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Review

Half-open metallocenes with heterodienyl ligands and related compounds☆

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This review is dedicated to Dr. Paul Powell in gratitude for allowing me to discover the pleasure of doing chemistry.

Contents

Abstract

This review surveys the chemistry of half-open metallocenes, half-sandwich and related compounds which include in their structure heterodienyl ligands, including oxygen, nitrogen, sulfur and phosphorus as heteroatoms. It covers the chemistry of the corresponding heterodienyls as anions,

☆ Note added after review of the manuscript by the referees: after submission of this manuscript, an interesting review concerned to the heteropentadienyl-transition metal complexes has been published by Bleeke [224].

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with main group, transition metals and the study of their reactivity; also some related compounds which contain heteroallyls, heterodiene or heterodienyl ligands are included.

Keywords: Half-open metallocenes; Heterodienyl ligands; Oxopentadienyl; Azapentadienyl; Thiapentadienyl; Phosphapentadienyl

1. Introduction

Although heterodienyl complexes were known early in the development of organometallic chemistry, it is only over the last 15 years that special attention has been devoted to their preparation and properties. It was generally assumed that properly designed heterodienyl complexes would provide new reactivity patterns and physical properties that could not be achieved with similar allyl, pentadienyl and cyclopentadienyl complexes. Heterodienyl ligands were expected to present different electronic interactions among them and metals. These and other expectations led to the progress in the field.

On one hand, cyclopentadienyl and allyl complexes have played a key role in the development of organometallic chemistry [1–3]. On the other hand, more recently developed pentadienyl ligands [1–5], which compared to allyls contain an extra double bond, are better chelates; therefore they may be expected to have higher thermal stability than allyls and higher reactivity than cyclopentadienyls. This is exactly what is expected of the corresponding heteropentadienyls, which are obtained by replacing one of the carbon atoms of the pentadienyl ligand with a heteroatom, such as oxygen, nitrogen, sulfur or phosphorus. This characteristic makes the heteropentadienyls the most versatile ligands. Moreover, they are able to formally donate a variable number of electrons to the metal.

At this stage, the chemistry of the heterodienyl metal compounds appears clearly under developed as much remains to be explored throughout the transition metal series with the various oxidation states. The systematic exploration of the potentiality of these ligands in organometallic chemistry is just beginning, and further studies will afford interesting results.

For the purposes of this review, the chemistry of the heterodienyl compounds is divided into four categories according to the heteroatom involved, specifically oxygen, nitrogen, sulfur or phosphorus, which will give the corresponding oxo-, aza-, thia- or phosphadienyl ligands. Most of the compounds discussed have the heteroatom at the terminal position of the heterodienyl ligands.

A discussion of the structural features and coordination modes of the heterodienyl group with special attention to transition metals is presented. The reactivity studies include chemical, photochemical and electrochemical processes with transmetallation, insertion, coupling, addition and oxidative addition reactions with the selective activation of C–H, C–C, C–X (X = O, N, S, P, Br) or O–O molecules.

2. Oxopentadienyl compounds

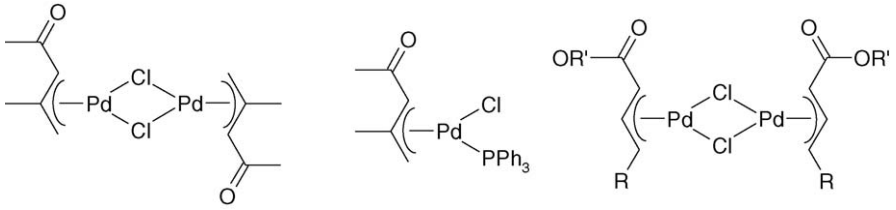
2.1. Oxopentadienyl anions with alkaline metals and cations

Although oxopentadienyl anions are useful reagents, most of them have not been studied in detail. A couple of reports refer to the abstraction of a proton from crotonaldehyde [6], *trans*-pent-2-enal [7], 2-methyl-pentenal and 2-methyl-2-butenal (tiglic aldehyde) [8], in the presence of potassium amide in liquid ammonia at low temperature, which afford the corresponding oxopentadienyl, 1-methyl-, 1,3-dimethyl- and 3-methyl-oxopentadienyl anions. However, the proposed conformations of these anions should be confirmed. Also, the electrocyclic ring opening dienolate anion, *cis*-1, *trans*-2-buta-1,3-dien-2-olate [9], from addition of *n*-BuLi [10] or KNH_2/NH_3 [9] to the 2,5-dihydrofuran showed the formation of a very stable isomer [9,10], which was unable to interconvert even at high temperature or prolonged times, which suggests a barrier to rotation of at least 23 kcal/mol [10].

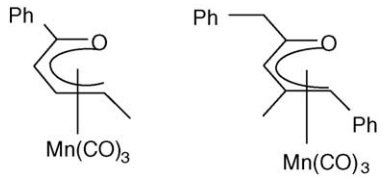
Quantum chemical DFT calculations have been used to gain insight into the conformational and energy properties of the oxopentadienyl ($CH_2CHCHCHO$) and oxoheptatrienyl (CH_2-CHCHCHCHCHO) cations and their corresponding cyclization reactions [11].

2.2. Oxopentadienyl compounds with transition metals

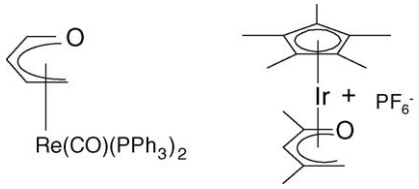
In the past, a few acyclic 1-oxopentadienyl transition metal compounds were described as unexpected products from various chemical reactions. For instance, the reaction of different palladium salts with α,β-unsaturated ketones or esters allows the formation of complexes $[PdCl\{\eta^3\text{-}CH_2C(Me)CHC(Me)O\}]_2$, $[PdCl(PPh_3)\{\eta^3\text{-}CH_2C(Me)CHC(Me)O\}]$ and $[PdCl\{\eta^3\text{-}CH(R)CHCHC(OR')O\}]_2$ (Scheme 1) [12,13].



Scheme 1.



Scheme 2.



Scheme 3.

Oxopentadienylmanganese complexes of the type $[Mn(CO)_3\{\eta^5\text{-}CH(Me)CHCHC(Ph)O\}]$ and $[Mn(CO)_3\{\eta^5\text{-}CH(Ph)C(Me)CHC(CH_2Ph)O\}]$ have been obtained from the reaction of $RMn(CO)_5$ with 1,3-butadiene [14,15] or by condensation of 1-phenylpropanone in the presence of $MeMn(CO)_5$ [16] respectively (Scheme 2).

Another unexpected reaction was the opening of furan by $Re(PPh_3)_2H_7$ to yield $[Re(\eta^5\text{-}C_4H_5O)(CO)(PPh_3)_2]$ (Scheme 3) [17].

The first report of half-open sandwich complexes containing acyclic 1-oxodienyl ligands corresponds to $[Cp^*Ir\{\eta^5\text{-}CH_2C(Me)CHC(Me)O\}][PF_6]$ and it was obtained by the reaction of cationic $[Cp^*Ir(Me_2CO)_3]^{2+}$ with 4-methylpent-3-en-2-one (mesityl oxide), which was formed in situ by a catalyzed aldol condensation (Scheme 3) [18,19].

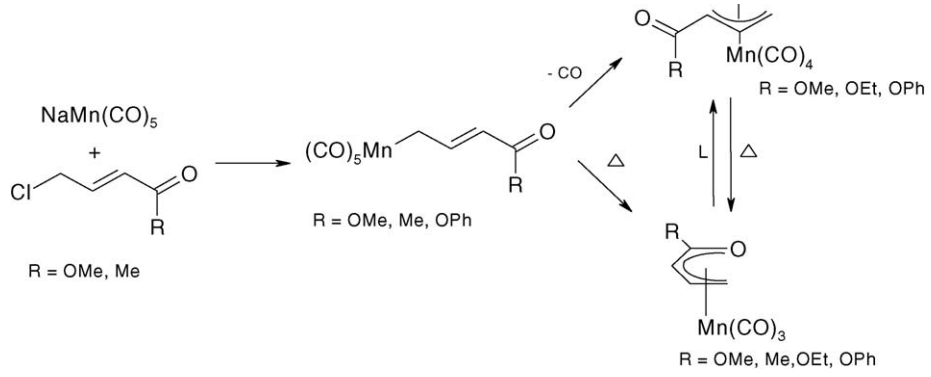
A similar metal-catalyzed aldol condensation is involved in the formation of the oxodienyl ligand in the complex $[NBu_4][(C_6F_5)_2Pd\{\eta^5\text{-}CH_2C(Me)CHC(Me)O\}]$ as a result of the reaction of di-μ-hydroxo palladium complex $[NBu_4]_2[(C_6F_5)_2Pd(\mu\text{-}OH)_2Pd(C_6F_5)_2]$ in acetone under reflux [20].

The interest in the chemistry of this kind of complexes based on specific designed synthetic procedures began around 1990s. Liu proposed a synthesis of oxopentadienylmanganese compounds, which consists in the use of halo-unsaturated esters or ketones in the presence of $NaMn(CO)_5$, in order to afford complexes $[(\eta^1\text{-}CH_2CHCHCOR)Mn(CO)_5]$, $[(\eta^3\text{-}CH_2CHCHCOR)Mn(CO)_4]$ and $[(\eta^5\text{-}CH_2CHCHCOR)Mn(CO)_3]$ (R = Me, OMe) (Scheme 4) [21].

