2$(PMe$_3$)}(dppm)][PF_6] and [Ru(η^5-$C_9H_4Me_3$)-{C≡CCPh$_2$(PMe$_3$)}(CO)(PPh_3)][BF_4] slowly rearrange in THF at room temperature to give the thermodynamically more stable allenyl-phosphonio derivatives [Ru(η^5-C_9H_7){C(PMe$_3$)=C=CPh$_2$}{κ^2-(*P*,*P*)dppm}][PF_6] and [Ru(η^5-$C_9H_4Me_3$){C(PMe$_3$)=C=CPh$_2$}(CO)(PPh_3)][BF_4], respectively (Scheme 22) [85,86,121]. These isomerization processes are promoted by the steric requirements of the two bulky phenyl groups at the C_γ atom. The subtle competence in the steric control between the ancillary ligands and the substituents in the C_γ atom is also confirmed in the nucleophilic addition of PMe$_2$Ph to [Ru(η^5-C_9H_7)(=C=C=CPh$_2$){κ^2-(*P*,*P*)dppm}]-[PF_6] which selectively takes place at the ca. atom of the allenylidene chain to yield [Ru(η^5-C_9H_7){C(PMe$_2$Ph)=C=CPh$_2$}{κ^2-(*P*,*P*)dppm}][PF_6] [86].

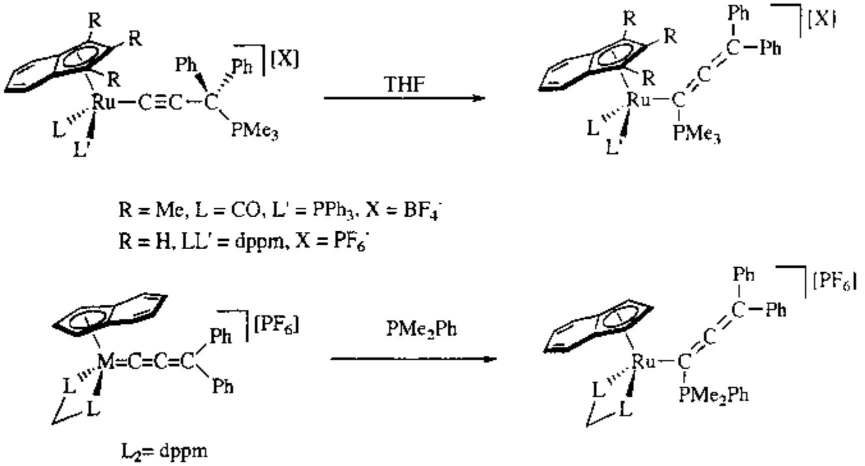
7.2.2.2. Additions of anionic nucleophiles. Complexes [Ru(η^5-C_9H_7){=C=C=C(R)-Ph}L$_2$][PF_6] undergo regioselective additions of a large variety of anionic nucleophiles to the more accessible C_γ atom to give neutral functionalized σ-alkynyl derivatives [Ru(η^5-C_9H_7){C≡CC(Nu)(R)Ph}L$_2$] (representative examples are shown in Scheme 23) [85,86,89,133]. As expected (see Section 7.1.1), protonation of most of these alkynyl complexes yields the corresponding cationic vinylidene derivatives in high yields [86,89,123,127,133].



R = H, L_2 = 2PPh$_3$, PR$_3$ = PMe$_3$, PMe$_2$Ph, PMePh$_2$, PPh$_3$
R = Ph, L_2 = 2PPh$_3$, PR$_3$ = PMe$_3$, PMe$_2$Ph
R = Ph, L_2 = dppe, PR$_3$ = PMe$_3$
R = Ph, L_2 = dppm, PR$_3$ = PMe$_3$

R = Me, PR$_3$ = PPh$_3$, P^{i}Pr$_3$.
R = H, PR$_3$ = P^{i}Pr$_3$

Scheme 21.



Scheme 22.

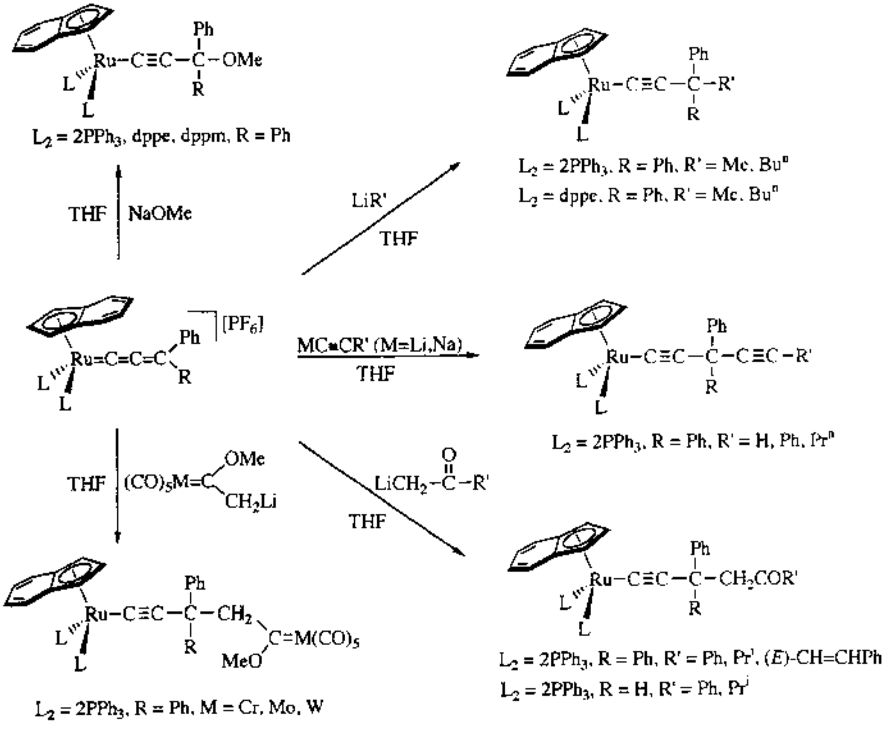
Diphenylallenylidene complexes $[Ru(\eta^5\text{-}C_9H_7)({=}C{=}C{=}CPh_2)L_2][PF_6]$ ($L_2 = 2PPh_3$, dppe, dppm) also react with sodium 2-methylthiophenolate, the position of the addition (C_α or C_γ) being controlled by the ancillary ligands on the ruthenium atom [86]. Thus, while $[Ru(\eta^5\text{-}C_9H_7)({=}C{=}C{=}CPh_2)(PPh_3)_2][PF_6]$ adds the thiolate anion at the C_γ to yield $[Ru(\eta^5\text{-}C_9H_7)\{C{\equiv}CCPh_2[S(C_6H_4Me\text{-}2)]\}(PPh_3)_2]$, the reaction of complex $[Ru(\eta^5\text{-}C_9H_7)({=}C{=}C{=}CPh_2)(\{\kappa^2\text{-}(P,P)\text{-dppm}\}][PF_6]$ takes place at the C_α to afford the allenyl derivative $[Ru(\eta^5\text{-}C_9H_7)\{C[S(C_6H_4Me\text{-}2)]{=}C{=}CPh_2\}\{\kappa^2\text{-}(P,P)\text{-dppm}\}]$. Apparently, the substitution of the two bulky triphenylphosphine ligands by the small-bite chelating dppm decreases the steric protection of the electrophilic ca. atom. Accordingly, the treatment of $[Ru(\eta^5\text{-}C_9H_7)({=}C{=}C{=}CPh_2)\{\kappa^2\text{-}(P,P)\text{-dppe}\}][PF_6]$ with this anionic nucleophile yields a mixture of the corresponding σ-alkynyl and allenyl complexes. In contrast, we have found that the diphenylallenylidene derivatives $[Ru(\eta^5\text{-}C_9H_4R_3)({=}C{=}C{=}CPh_2)(CO)(L)][BF_4]$ ($R = Me$, $L = PPh_3$; $R = H$, $L = P^iPr_3$), containing a carbonyl ligand which is less sterically demanding than a phosphine, do not react with nucleophiles at the C_α to afford allenyl species yielding instead σ-alkynyl complexes (e.g. $[Ru(\eta^5\text{-}C_9H_4R_3)\{C{\equiv}CC(Nu)Ph_2\}(CO)(L)][BF_4]$ ($R = Me$, $L = PPh_3$, $Nu = OMe$, $C{\equiv}CH$; $R = H$, $L = {}^iPPr_3$, $Nu = OMe$, $C{\equiv}CPh$; $R = H$, $L = PCy_3$, $Nu = OMe$, OEt) [73,121].

Intramolecular C_α additions to afford allenyl-metallacycle derivatives, via initial deprotonation of one auxiliary phosphine ligand, have also been reported to occur in complexes $[Ru(\eta^5\text{-}C_9H_7)({=}C{=}C{=}CPh_2)(\{\kappa^2\text{-}(P,P)\text{-dppm}\}][PF_6]$ and $[Ru(\eta^5\text{-}C_9H_7)({=}C{=}C{=}CPh_2)(PPh_3)\{\kappa\text{-}P\text{-}Ph_2PCH_2C({=}O)^tBu\}][PF_6]$ (Scheme 24). For the latter the transformation is diastereoselective since only one pair of enantiomers are obtained $S_{Ru},R_C/R_{Ru},S_C$, as it is confirmed by the X-ray crystal structure determination [79,86].

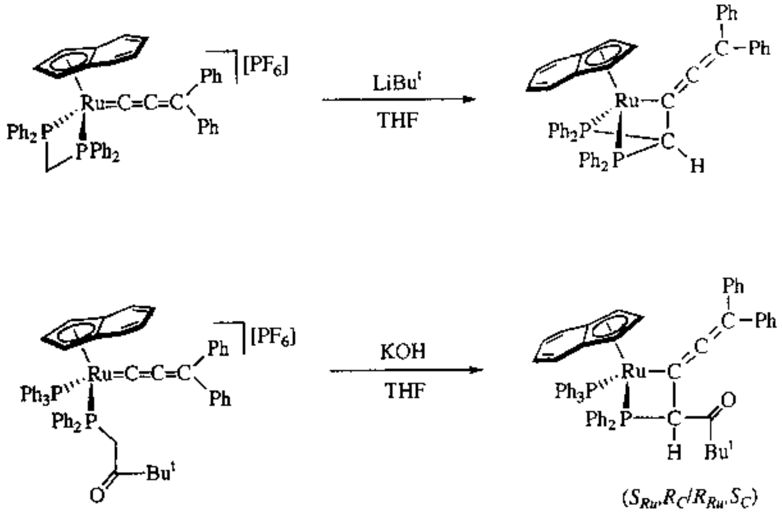
7.2.2.3. Wittig reactions. The alkynyl-phosponio complexes [Ru(η^5-C_9H_7)-{C≡CC(R)H(PR_3)}(PPh_3)$_2$][PF_6] containing an acidic hydrogen atom at C_γ, are excellent substrates for Wittig reactions leading to the formation of new double carbon–carbon bonds (Scheme 25). Thus, the treatment of THF solutions of these complexes with Li^{n}Bu generate the highly unstable phosphorus-ilyde alkynyl species [Ru(η^5-C_9H_7){C≡CC(R)=PR_3}(PPh_3)$_2$]. Although they can not be isolated, the treatment in situ with aldehydes or ketones affords neutral σ-enynyl derivatives [Ru(η^5-C_9H_7){C≡CC(R)=CR′R″}(PPh_3)$_2$] in high yields [88,89,121]. When aldehydes are used, mixtures of the corresponding *E* and *Z* stereoisomers are obtained. Similarly, the σ-keteniminyl complex [Ru(η^5-C_9H_7){C≡CC(Ph)=C=NPh}(PPh_3)$_2$] has been obtained starting from [Ru(η^5-C_9H_7){C≡CC(Ph)H(PMe_3)}(PPh_3)$_2$][PF_6] and phenylisocyanate [89].