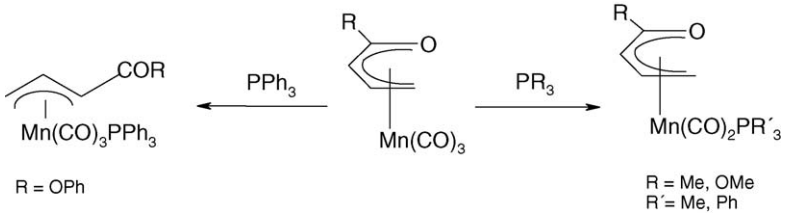
Similar complexes have been synthesized and crystal structures report the interconversion of η^1-, η^3- and η^5-ester dienolate complexes of manganese carbonyls with (R = OEt, OPh), as described in Scheme 4. The reaction of the complex $Mn[\eta^5\text{-}CH_2CHCHC(OPh)O](CO)_3$ with triphenylphosphine affords the corresponding $Mn(CO)_3(PPh_3)(\eta^3\text{-}CH_2CHCHCOOPh)$ [22] and the decarbonylation products $Mn(CO)_2(PR_3)(\eta^5\text{-}CH_2CHCHCOR)$ [21] (Scheme 5).

Convenient syntheses of half-open sandwich compounds with oxodienyl ligands have been reported by Ernst. The reaction of $[Cp^*RuCl]_4$ with enones or enals in the presence of K_2CO_3 leads to the formation of $[Cp^*Ru\{\eta^5\text{-}CH(R_4)C(R_3)C(R_2)C(R_1)O\}]$. In addition to these oxopentadienyl complexes, it is possible, in some cases, to observe other compounds as a result of the abstraction of CO from the oxodienyl ligand, which coordinates to ruthenium centers along with the remaining fragment of the ligand (Scheme 6) [23,24].

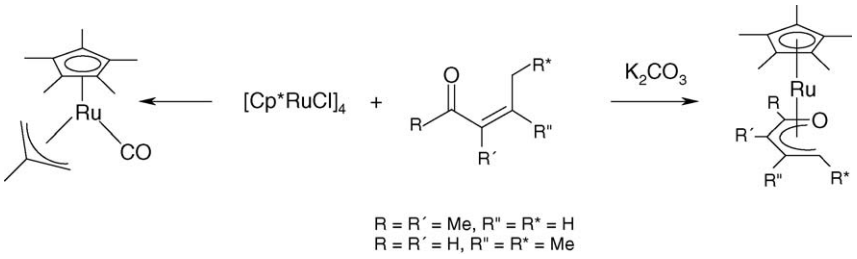
So, these results have been showing that methyl substituents in different positions of the ligand are important to stabilize the oxopentadienyl complexes [23,24].



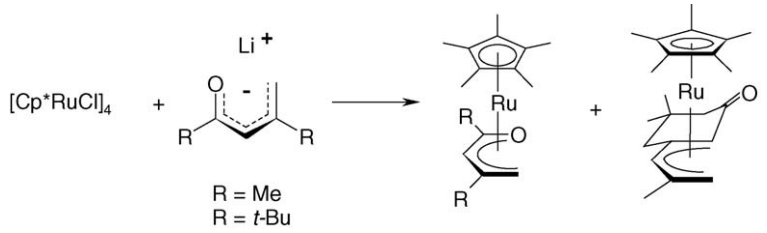
Scheme 4.



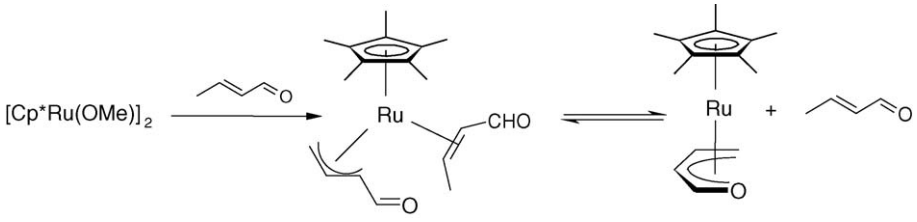
Scheme 5.



Scheme 6.



Scheme 7.



Scheme 8.

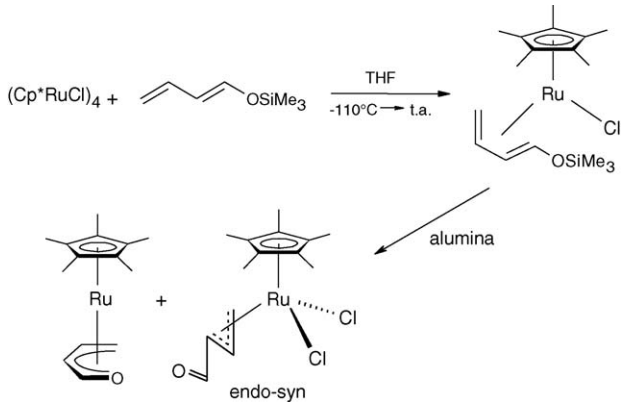
Lithium oxopentadienide reagents have been also reported as building blocks. The reactions of $[Cp^*RuCl]_4$ with $Li[CH_2C(R)CHC(R)O]$ (R = Me, *t*-Bu) lead to the formation of $[Cp^*Ru\{\eta^5\text{-}CH_2C(R)CHC(R)O\}]$ (Scheme 7) [25]. It is interesting to mention that during the formation of the η^5-oxopentadienyl complex, a second product was isolated in a minimum amount, and the crystallographic study showed the formation of a substituted pentadienyl complex $Cp^*Ru[\eta^5\text{-}CH_2C(Me)CHC\{CH_2C(Me)_2CH_2C(O)\}CH]$ (Scheme 7) [26].

Unsuccessful attempts to isolate $Cp^*Ru(\eta^5\text{-}CH_2CHCH\text{-}CHO)$ from $[Cp^*Ru(OMe)]_2$ and crotonaldehyde were explained on the basis of the absence of methyl groups as substituents on the oxopentadienyl ligand (Scheme 8) [27].

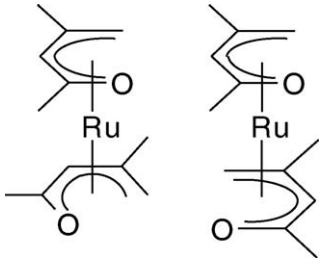
However, the isolation of $Cp^*Ru(\eta^5\text{-}CH_2CHCHCHO)$ in reasonable yield (67%) was obtained from the reaction of $Cp^*Ru(\eta^4\text{-}CH_2CHCHCHOSiMe_3)$ which in presence of alumina affords the mixture of compounds $Cp^*RuCl_2(\eta^3\text{-}CH_2CHCHCHO)$ and $Cp^*Ru(\eta^5\text{-}CH_2CHCHCHO)$ (Scheme 9) [26,28].

In 1991, the first homoleptic open ruthenocenes with η^5-oxopentadienyl ligands were obtained from the reduction of $RuCl_3{\cdot}xH_2O$ and an excess of mesityl oxide. The products were two isomers of $Ru[\eta^5\text{-}CH_2C(Me)CHC(Me)O]_2$ with different arrangements between the oxopentadienyl ligands, the *syn-gauche* and *anti-eclipsed* forms (Scheme 10) [29].

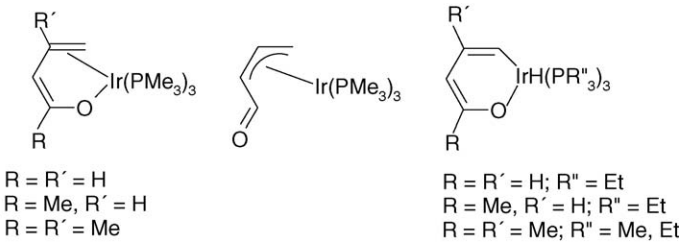
A systematic exploration of the synthesis of heterodienyl metal complexes has been carried out by Bleeke using halo-



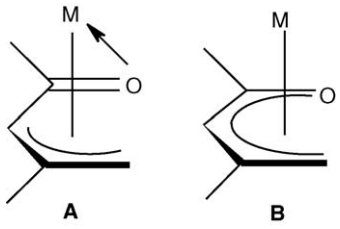
Scheme 9.



Scheme 10.



Scheme 11.



Scheme 14.

metal phosphine precursors. Specifically, potassium oxopentadienide reagents have been reported for iridium and rhodium compounds. The formation of isomers (1,2,5-η-), (1-3-η-) or (1,5-η-) oxopentadienyl iridium complexes has been proved (Scheme 11) [30,31].