The related polyunsaturated σ-alkynyl complexes [Ru(η^5-C_9H_7){C≡CC-(R)=CH(CH=CH)$_n$R′}(PPh_3)$_2$] which are the first examples of transition-metal σ-polyenynyl derivatives, have been also prepared (Scheme 25) as mixtures of the *E* and *Z* isomers by reaction of the in situ generated ilyde-alkynyl species with unsaturated aldehydes R′(CH=CH)$_n$CHO [121].

A series of Wittig reactions using unsaturated aldehydes and ketones bearing strong electron withdrawing groups (e.g. NO_2) or efficient bridging groups (e.g.

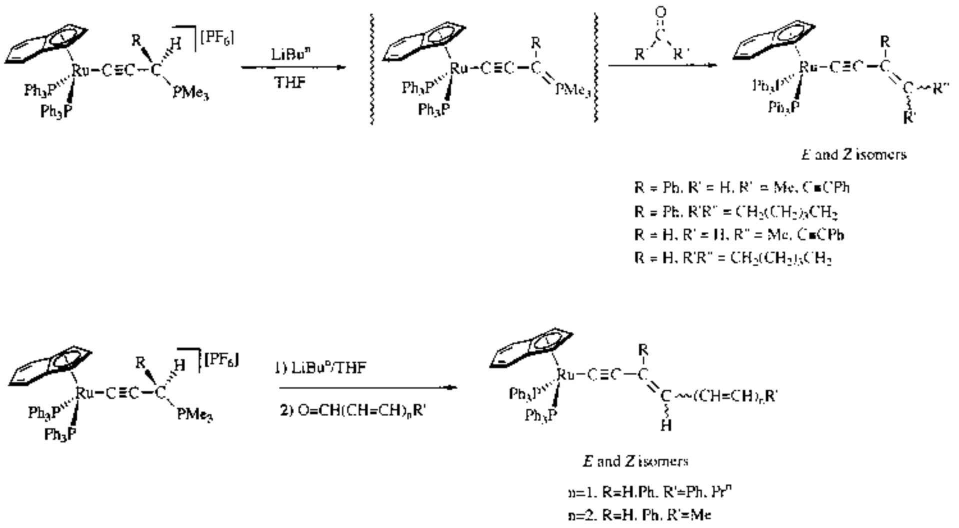


Scheme 23.



Scheme 24.

C ≡ N) capable to coordinate metallic acceptor fragments (e.g. $M(CO)_5$, M = Cr, W) have been reported (Scheme 26) These reactions provide a synthetic methodology of novel σ-enynyl complexes with donor–acceptor properties which are of interest as materials with good second-order nonlinear optical (NLO) properties [80,122]. Determination of the molecular quadratic hyperpolarizabilities (β) for the resulting donor–acceptor σ-enynyl derivatives yields resonantly enhanced values

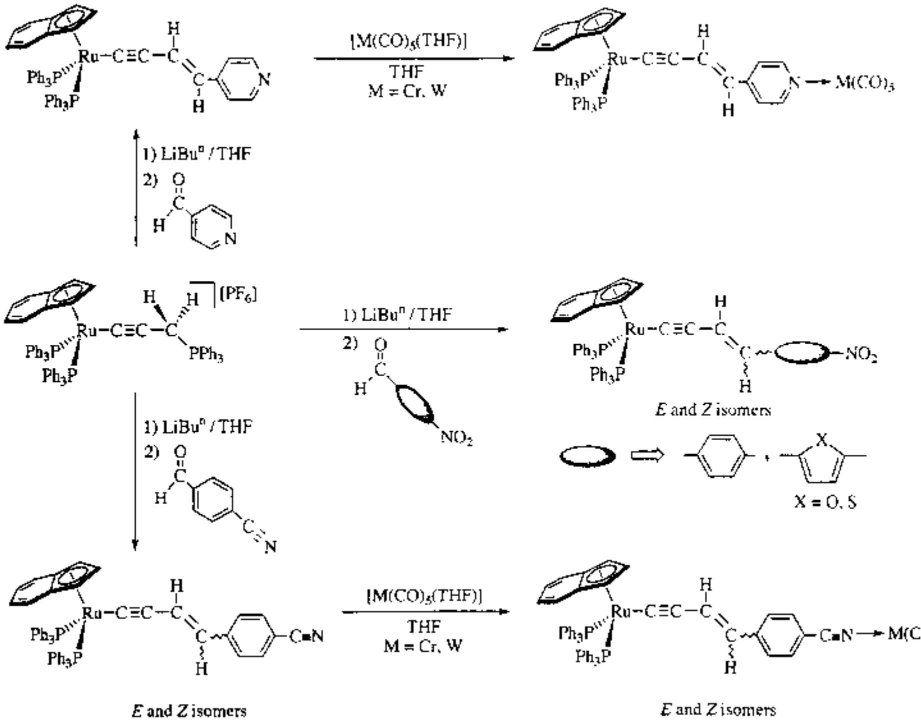


Scheme 25.

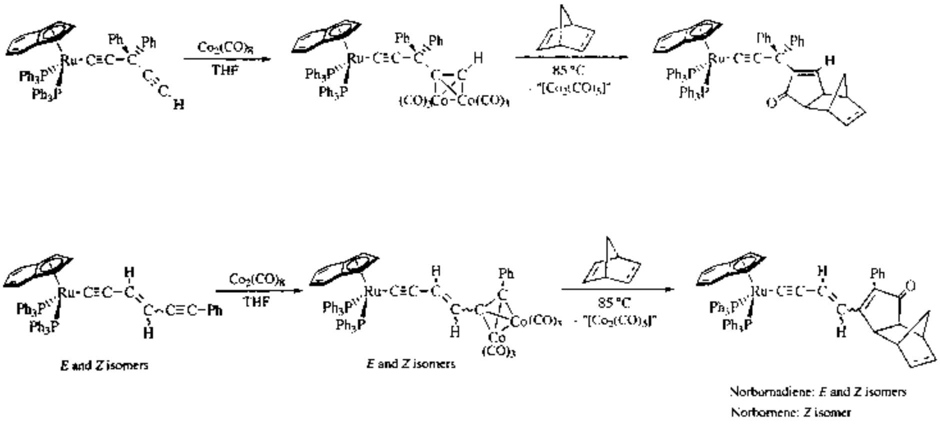
significantly larger than those of the more commonly studied organometallic chromophores ($\beta_{1064\text{nm}} = 10\text{–}1320(10^{-30}$ esu) [134,135]. Representative examples of these complexes are shown in Scheme 26.

7.2.2.4. Pauson–Khand reactions. Indenyl ruthenium(II) σ-alkynyl derivatives $[\text{Ru}(\eta^5\text{-C}_9\text{H}_7)\{\text{C}{\equiv}\text{CCPh}_2(\text{C}{\equiv}\text{CH})\}(\text{PPh}_3)_2]$ and (*E*, *Z*)-$[\text{Ru}(\eta^5\text{-C}_9\text{H}_7)\{\text{C}{\equiv}\text{CC(H)}{=}\text{CH-}(\text{C}{\equiv}\text{CPh})\}(\text{PPh}_3)_2]$ which bear a triple bond functionality at the end of the alkynyl chain react with dicobalt octacarbonyl leading to the selective coordination of the $[\text{Co}_2(\text{CO})_6]$ moiety on the less sterically hindered terminal C≡C bond (Scheme 27). The reactions between the resulting dicobalt adducts and strained cyclic alkenes (norbonadiene and norbornene) leads to the formation of novel σ-alkynyl derivatives containing tricyclic cyclopentenone fragments [88]. These processes are examples of Pauson–Khand reactions which allow an efficient entry to the selective synthesis of organometallic cyclopentenones.

Protonation of these species with HBF_4 affords the corresponding cationic vinylidene derivatives in high yields. Nevertheless, the scope of this cycloaddition process is quite limited since the displacement of the coordinated alkyne by the alkenes only takes place when unstrained olefines are used.

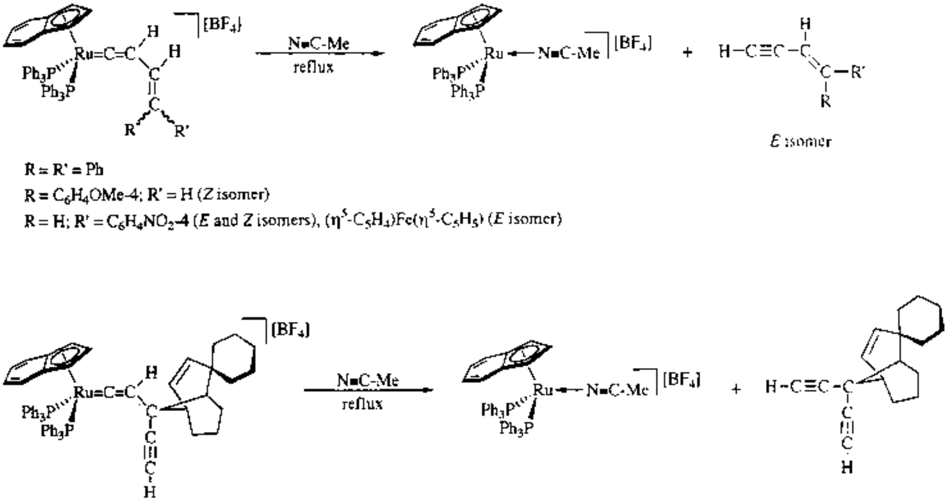


Scheme 26.



Scheme 27.

7.2.2.5. Synthesis of functionalized terminal alkynes. As is described in the Section 7.1.2, the vinylidene moiety in [Ru(η^5-C_9H_7){=C=C(H)R}(PPh_3)$_2$][PF_6] is labile, being easily obtained the corresponding terminal alkyne by the treatment with nitriles. This behaviour has proven to be general as shown by the analogous reactions of vinylvinylidene complexes [Ru(η^5-C_9H_7){=C=C(H)C(H)=CRR′}-(PPh_3)$_2$][BF_4] (Scheme 28) The heating of these complexes, (see Section 7.2.2) in refluxing acetonitrile, afford stereoselectively, through a demetallation process, the thermodynamically more stable (*E*)-1,3-enynes HC≡CCH=CRR′, in high yields. The potential utility of this process for the preparation of novel terminal alkynes is demonstrated in the synthesis of the unprecedented diyne $(HC{\equiv}C)_2CC_{13}H_{20}$ (Scheme 28) [123].

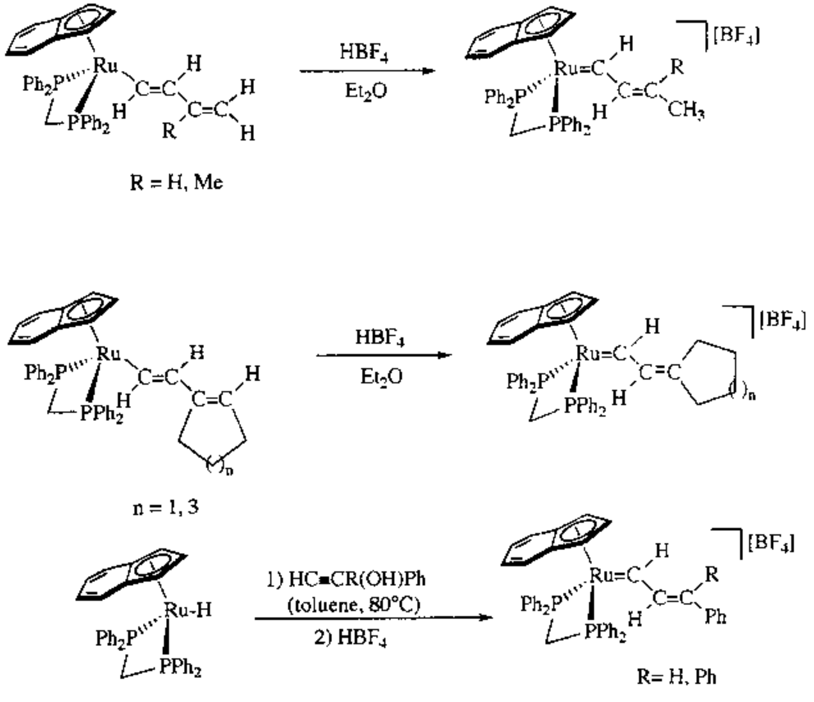


Scheme 28.