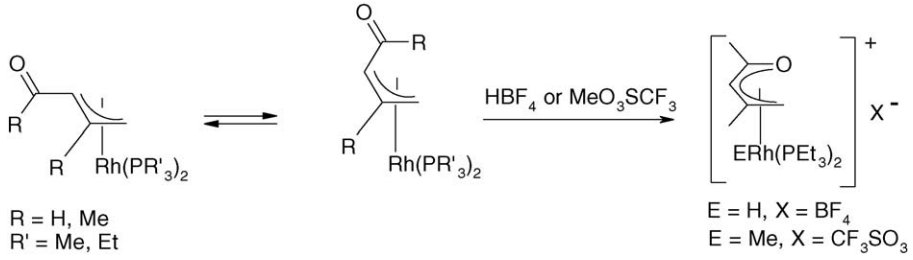
However, in the case of rhodium, treatment of $[Rh(\mu\text{-}Cl)(PR'_3)_2]_2$ (R′ = Me, Et) with potassium oxapentadienides leads to the production of $[Rh(PR'_3)_2\{\eta^3\text{-}CH_2C(R)CHC(R)O\}]$ (R = H, Me), which were observed as equilibrium mixtures of *anti* and *syn* isomers (R = H) or predominantly *anti* (R = Me). The complex $[Rh(PEt_3)_2\{\eta^3\text{-}CH_2C(Me)CHC(Me)O\}]$ reacted with electrophiles (HBF_4 and MeO_3SCF_3) to yield the corresponding η^5-oxopentadienyl derivatives $[Rh(PEt_3)_2(E)\{\eta^5\text{-}CH_2C(Me)CHC(Me)O\}][X]$ (E = H, X = BF_4; E = Me, X = CF_3SO_3) (Scheme 12) [32].

The crystal structure of the triflate salt of the η^5-derivative (Scheme 12) shows the nonplanarity of the oxopentadienyl ligand, and it is proposed that the (1-3,5-η) resonance structure (Scheme 14A) is an important contributor, along with the corresponding η^5 (Scheme 14B), to the overall bonding picture of this cation [32].

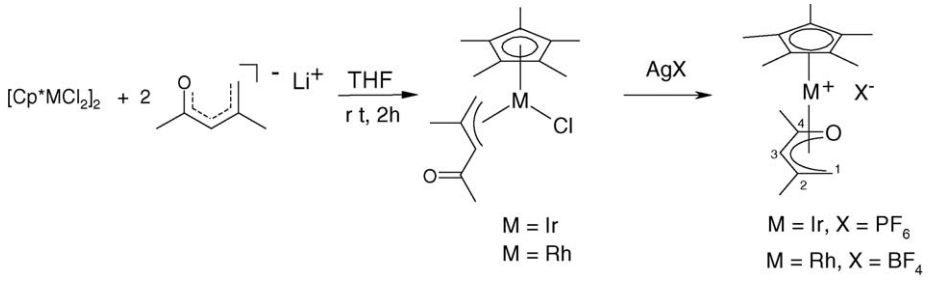
Treatment of $[Cp^*MCl_2]_2$ (M = Rh, Ir) with lithium 2-methyl-4-oxopentadienide produces η^3-oxopentadienyl-rhodium or iridium compounds $Cp^*MCl[\eta^3\text{-}CH_2C(Me)CHC(Me)O]$ [M = Ir, Rh] which in the presence of AgX, can be converted into the η^5 derivatives $[Cp^*M\{\eta^5\text{-}CH_2C(Me)CHC(Me)O\}][X]$ (M = Ir, X = PF_6; M = Rh, X = BF_4) (Scheme 13) [19].

In the $^{13}C\{^1H\}$ NMR spectrum of $[Cp^*Rh\{\eta^5\text{-}CH_2CH(Me)CHC(Me)O\}][BF_4]$ the signals for carbons C1 (δ = 72.3), C2 (δ = 121.5), and C3 (δ = 85.2) are doublets with J = 9.1, 5.9, and 4.1 Hz, respectively. The coupling indicates that C1, C2, and C3 are coordinated to the rhodium atom, while C4 from the CO group showed a singlet at δ = 171.4. The frequency of the C4 from the CO group is extremely high contrasted to the corresponding chemical shift C4 (δ = 158.7) in the iridium compound $[Cp^*Ir\{\eta^5\text{-}CH_2CH(Me)CHC(Me)O\}][PF_6]$. This indicates that the rhodium derivative experiences a strong inductive effect, and C4 is distinctly the most positively charged atom. This fact could point to a contribution from a resonance hybrid A in which there is an η^3-allylic bond, as well as the donation of the electron pair from the oxygen to the rhodium atom (1-3,5-η); meanwhile the resonance hybrid B is proposed for the iridium complex as described in Scheme 14. However, the X-ray diffraction studies show that there are similar interactions of the oxodienyl ligand for both compounds [19].

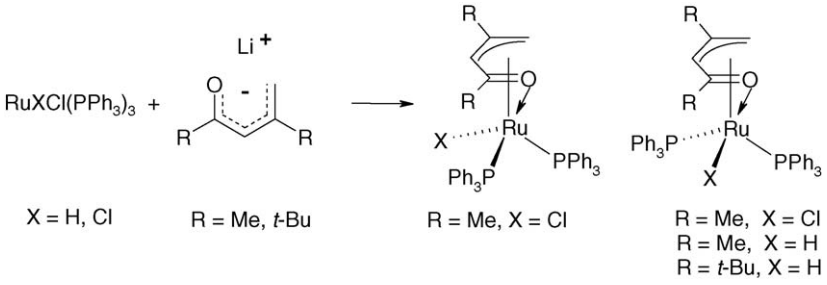
Lithium oxopentadienides and $[RuXCl(PPh_3)_3]$ have been used to obtain half-sandwich complexes of the type $[RuX(PPh_3)_2\{1\text{-}3,5\text{-}\eta\text{-}CH_2C(R)CHC(R)O\}]$ (X = Cl, R = Me;



Scheme 12.



Scheme 13.



Scheme 15.

X = H, R = Me; X = H, R = *t*-Bu) (Scheme 15) [33,34]. It is important to mention that the synthesis, with $RuCl_2(PPh_3)_3$ and the corresponding lithium 2,4-dimethyloxopentadienide, always shows the formation of both compounds with Ru–Cl and Ru–H bonds. The formation of $RuHCl(PPh_3)_3$ in situ, previously to the reaction with the lithium salt, is responsible for the hydride derivative, which in presence of chloroform could be partially transformed to the Ru–Cl complex (Scheme 15) [35]. There is also crystallographic evidence of the orthometallation product $(C_6H_4PPh_2)$Ru(2,4-dimethyl-η^5-oxopentadienyl)(PPh_3) [35].

A similar behaviour, as the one described for the oxopentadienyl Cp^*Rh and Cp^*Ir compounds, was observed in solid state and solution for the ruthenium complexes, where two resonance structures, as those described in Scheme 14, are proposed for the neutral compounds. Even though there is a delocalization over the oxopentadienyl ligands, and they are nearly planar structures, the 1-3,5-η-mode predominates in the solid state and in solution, according to the comparison to some related $Cp^*Ru(\eta^5$-oxopentadienyl) [23–26] $[Cp^*M(\eta^5$-oxopentadienyl$)]^+$ [M = Rh, Ir] [19] and (η^5-oxopentadienyl)$Mn(CO)_2L$ (L = CO, PPh_3) [21] compounds.

The trimethylsilyloxybuta-1,3-diene reacts with molybdenum or ruthenium precursors $[Cp^*Mo(NCMe)_2(CO)_2][BF_4]$, $[CpRu(NCMe)_2(CO)][OTf]$ to produce a mixture of isomers $[Cp^*Mo(CO)_2\{\eta^3$-$CH_2CHCHCHO\}]$ and $[CpRu(CO)\{\eta^3$-$CH_2CHCHCHO\}]$, respectively. The different conformation in such isomers has been established as *exo-syn*, *exo-anti* and *endo-syn* [36,37]. A theoretical study concerning the energy of the *exo* and *endo* conformations has recently appeared in the literature for $CpM(CO)(\eta^3$-$C_3H_5)$ (M = Fe, Ru) and $CpMo(CO)_2(\eta^3$-$C_3H_5)$ [38]. Quite recently, the silylated dienes have been also proved useful in the synthesis of new Cp^*Ru compounds [28]. The well known $(Cp^*RuCl)_4$ and $[Cp^*RuCl_2]_2$ react with trimethylsilyloxybuta-1,3-diene to afford compound $Cp^*RuCl(\eta^4$-$CH_2CHCHCHOSiMe_3)$ which treated under alumina affords $Cp^*Ru(\eta^5$-$CH_2CHCHCHO)$ and the *endo-syn* isomer of $Cp^*RuCl_2(\eta^3$-$CH_2CHCHCHO)$ (Scheme 9). The same ligand in ethanolic or methanolic solutions of $(Cp^*RuCl_2)_2$ affords compounds $Cp^*RuCl_2[\eta^3$-CH(Me)CHCH(OR)] (R = Me, Et), $Cp^*RuCl_2[\eta^3$-$CH_2CHCHCH(OR)_2]$ (R = Me, Et) and the *endo-syn* isomer $Cp^*RuCl_2(\eta^3$-$CH_2CHCHCHO)$ (Scheme 16) or $[Cp^*Ru(\eta^5$-$CH_2CHCHCHO)]_2(\mu_2$-$ZnCl_2)$ and $Cp^*RuCl[\eta^4$-$CH_2CHCHCH(OEt)]$ which can be prepared and isolated under different experimental conditions (Scheme 17) [28].