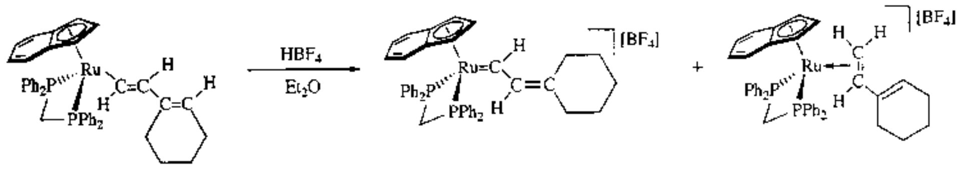
7.3. Alkenyl alkylidene complexes

Neutral vinyl-alkenyl derivatives $[\mathrm{Ru}(\eta^5\text{-}C_9H_7)\{(E)\text{-}CH{=}CHCR{=}CH_2\}\{\kappa^2\text{-}(P,P)\text{-dppm}\}]$ and $[\mathrm{Ru}(\eta^5\text{-}C_9H_7)\{(E)\text{-}CH{=}CHR\}\{\kappa^2\text{-}(P,P)\text{dppm}\}]$ (R = 1-cycloalkenyl) (see Section 6.2) are excellent precursors of cationic α,β-unsaturated alkenyl alkylidene complexes $[\mathrm{Ru}(\eta^5\text{-}C_9H_7)({=}CHCH{=}CR'R'')\{\kappa^2\text{-}(P,P)\text{-dppm}\}][BF_4]$ (Scheme 29) via protonation with HBF_4 [90]. The electrophilic addition of the proton proceeds regioselectively at the C_δ atom of the vinyl-alkenyl group. Analogous complexes $[\mathrm{Ru}(\eta^5\text{-}C_9H_7)({=}CHCH{=}CRPh)(\{\kappa^2\text{-}(P,P)\text{-dppm}\}][BF_4]$ (R=H, Ph) have been also prepared via one-pot synthesis, by treatment of the hydride precursor $[\mathrm{Ru}(\eta^5\text{-}C_9H_7)H\{\kappa^2\text{-}(P,P)\text{-dppm}\}]$ with $CH \equiv CCR(OH)Ph$ (R = H, Ph) in refluxing toluene followed by the addition of HBF_4 to the resulting reaction mixture.

In contrast, protonation of $[\mathrm{Ru}(\eta^5\text{-}C_9H_7)\{(E)\text{-}CH{=}CHR\}\{\kappa^2\text{-}(P,P)\text{-dppm}\}]$ (R = 1-cyclohexenyl) leads to a mixture of the corresponding alkenyl alkylidene complex and the π-alkene derivative $[\mathrm{Ru}(\eta^5\text{-}C_9H_7)(\eta^2\text{-}CH_2{=}CHR)\{\kappa^2\text{-}(P,P)\text{-dppm}\}][BF_4]$ (R = 1-cyclohexenyl) (Scheme 30).The formation of this mixture can be explained as the result of the protonation at the C_β atom of the vinylalkenyl chain to give the transient alkylidene complex $[\mathrm{Ru}(\eta^5\text{-}C_9H_7)({=}CHCH_2R)\{\kappa^2\text{-}(P,P)\text{-dppm}\}][BF_4]$ which undergoes a thermodynamically favorable isomerization via an [1,2]-H shift, to afford the final π-alkene complex.



Scheme 29.



Scheme 30.

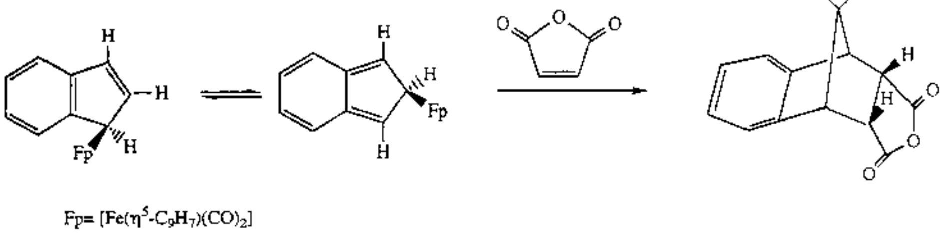
The formation of these α,β-unsaturated alkylidene complexes are the result of the competitive electrophilic addition at either the C_γ or the C_δ atom, revealing the remarkably high electron density on these positions of the vinylalkenyl moiety. These cationic indenyl ruthenium(II) alkenyl alkylidene complexes are related to those of the type $[RuCl_2(=CH-CH=CPh_2)(PR_3)_2]$ and $[RuCl_2(=CHC_6H_4X\text{-}4)(PR_3)_2]$ (Grubbs metathesis catalysts) which are efficient catalysts for ring-opening metathesis polymerization (ROMP).

8. Ring additions

The following addition reactions to the indenyl ring have been described.

8.1. Cycloadditions

The iron complex $[Fe(\eta^5\text{-}C_9H_7)(\eta^1\text{-}C_9H_7)(CO)_2]$ undergoes Diels–Alder cycloaddition reactions with maleic anhydride and tetracyanoethylene in the η^1-indenyl group to form benzonorbornene derivatives (Scheme 31). Although a [3 + 2] cycloaddition mechanism was originally invoked [105c] further studies show that the reaction proceeds through the initial formation of the isoindene complex via 1,5 shift of the η^1-C_9H_7 ligand followed by a [4 + 2] addition [98].



Scheme 31.

8.2. Catalytic hydrogenations

Catalytic transformations of the η^5-indenyl group in the corresponding η^5-tetrahydroindenyl complex occurs through the hydrogenation of η^5-C_9H_7 ring at atmospheric pressure and in the presence of palladium on charcoal or PtO_2. Examples of these reactions have been described for $[Fe(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_5H_5)]$ [19] and $[Fe_2\{(\eta^5\text{-}C_9H_6)_2E\}(CO)_2(\mu\text{-}CO)_2]$ ($E = Me_2Si$, $Me_2SiOSiMe_2$, $Me_2SiSiMe_2$) [64,136].

8.3. Protonations

Proton additions lead to $\eta^5 \rightarrow \eta^6$ indenyl rearrangements. The first reported example was the conversion of $[Fe(\eta^5\text{-}C_9H_7)_2]$ into $[Fe(\eta^5\text{-}C_9H_7)(\eta^6\text{-}C_9H_8)]^+$ upon reaction with $BF_3{\cdot}OEt_2$ [12]. This transformation along with the related formation of $[Fe(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_9H_8)]^+$ was later reported to occur by using protic acids such as CF_3CO_2H [13].

8.4. Intramolecular additions

These types of processes which had also been previously reported for the cyclopentadienyl ring are take place in the base induced migration of the SiR_3 group and analogous species Si_nMe_m to the η^5-C_9H_7 ring in the complexes $[Fe(\eta^5\text{-}C_9H_7)E(CO)_2]$ ($E = SiR_3$, Si_nMe_m). The reactions are promoted by lithium diisopropylamide (LDA) and take place in the presence of Ph_3SnCl to give $[Fe(\eta^5\text{-}C_9H_6R)(SnPh_3)(CO)_2]$. A second treatment with LDA in the case of $[Fe(\eta^5\text{-}C_9H_6SiMe_3\text{-}1)(SnPh_3)(CO)_2]$ followed by addition of Ph_3SnCl or MeI produced $[Fe(\eta^5\text{-}1\text{-}SiMe_3\text{-}3\text{-}SnPh_3C_9H_5)E(CO)_2]$ ($E = SnPh_3$, Me) [39].

9. Kinetic studies

Kinetic studies on indenyl transition metal complexes are related with the *indenyl ligand effect*. As far as Group 8 metals is concerned, kinetics have been studied in ligand substitution and insertion reactions using a number of η^5-indenyl iron(II) and ruthenium(II) complexes:

9.1. Ligand substitutions

Early kinetic studies [2] on the indenyl effect were performed on the substitution of CO in $[Fe(\eta^5\text{-}C_9H_7)I(CO)_2]$ by phosphites $P(OR)_3$ (R = Et, Ph). The reactions, which are independent of the incoming ligand, proceed by an S_N1 mechanism and are faster than those analogous of a cyclopentadienyl complex by a factor of 5.7×10^2. Electrochemical studies have established that similar CO substitution in the 19-electron radical $[Fe(\eta^5\text{-}C_9H_7)(CO)_3]$ are also dissociative [61] but the reactions are slower than that of $[Fe(\eta^5\text{-}C_5H_5)(CO)_3]$ by at least 10^6 times. Kinetic studies on the basis of electrochemical results provide evidence that the reduction of $[Fe(\eta^5\text{-}C_9H_7)(CO)_3]^+$ in the presence of nucleophiles proceeds through the following ETC mechanism in which the rate determining step is CO dissociation from the 19 electron $[Fe(\eta^5\text{-}C_9H_7)(CO)_3]$ to give the 17-electron intermediate $[Fe(\eta^5\text{-}C_5H_5)(CO)_2]$ which is rapidly trapped by L.

$$[Fe(\eta^5\text{-}C_9H_7)(CO)_3]^+ \overset{e^-}{\rightleftharpoons} [Fe(\eta^5\text{-}C_9H_7)(CO)_3]$$

$$[Fe(\eta^5\text{-}C_9H_7)(CO)_3]^+ \xrightarrow{k_{-CO}} [Fe(\eta^5\text{-}C_9H_7)(CO)_2] + CO$$

$$[Fe(\eta^5\text{-}C_9H_7)(CO)_3] + L \xrightarrow{k_L} [Fe(\eta^5\text{-}C_9H_7)(CO)_2L]$$

$$[Fe(\eta^5\text{-}C_9H_7)(CO)_2L]^+ \overset{-e^-}{\rightleftharpoons} [Fe(\eta^5\text{-}C_9H_7)(CO)_2L]^+$$

Hückel MO calculations provide an explanation of this reduced reactivity (*inverse indenyl effect*) as compared with the enhanced reactivity, observed for most of the associative substitution reactions in 18-electron indenyl complexes, for which the $\eta^5 \rightarrow \eta^3$ ring slippage is invoked. According to these theoretical studies the LUMO, which is for both cyclopentadienyl and indenyl complexes, Fe–CO antibonding has a significant localization on the benzo ring of the indenyl ligand. Therefore, it reduces the localization on the CO ligands and accordingly the rate of dissociation of CO is much slower.

A comparison for the reactivity of indenyl and cyclopentadienyl compounds is also available from the exchange of PPh_3 in $[Ru(\eta^5\text{-}C_9H_7)Cl(PPh_3)_2]$ and $[Ru(\eta^5\text{-}C_5H_5)Cl(PPh_3)_2]$ by alkyl–aryl phosphines [78]. The mechanisms are also dissociative and the extrusion of PPh_3 is rate determining, which excludes the formation of η^3 intermediates. Kinetics show a rate constant for the indenyl complex, which is one order of magnitude greater than for the cyclopentadienyl complex, indicating more efficient stabilization of the 16-electron intermediate. This behaviour likely arises from the ability of the indenyl ligand to act as an electron sink towards the metal fragments $[Fe(CO)_3]$ and $[RuCl(PPh_3)_2]$ favoring the cleavage of the metal–CO and PPh_3 bond respectively or alternatively stabilizing the 16-electron intermediate[9].