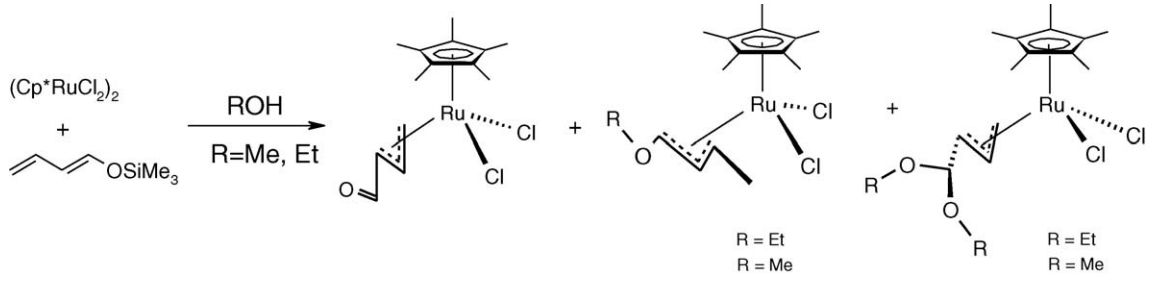
Under specific conditions the reaction of a mixture of isomers, 1,3-dimethylbutadienyloxytrimethylsilane and 4-methyl-2-trimethylsililoxy-1,3-pentadiene, with $[Cp^*RuCl]_4$ or $(Cp^*RuCl_2)_2$ affords compounds such as the oxopentadienyl $Cp^*Ru[\eta^5$-$CH_2C(Me)CHC(Me)O]$, the pentadienyl $Cp^*Ru[\eta^5$-$CH_2C(Me)CHC(OSiMe_3)CH_2]$, the oxodienyl $Cp^*RuCl_2[\eta^3$-$CH_2C(Me)CHC(Me)O]$ (Scheme 18) and $[Cp^*Ru(\eta^5$-$CH_2C(Me)CHC(Me)O)]_2(\mu_2$-$ZnCl_2)$, and the hydroxybutadiene complex $Cp^*RuCl[\eta^4$-$CH_2C(Me)CHC(Me)OH]$ (Scheme 19), respectively [28].

The photoelectron spectroscopic studies of $Cp^*Ru[\eta^5$-CH(R′)C(R)C(R′)C(R)X] (X=CH_2, R=Me, R′=H; X=O, R=Me, *t*-Bu, R′ = H; X = N(*t*-Bu), R = H, R′ = Me) show interesting features in their electronic structure of the pentadienyl, oxopentadienyl and azapentadienyl (Section 3.3) compounds [39].

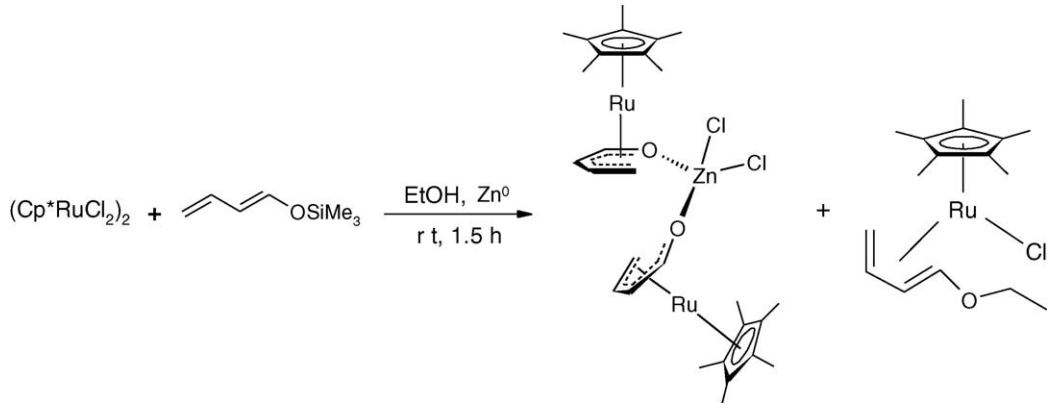
2.3. Reactions of oxopentadienyl transition metal compounds

2.3.1. Reactions with tertiary phosphines, carbon monoxide and alkynes

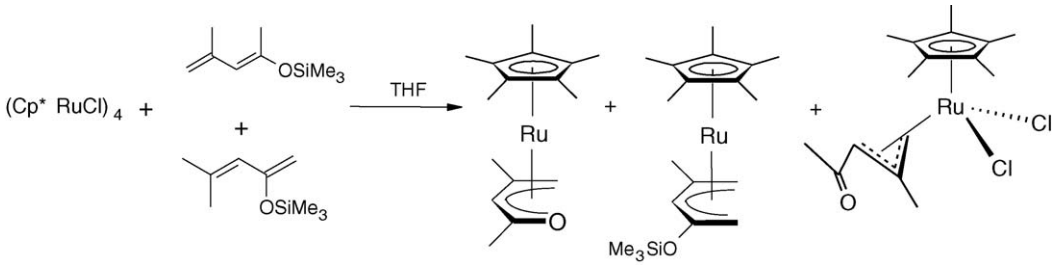
2.3.1.1. Phosphines. Reactivity studies on acyclic 1-oxopentadienyl transition metal complexes have been scarce.



Scheme 16.



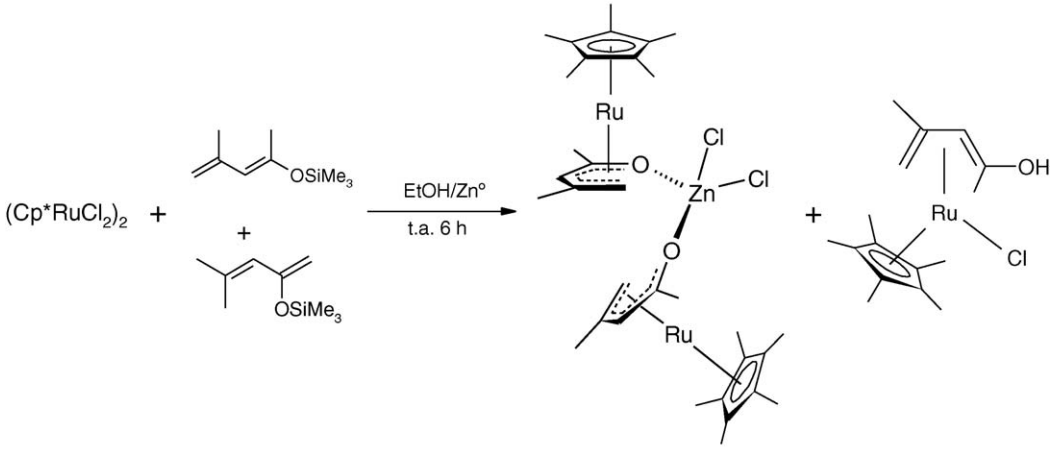
Scheme 17.



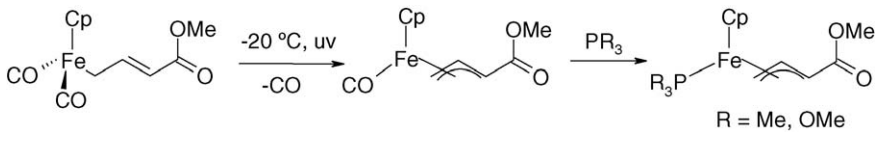
Scheme 18.

However, they have shown that such compounds revealed easy $\eta^5 \rightleftarrows \eta^3$ interconversion of the ligand promoted by the presence of the oxygen atom, which gives a variety of derivatives. For instance, the decarbonylation of $CpFe(CO)_2[\eta^1$-$CH_2CHCHC(OMe)O]$ in which the $\eta^1 \rightleftarrows \eta^3$ transformation occurs to produce $CpFe(CO)[\eta^3$-$CH_2CHCHC(OMe)O]$. The CO in the latter, can be substituted by PMe_3 or $P(OMe)_3$ in order to get $CpFe(PR_3)[\eta^3$-$CH_2CHCHC(OMe)O]$ [R = Me, OMe] (Scheme 20) [40].

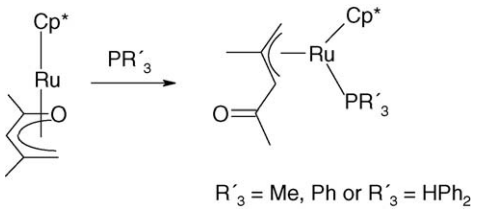
Another example is the reactivity of $[Cp^*Ru\{\eta^5$-$CH_2C(R)CHC(R)O\}]$ (R = Me) with PR_3, under refluxing cyclohexane, to yield complexes $[Cp^*Ru(PR'_3)\{\eta^3$-$CH_2C(Me)$-



Scheme 19.



Scheme 20.



Scheme 21.

CHC(Me)O}] (R′ = Me, Ph or R'_3 = HPh_2) in which only the conformation *exo-syn* was observed. In contrast to the previous example in which R = Me, the oxopentadienyl compound with bulky *tert*-butyl groups (R = *t*-Bu) yields no adducts with PPh_3 or PMe_3 even under THF reflux during 13 h (Scheme 21) [25].