9.2. Insertion reactions

Following the pioneering work [1a] in which the S_N^2 nature of the reaction of $[Mo(\eta^5\text{-}C_9H_7)Me(CO)_3]$ with PPh_3 to give $[Mo(\eta^5\text{-}C_9H_7)(COMe)(CO)_2(PPh_3)]$ was attributed to the ability of the indenyl ring to undergo the η^5- to η^3-coordination, Bassetti and Monti have studied [59,137] the CO migratory insertion reactions on the complex $[Fe(\eta^5\text{-}C_9H_7)Me(CO)_2]$ induced by phosphines. On the basis of kinetic and spectroscopic data they have shown that the reaction also proceeds through an associative pathway. However, they propose the rapid formation of a weak

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[9] CO substitutions for the cyclopentadienyl complex $[Mo(\eta^5\text{-}C_5H_5)X(CO)_3]$ ($X = Cl, Br, I$) proceed by a dissociative (S_N^1) pathway whereas the indenyl analogue is substituted by both an S_N^1 and S_N^2 mechanisms with a rate enhancement of ca. 6000 for the S_N^1 path only: see Ref. [1b].

molecular complex $[\mathrm{Fe}(\eta^5\text{-}\mathrm{C_9H_7})\mathrm{Me(CO)_2(PPh_3)}]$ as intermediate which precedes the rate determining alkyl migration step.

$$[\mathrm{Fe}(\eta^5\text{-}\mathrm{C_9H_7})(\mathrm{CO})_2R] + \mathrm{L} \overset{k}{\rightleftharpoons} [\mathrm{Fe}(\eta^5\text{-}\mathrm{C_9H_7})(\mathrm{CO})_2\mathrm{R, L}]$$

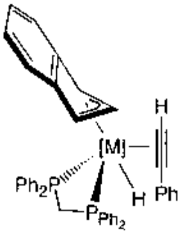
$$[\mathrm{Fe}(\eta^5\text{-}\mathrm{C_9H_7})(\mathrm{CO})_2\mathrm{R, L}] \xrightarrow{k_2} [\mathrm{Fe}(\eta^5\text{-}\mathrm{C_9H_7})(\mathrm{COR})(\mathrm{L})]$$

$\mathrm{R} = \mathrm{CHMe_2}$, Me; L = alkyl, aryl and mixed alkyl–aryl phosphines

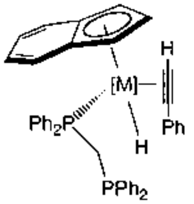
A wide series of phosphine ligands with different steric and electronic properties have been used which do not induce any change in the η^5-coordination mode of the indenyl ligand. In contrast to the most commonly proposed intermediates in the reactions of indenyl complexes, no evidence has been found of the formation of η^3-indenyl intermediates. These studies also indicate a different pathway from the classic two-step mechanism for migratory insertion i.e. alkyl migration and attack of the phosphine on the coordinatively unsaturated acyl intermediate. The nature of the active intermediates has been thoroughly studied concluding that the molecules interact through an electron donor–acceptor mechanism, where the iron complex is the donor and the phosphine the acceptor. The formation of the weak intermolecular complex is favoured by increased electron donation on the metal and by decreased phosphine basicity. The comparative reactivity of the corresponding cyclopentadienyl complexes has also been studied [138]. Acyl derivatives $[\mathrm{Fe}(\eta^5\text{-}\mathrm{C_5H_5})(\mathrm{COR})(\mathrm{CO})(\mathrm{PR'_3})]$ are also formed through an associative mechanism similar to that established for the indenyl complexes but the reactions are one order of magnitude slower. The crown ether functionalized phosphine $[\mathrm{Ph_2PCH_2}$-(aza-15-crown-5)] (L) reacts similarly with $[\mathrm{Fe}(\eta^5\text{-}\mathrm{C_9H_7})\mathrm{Me(CO)_2}]$ to give the corresponding acyl derivative $[\mathrm{Fe}(\eta^5\text{-}\mathrm{C_9H_7})(\mathrm{COMe})(\mathrm{CO})\mathrm{L}]$ [139]. The presence of the salts NaI, $\mathrm{NaPF_6}$ or $\mathrm{CaI_2}$ increases twice or three times the rate of reaction, whereas that of the corresponding cyclopentadienyl derivative remains unaffected.

Kinetic studies on the photodecarbonylation of acetyl complexes $[\mathrm{Fe}(\eta^5\text{-}\mathrm{C_9H_7})(\mathrm{COMe})(\mathrm{CO})_2]$ and $[\mathrm{Fe}(\eta^5\text{-}\mathrm{C_5H_5})(\mathrm{COMe})(\mathrm{CO})_2]$ reveal [140] that the indenyl intermediate is about 5 times more reactive towards methyl migration and towards trapping by various ligands than the cyclopentadienyl analog is. Since only this modest rate acceleration is observed it is proposed that a ring slippage intermediate leading to the formation of the η^3-complex does not play a significant role. This is in accordance with the results reported by Bassetti et al. for the related CO migratory insertions of $[\mathrm{Fe}(\eta^5\text{-}\mathrm{C_9H_7})\mathrm{Me(CO)_2}]$ assisted by phosphines under thermal conditions (see above).

We have recently described [75] the synthesis of σ-alkenyl ruthenium(II) complexes through insertion reactions of the hydride complexes $[\mathrm{Ru}(\eta^5\text{-}\mathrm{C_9H_7})\mathrm{HLL'}]$ with terminal alkynes. A kinetic study has been performed for the reaction of the complexes $[\mathrm{Ru}(\eta^5\text{-}\mathrm{C_9H_7})\mathrm{X}\{\kappa^2\text{-}(P,P)\mathrm{dppm}\}]$ (X = H, D) with phenylacetylene. The reactions, which are first order with respect to the ruthenium complex and to the alkyne, proceed via an associative mechanism. Although no intermediate is detectable, it is proposed that either an η^3-indenyl π-alkyne complex (**A**) or κ-*P*-dppm complex (**B**) (Chart IV) is likely formed as a transient reactive species. Since the analogous cyclopentadienyl hydride complex $[\mathrm{Ru}(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{H}\{\kappa^2\text{-}(P,P)\mathrm{dppm}\}]$ is unreactive the reaction represent a case of the *indenyl ligand effect*.



(A)



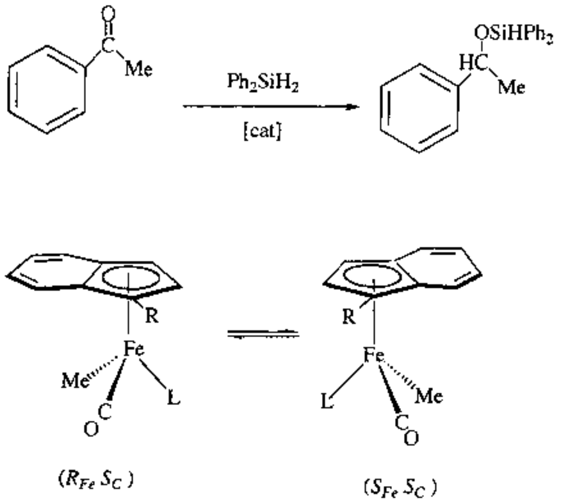
(B)

10. Catalytic reactions

Reactions catalyzed by indenyl Group 8 metal complexes are very scarce [4a,c,f,141]. Most of them are concerned with the studies on the catalytic activity of the complex [Ru(η^5-C_9H_7)Cl(PPh_3)$_2$] as compared to that shown by the analogous [Ru(η^5-C_5H_5)Cl(PPh_3)$_2$]. In general, an enhancement of the catalytic activity is achieved by using the indenyl derivative. This behaviour was first observed by Trost and co-workers [142] as part of the investigation on the ruthenium-catalyzed redox isomerization of allyl alcohols. By switching the catalyst from the cyclopentadienyl complex to the indenyl one the scope of the reaction is expanded significantly while most of the selectivity is mantained. A very efficient catalytic process has also been reported involving the redox isomerization of propargyl alcohols to enals and enones with an excellent chemoselectivity [143]. Recently, [Ru(η^5-C_9H_7)Cl(PPh_3)$_2$] has been used as a catalyst in the transformation of α-diazo carbonyl compounds in *cis*-enediones [144] and the tandem $[2+2+2]/[4+2]$ cycloaddition of 1,6-heptadiyne with norbornene [145]. Significant improvements of the reactivity and selectivity with respect to the cyclopentadienyl derivative are reported.

The use of the optically active (+)- and (−)-methyl and (+)- and (−)-acetyl iron complexes [Fe(η^5-C_9H_6R)Me(CO)L] and [Fe(η^5-C_9H_6R)(COMe)(CO)L] (R = H, 1-Bu^t; L = (*S*)-(+)-P(Ph)$_2$N(Me)CH(Me)Ph) as catalysts for hydrosilylation or hydrogenation of acetophenone with diphenylsilane has been described (Scheme 32) [4d]. Reactions for 24 h proceed in a selective and quantitative formation of the silylated 1-phenylethanol (hydrogenation to give the silylated enol derivative $Ph_2(H)SiOC(Ph){=}CH_2$ was not observed in any case). The required temperatures are dependent on the catalyst and are coincident with those necessary for the epimerization at the Fe atom of the catalyst. It is proposed that the dissociation of the phosphine from the catalyst is the rate-determining step for both the epimerization and the formation of the catalytically active species.

A brief report on the catalytic activity of [Fe(η^5-C_9H_7)$_2$] in the photoreduction of methylviologen in methanol solutions under near ultraviolet light is also known [11].



Scheme 32.

11. Conclusions

In this review article it is shown that experimental and theoretical studies on indenyl Group 8 metal complexes display special features. This particular behaviour has increased the interest in this chemistry mainly arising, as for other indenyl transition metal derivatives, from the potential enhanced reactivity generally referred to as the *indenyl effect*. Although the chemistry is still less developed than that of analogous cyclopentadienyl derivatives, a high number of indenyl complexes are known to date (Table 1), most of them η^5-iron and ruthenium complexes. However, the particular electronic and steric properties of the indenyl ring provide singular properties, as is evidenced by kinetic, catalytic and reactivity studies which in general confirm that these derivatives show an enhanced and more selective reactivity. Thus, ligand exchange processes and insertion reactions proceed at a faster rate, whereas the presence of the benzo ring may control the steric protection of reactive sites giving rise to regio and stereoselective processes. Nevertheless, it is apparent that the chemistry of these derivatives has not been exploited yet. This is specially notorious for osmium complexes and for the potential utility in catalytic processes for which only preliminar investigations have been reported. In summary, it may be foreseen for the coming years that the chemistry of these derivatives will undergo a further development and will appear useful applications.

12. Notes added in proof

(i) Alkynyl iron complexes $[Fe(\eta^5\text{-}C_9H_7)(C\equiv CR)(CO)_2]$ react with an excess of phosphines and $P(OMe)_3$ to give indenyl vinylidene complexes which are formed by an intramolecular transfer of the indenyl ligand from the iron to the C_β atom of the alkynyl ligand [146].

(ii) The ruthenium complexes $[Ru(\eta^5\text{-}C_9H_7)(X)(dppm)]$ (X = H, C≡CPh, (E)-CH=CHPh), $[Ru(\eta^5\text{-}C_9H_7)(X)L_2]$ (X = H, C≡CPh; L = PPh_3; L_2 = dppe), $[Ru(\eta^5\text{-}C_9H_7)Cl(COD)]$, (dppm = bis(diphenylphosphino)methane; dppe = 1,2 bis(diphenylphosphino)ethane; COD = 1,5 cyclooctadiene) catalyze the dimerization of phenylacetylene to E and Z 1,4 diphenyl-1-buten-3-yne. The cyclopentadienyl complex $[Ru(\eta^5\text{-}C_5H_5)H(dppm)]$ is inactive [147].

Acknowledgements

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