As part of an effort to understand the reactivity of the oxodienyl ligand, the reactivity of cationic isoelectronic compounds [$Cp^*M\{\eta^5$-$CH_2C(Me)CHC(Me)O\}$][X] (M = Ir, X = PF_6; M = Rh, X = BF_4) was explored and compared to the one of ruthenium. The addition of phosphines PR_3 to the rhodium or iridium compounds led to the formation of isomers $Cp^*M(PR_3)$[1,5-η-$CH_2C(Me)CHC(Me)O$][X] (M = Ir, X = PF_6, R = Me, Ph) (M = Rh, X = BF_4: R = Ph) and $Cp^*M(PR_3)[\eta^3$-$CH_2C(Me)CHC(Me)O$][X] (M = Ir, X = PF_6: R = Me, Ph, R_3 = HPh_2; M = Rh, X = BF_4: R = Me, Ph) (Scheme 22). The 1,5-η and 1-3-η isomers were the kinetic and thermodynamic products, respectively. The η^3-oxopentadienyl-iridium complexes were established as *exo-anti* or *exo-syn* conformations, whereas the rhodium complexes formed *exo-syn* isomers, exclusively [19].

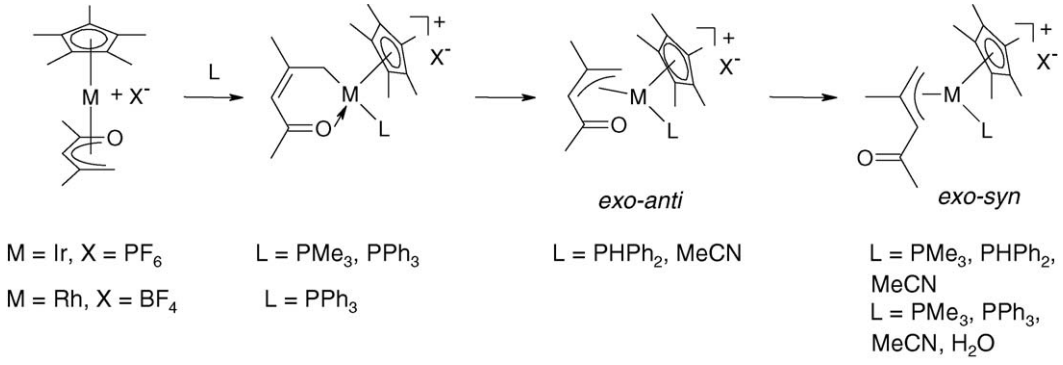
The addition reactions of phosphines to cationic iridium and rhodium compounds generally proceed much faster than those observed for the neutral ruthenium complex. The selectivity of rhodium and iridium compounds is evident and it is interesting to contrast the strongly preferred *exo-syn* conformation for rhodium and ruthenium complexes, meanwhile for iridium analogs both isomers can be presented as a mixture, depending on the reaction conditions.

Compounds $Cp^*M[\eta^5$-$CH_2C(Me)CHC(Me)O$][X] (M = Ir, X = PF_6; M = Rh, X = BF_4) also reacted with acetonitrile, and the rhodium complex also reacted with water to lead η^3-oxopentadienyl [$Cp^*M(L)\{\eta^3$-$CH_2C(Me)CHC(Me)O\}$][X] (M = Ir, X = PF_6: L = CH_3CN; M = Rh, X = BF_4: L = CH_3CN, H_2O) (Scheme 22) [19].

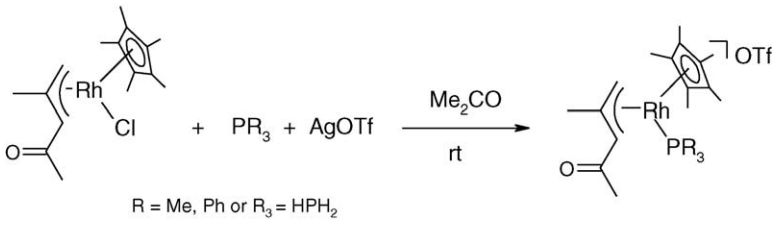
Exclusive transformation of the *exo-syn* derivatives [$Cp^*Rh(PR_3)\{\eta^3$-$CH_2C(Me)CHC(Me)O\}$][OTf] [R = Me, Ph or R_3 = HPh_2] can also be obtained by firstly adding AgOTf, and then, the corresponding phosphine PR_3 (R = Me, Ph or R_3 = HPh_2) to compound $Cp^*RhCl[\eta^3$-$CH_2C(Me)CHC(Me)O$] as described in Scheme 23 [19].

2.3.1.2. Carbon monoxide. The addition of CO, at atmospheric pressure, to a solution of compounds $Cp^*Ru(\eta^5$-$CH_2C(R)CHC(R)O)$ (R = H, Me) in refluxing THF gave the corresponding carbonyl products in a selective manner. The most stable compound is the one with an η^3-*anti* conformation (R = H) [28]; whereas the η^3-*exo-syn* complex is always preferred when R = Me [25]. However, the last complex is in equilibrium with the 2,4-dimethyl-η^5-oxopentadienyl complex, being unable to be isolated as a pure compound (Scheme 24).

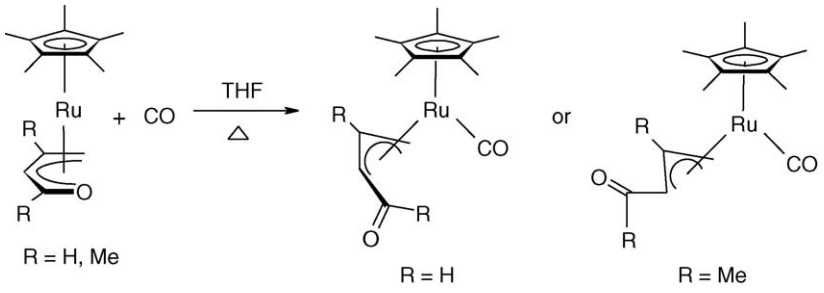
2.3.1.3. Alkynes. The diphenylacetylene reacts with compounds $Cp^*Ru(\eta^5$-$CH_2CHCHCHO)$, $Cp^*RuCl_2(\eta^3$-*endo-syn*-



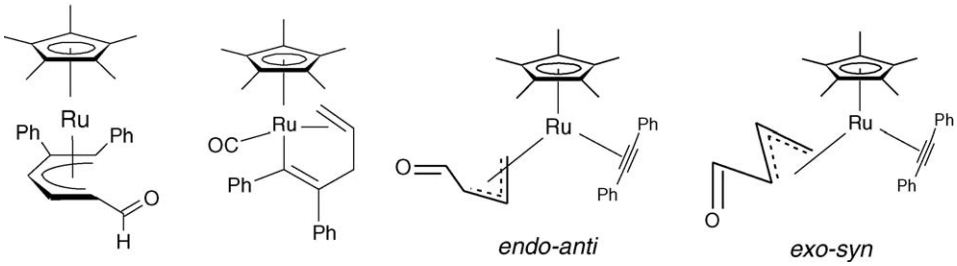
Scheme 22.



Scheme 23.



Scheme 24.



Scheme 25.

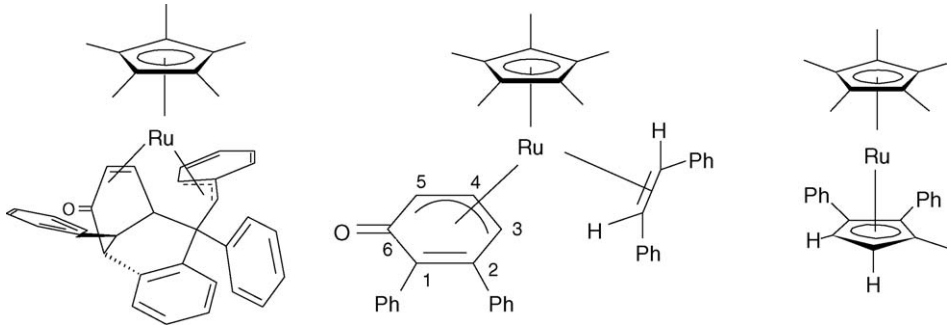
$CH_2CHCHCHO$) and $Cp^*RuCl_2[\eta^3$-*endo-syn*-CH(Me)CHCH-(OEt)] to afford a variety of acyclic $Cp^*Ru[\eta^5$-CH(Ph)C(Ph)CHCHCH(CHO)], $Cp^*Ru[1,4,5$-η-C(Ph)C(Ph)CH_2CH-CH_2]CO, *endo-anti* and *exo-syn* isomers of $Cp^*Ru(\eta^3$-$CH_2CHCHCHO)(\eta^2$-PhCCPh) (Scheme 25) [26,28] and compounds with cyclic structures, such as $Cp^*Ru[1,6,7,10,11$-η-CH-$(CH)_4$CCHC(Ph)CH$(CH)_2$C(O)CH(C_6H_4)CH(Ph)], Cp^*Ru-[3,4,5-η-C(Ph)C(Ph)-CHCHCHC(O)]$(\eta^2$-PhCH=CHPh) and $Cp^*Ru[\eta^5$-C(Ph)C(Ph)C(Me)CHCH] (Scheme 26) [26]. Compound $Cp^*Ru(\eta^3$-*exo-syn*-$CH_2CHCHCHO)(\eta^2$-PhCCPh) (Scheme 25) has also been reported in the presence of the dimer $[Cp^*Ru(\mu$-η^3-$O(CH_2)_2CH{=}CH_2)]_2$ and diphenylacetylene [41], and it has recently been established as the intermediate in the coupling reaction of $Cp^*Ru[\eta^5$-CH(Ph)C(Ph)CHCHCH(CHO)] [26].

The study of the reactivity of the 2,4-dimethyl-oxopentadienyl of $Cp^*Ru[\eta^5$-CH_2C(Me)CHC(Me)O] with excess of diphenylacetylene or dimethyl acetylenedicarboxylate showed the oxopentadienyl/alkyne coupling products $Cp^*Ru[\eta^5$-*syn*-CH(Ph)C(Ph)CHC(Me)CH(COMe)] and $Cp^*Ru[\eta^5$-*syn*-CH(COOMe)C(COOMe)CHC(Me)CH(COMe)], along with small amounts of $Cp^*Ru[\eta^5$-*syn*-CH(Ph)C(Ph)CHC{CH_2C(Ph)CH-(Ph)}CH(COMe)] and $Cp^*Ru[\eta^5$-*syn*-CH(COOMe)C(COO-Me)CHC{CH_2C(COOMe)CH(COOMe)}CH(COMe)]. The last two are products of a second coupling reaction which is the consequence of the activation of one of the C–H bonds of the 2-methyl substituent (Scheme 27) [26].

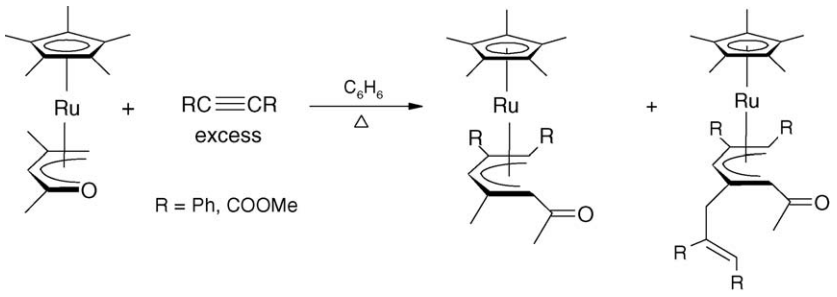
2.3.2. Oxidative addition reactions with halides, oxygen and tin tetrachloride

In the literature there is only one example of the bromation of compound $Cp^*RuBr[\eta^4$-$CH_2CHCHCH(OMe)]$ which yields the corresponding $[Cp^*Ru(Br)_2\{\eta^3$-$CH_2CHCHCHO\}]$ by losing MeBr (Scheme 28) [42].

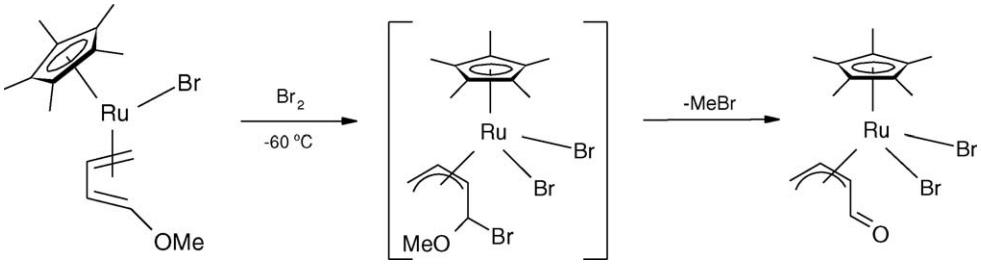
As mentioned before, the addition reactions of half-open ruthenocene of the type $[Cp^*Ru\{\eta^5$-CH_2C(Me)CHC(Me)O}] have been extensively explored. The oxidative addition reactions were also studied in detail and it was found that this complex reacts with $CHCl_3$, I_2, O_2 and $SnCl_4$, to lead stable ruthenium(IV) products $[Cp^*Ru(X_1)(X_2)\{\eta^3$-$CH_2$C(Me)CHC(Me)O}] ($X_1 = X_2 = Cl$; $X_1 = X_2 = I$; $X_1 = Cl$, $X_2 = SnCl_3$) and a peroxo compound $[Cp^*Ru(O_2)\{\eta^3$-



Scheme 26.



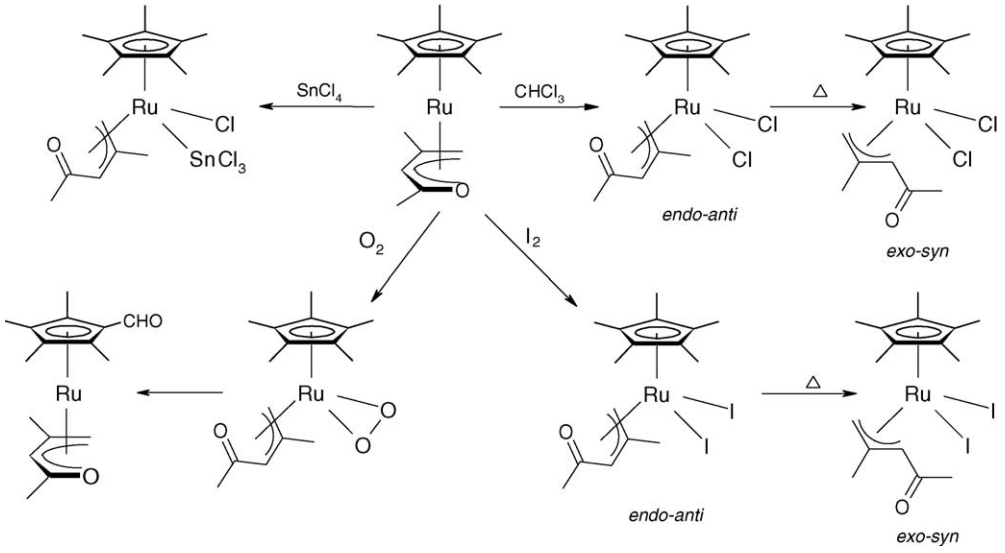
Scheme 27.



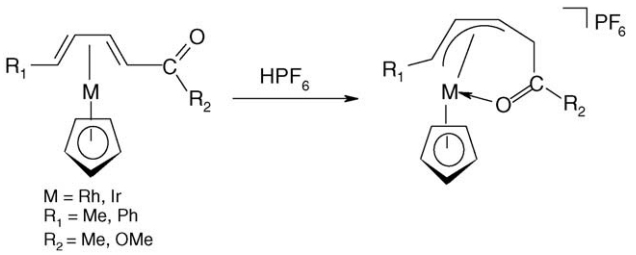
Scheme 28.

$CH_2C(Me)CHC(Me)O\}$] readily [20]. The transformation of kinetic *endo-anti* isomers to thermodynamics *exo-syn* ones was observed. It is important to mention that the formation of the peroxo complex by oxygen activation allowed the subsequent intramolecular C–H activation and oxidation of the Cp^* ligand to lead (η^5-C_5Me_4CHO)Ru[η^5-$CH_2C(Me)CHC(Me)O$] (Scheme 29). Peroxo compounds [$Cp^*Ru(O_2)\{\eta^3$-$CH_2C(R)CHC(R)X\}$] (X = O, R = Me, *t*-Bu; X = CH_2, R = Me) could be obtained through chemical [25,43] or electrochemical techniques [43,44]. The electrochemical oxidation of Cp^*Ru[η^5-$CH_2C(R)CHC(R)X$] (X = O, R = Me [25], *t*-Bu [43]; X = CH_2, R = Me [45]) in acetonitrile, under argon, has also been studied and crystal structures of Cp^*Ru[η^5-$CH_2C(Me)CHC(Me)CH_2$] [46] and [$Cp^*Ru(O_2)\{\eta^3$-$CH_2C(t$-Bu)$CHC(t$-Bu)$O\}$] [43] are solved.

In the case of the oxopentadienyl complex Cp^*Ru[η^5-$CH_2C(t$-Bu)$CHC(t$-Bu)O], the corresponding oxidative addition reactions proceeded in a more restrained way because of the bulkiness of *t*-Bu groups. Analogous stable ruthenium(IV) complexes were formed with $X_1 = X_2 = Cl$, $X_1 = X_2 = I$ and $X_1 = X_2 = O$ under chemical reaction conditions [25,43]. However, analogous peroxide complex [$Cp^*Ru(O_2)\{\eta^3$-$CH_2C(t$-Bu)$CHC(t$-Bu)$O\}$] was obtained in better yield by electrochemical techniques [43] as described above.



Scheme 29.



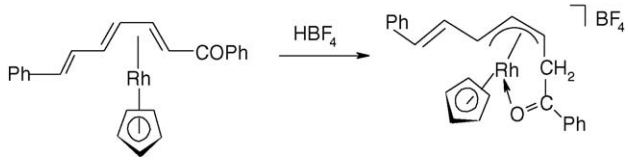
Scheme 30.

In contrast to neutral ruthenium complexes, cationic isoelectronic rhodium or iridium compounds were not stable in higher oxidation state, and the reactions with I_2 or $SnCl_4$ led to the loss of the oxopentadienyl ligand and the formation of Rh or Ir(III) products [19].

2.4. Related compounds with oxoallyl, oxodiene or oxodienyl ligands

The protonation of η^4-dienone or -dienoate complexes as $Cp^*M[\eta^4$-CH(R)CHCHCHC(R′)O] (M = Rh, Ir; R = Me, Ph; R′ = Me, OMe) affords crystalline salts of $[CpM\{\eta^3$-CH(R)-CHCHCH$_2$C(R′)O}][PF_6] (M = Rh, Ir, R = Me, Ph, R′ = Me, OMe in which the acyl CO group is coordinated to the metal) (Scheme 30) [47]. A similar coordination of the acyl group has been proposed for complex [η^4-CH(COPh)CHCHCH-(CH=CHPh)] which reacts with HBF_4 to give the salt $CpRh[\eta^3$-CH(CH$_2$COPh)CHCH(CH=CHPh)][BF_4] (Scheme 31) [48].

Treatment of [(1,2,5-η)-4-methyl-5-oxopentadienyl]Ir-(PMe_3)$_3$ with HBF_4·Et_2O leads to protonation at the central carbon of the heterodienyl ligand to afford [{(1,2,5-η)-4-methyl-5-oxopenta-1,4-diene}Ir(PMe_3)$_3$]BF_4, which at room temperature rearranges to the iridafuran complex [49]. A similar cationic intermediate, but with the tris-PEt_3, could be formed from a different precursor to afford analogous iridafuran complex under reflux of THF (Scheme 32) [31,49].



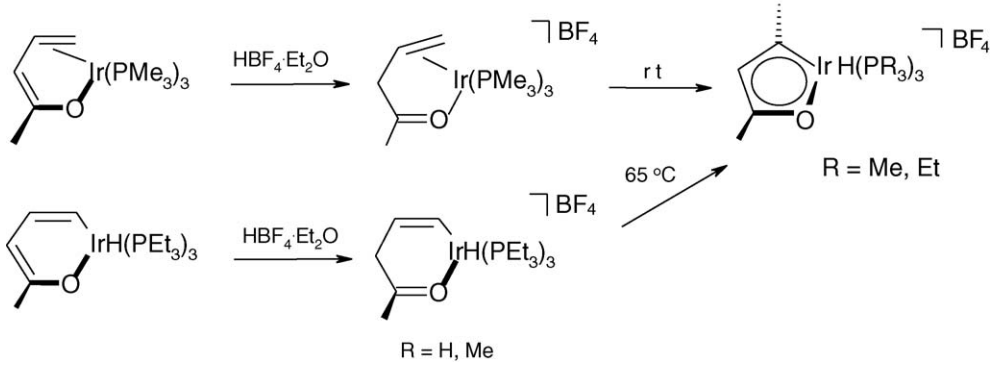
Scheme 31.

Meanwhile, the dimethylated compound [(1,5-η)-2,4-dimethyl-5-oxopentadienyl]Ir(H)(PEt_3)$_3$, described previously in Scheme 11 [31], reacts with $AgBF_4$ to afford a mixture of iridapyrylium and the protonated ring compound [Ir{1,5-η-CHC(Me)CH$_2$C(Me)O}][BF_4] (Scheme 33) [50,51]. Treatment of the metallapyrylium complex [(PEt_3)$_3$Ir{CHC(Me)CHC(Me)O}]BF_4 in presence of lithium tri-*tert*-butoxyaluminohydride [51] regenerates the metal-hydride precursor, as well as the reaction of the protonated ring in presence of LDA (Scheme 33) [50,51].

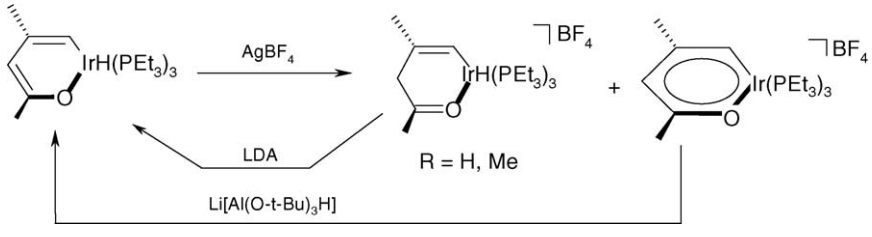
Some oxoallyl derivatives have been reported for several metals [52]. However there is only X-ray structural analysis for the manganese complex described in Scheme 34 [52–54].

Homoleptic tris(1-oxo-1,3-diene) molybdenum complexes Mo[CH$_2$CHC(O)NMe$_2$]$_3$ and Mo[CH$_2$C(Me)C(O)OMe]$_3$ in which the ligand bonding is best described as intermediate between η^4 and κ^2, η^2 coordination have been reported (Scheme 35) [55].

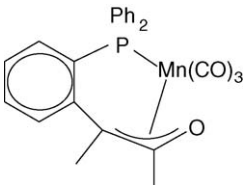
The reaction of Mo(CO)$_3$(MeCN)$_3$ with acrolein, crotonaldehyde and methyl vinyl ketone has been reported and the tentative characterization described needs to be reinforced [56]. However,



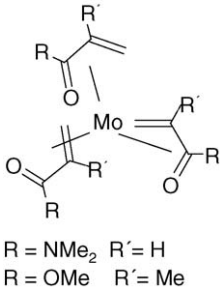
Scheme 32.



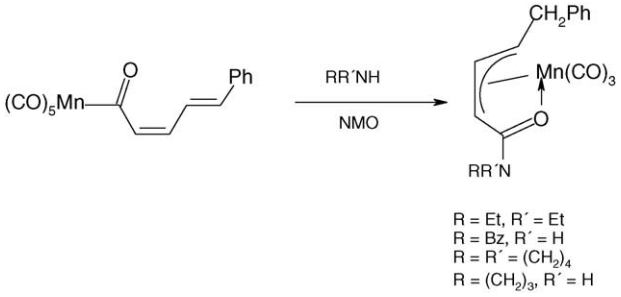
Scheme 33.



Scheme 34.



Scheme 35.

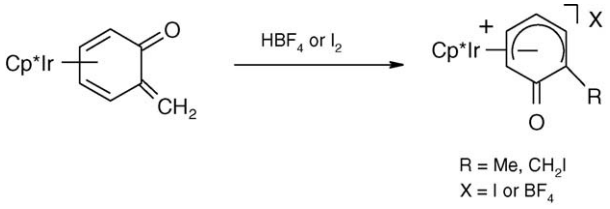


Scheme 36.

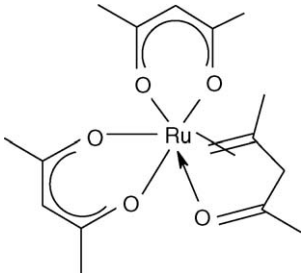
the crystal structure of the tris(methyl vinyl ketone)tungsten analogue has already been published [57].

Reaction of Li[$Mn(CO)_5$] and (2*Z*,4*E*)-5-phenylpentadienoyl chloride affords $Mn(CO)_5[\eta^1$-C(O)CH=CHCH=CH(Ph)]. Thermal and photochemical reaction attempts to affect the loss of terminal carbon ligands to give η^3- or η^5-pentadienoyl complexes were unsuccessful. Slow addition of *N*-methylmorpholine *N*-oxide (NMO) and selected amines to the $Mn(CO)_5[\eta^1$-C(O)CH=CHCH=CH(Ph)] gave $Mn(CO)_3$[1-3,5-η-$CH(CH_2Ph)CHCH(NRR')CO$] (Scheme 36) [58].

Coordination of 2-alkylphenols to $[Cp^*Ir(acetone)_3](BF_4)_2$ and subsequent deprotonation with Et_3N affords $(\eta^5$-$Cp^*)Ir[\eta^5$-(2-alkyl)oxodienyl$](BF_4)$ complexes; whereas after deprotonation with KO-*t*-Bu, it gives neutral *o*-quinone methide complexes such as $Cp^*Ir[\eta^4$-C_6H_4{=CH_2}O]. This Cp^*Ir-*o*-quinone methide complex exhibited unusual reactivity toward acids or electrophiles; for instance treatment with 1 equiv. of $HBF_4{\cdot}Et_2O$ or I_2 lead to the oxodienyl complexes $[Cp^*Ir(\eta^5$-$C_7H_7O)][BF_4]$ or $[Cp^*Ir(\eta^5$-$C_7H_6IO)][I]$, respectively (Scheme 37) [59,60].



Scheme 37.

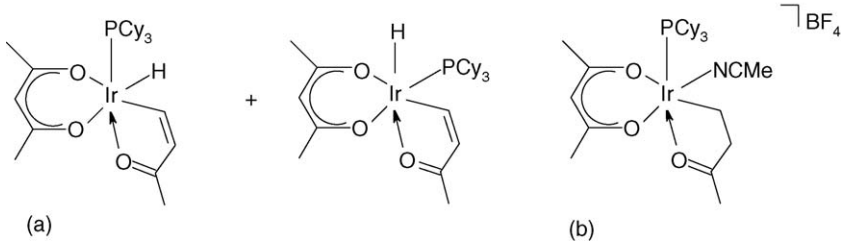


Scheme 39.

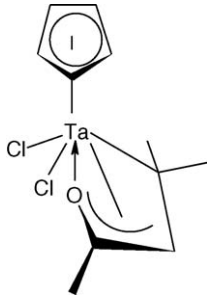
The cyclooctene ligand of Ir(acac)(cyclooctene)$(Pcy)_3$ is easily displaced by methyl vinyl ketone to give Ir(acac)[η^2-CH_2=CHC(O)Me](PCy_3). The nucleophilic character of the metallic center is revealed by means of the oxidative addition of the olefin CH bond, disposed *cis* to the –C(O)Me group of the coordinated methyl vinyl ketone molecule, to give a mixture of isomers of the hydrido-alkenyl complex Ir(acac)H[(*Z*)CH=CHC(O)Me](PCy_3), as described in Scheme 38a. The same reaction with HBF_4 and subsequent treatment with MeCN affords the compound described in Scheme 38b [61].

A chelate mono-alkene complex of $Ru(acac)_2[\eta^2$-$CH_2C(Me)CH_2C(Me)O]$ has been prepared from mesityl oxide (Scheme 39) [62].

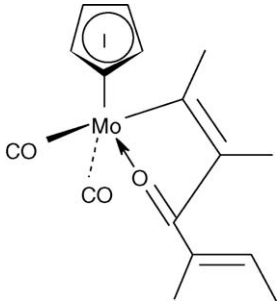
The tantalum compound $CpTa[OC(Me)CHC(Me)_2]Cl_2$ has been synthesized by reductive high-pressure carbonylation of $CpTaCl_4$ and subsequent treatment of the reactive intermediate with mesityl oxide (Scheme 40) [63].



Scheme 38.



Scheme 40.



Scheme 41.

Reaction of $[CpMo(CO)\{\eta^2\text{-}C(Me)C(Me)\}_2][BF_4]$ with lithium dimethylcuprate affords $CpMo(CO)[\eta^2\text{-}C(Me)C(Me)][\eta^1\text{-}C(Me)C(Me)_2]$, whereas reaction with $K[BH(sec\text{-}Bu)_3]$ followed by treatment of CO gives $CpMo(CO)_2[\eta^2\text{-}C(Me)C(Me)C(O)(R)]$ [R = C(Me)CHMe] (Scheme 41) [64].

3. Azapentadienyl compounds

3.1. Azapentadienyl anions with alkaline metals and magnesium

As an extension of pentadienyl [1,65–79] and oxopentadienyl [6–10] anion chemistry, the reactions and structures of azapentadienyl anions have attracted attention in both organic and inorganic chemistry. Würthwein et al. carried out the most systematic studies on experimental and theoretical chemistry of lithium 1-, 2-, and 3-azapentadienyls and related species [80–90].

Specifically, the stereochemistry of some lithium 1-azapentadienide was established through ^1H and ^{13}C NMR experiments (Scheme 42) as well as MNDO and ab initio calculations [80].

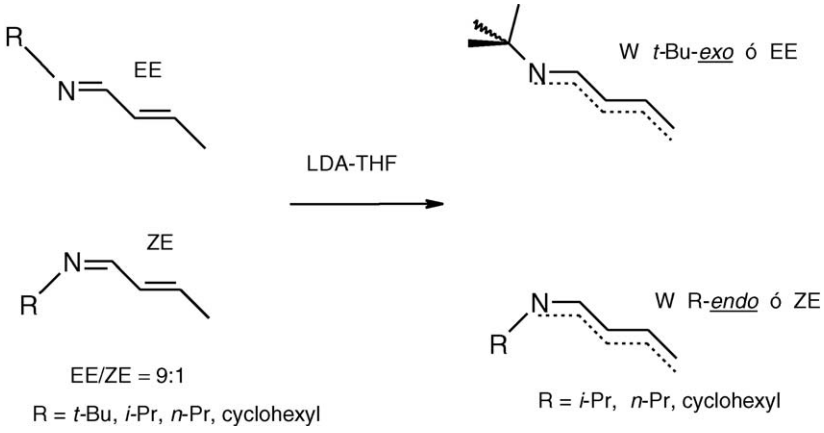
The mixture of α,β-unsaturated imines, as *EE*/*ZE* isomers, can be deprotonated by lithium diisopropylamide (LDA) in THF. In all cases the lithium azapentadienides adopt the W conformation. However, if the anion has a bulky substituent on nitrogen, such as the *t*-Bu group, the EE or *t*-Bu-*exo* W-shaped isomer will be favored; but if the anion has less bulky substituents on nitrogen, such as R = *i*-Pr, *n*-Pr or Cy, the major conformer will be *ZE* or R-*endo* W-shape isomer [80]. In presence of substituents on the lithium azapentadienide, particularly in the C2 and C4, the U conformation will be favored, as it has been observed for pentadienyl anions [66].

Treatment of α,β-unsaturated imines with potassium amide in liquid ammonia [91] affords the same W conformation as the lithium analogue [80]. The analogy has been established by comparison of the NMR data. According to that, there is a significant difference with the potassium pentadienide shape, which has a U preferential conformation [66].

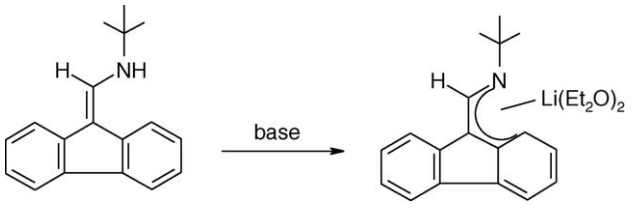
In the case of azapentadienides there is only evidence of U conformation in compounds with very bulky substituents, such as the anion of *N*-phenyl-1,3-diphenyl-2-butenaldimine [80,92].

Most of the azapentadienides studied have a lithium cation, only a few molecules have been reported with potassium, and there are no examples involving sodium as counterion. There is an interesting Cu(I) species of 1-azapentadienides [81] which in front of organic electrophiles affords exclusively the attack on the central carbon; whereas similar species using lithium as counterion afford the attack at the terminal carbon atom [81].

The electrophilic attack of $SiMe_3Cl$ on lithium azapentadienides affords trimethylsilylazapentadienes [93–95]. Some of these silicon derivatives suffer condensation with aldehydes in a γ-regioselective manner (terminal carbon) vide infra, Section 3.2 and contrastingly, the direct reaction of the lithium azapentadienide with an aldehyde affords products which are substituted at the central carbon atom [95,96].



Scheme 42.



Scheme 43.

The regiochemistry in the 1-azapentadienides is determined by the steric factors. In particular, the electrophile $SiMe_3^+$ almost always attacks at the terminal carbon, as observed for pentadienide anions for which a kinetic control has been established [66,97–99]. By analogy, it has been proposed that azapentadienides also show kinetic control and, according to it, Ahlbretch proposed that steric aspects are basically those which do not allow the attack on the most electrophilic places, such as the nitrogen atoms in these systems [92,100], even when sometimes nitrogen is the most electronegative atom in the molecule [81].

Generation of other 1-azapentadienyl [96,99,101–105] and 2-azapentadienyl anions [106–108] have been useful in organic synthesis and a number of studies have appeared.

Theoretical calculations predicted that 2-azapentadienides would be more reactive than the corresponding 1- and 3-azapentadienides, and that it would be unlikely to expect a direct electrophilic attack on the nitrogen atom because it is situated in a node of the conjugated 2-azapentadienide system [83].

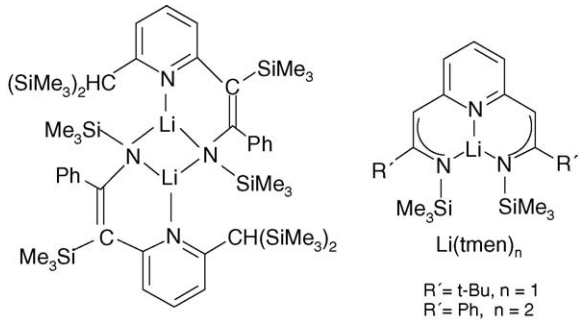
Treatment of the bis(silyl)allyllithium complexes [Li{η^3-CH(CHSiMe$_2$*t*-Bu)(CHSiMe$_2$R)}(Me$_2$NCH$_2$CH$_2$NMe$_2$)] (R = *t*-Bu, Me) and K[η^3-CH(CHSiMe$_2$*t*-Bu)$_2$] with *t*-BuCN yielded the 1-azapentadienyllithium or potassium compounds Li[N(SiMe$_2$R)C(*t*-Bu)CHCHCHSiMe$_2$*t*-Bu](Me$_2$NCH$_2$CH$_2$NMe$_2$) (R = *t*-Bu, Me) and [K{η^4-N(SiMe$_2$*t*-Bu)C(*t*-Bu)CHCHCH(SiMe$_2$*t*-Bu)$_2$}]$_\infty$, respectively [109]; and the synthesis of similar 1-azapenta-2,4-dienyllithium compounds and a series of potassium analogues was also published later [110].

Lithiation of 4-isopropylaminopent-3-en-2-one gave a 1-oxa-5-azapentadienyl tetrameric compound [N(*i*-Pr)C(Me)CHC(Me)OLi]$_4$ in which a heterocubane framework is formed with lithium–oxygen bonds and the nitrogen atoms are also coordinated to the corresponding lithium atoms. The addition of hexamethylphosphoric triamide produced a dimeric complex [N(*i*-Pr)C(Me)CHC(Me)OLi·OP(NMe)$_3$]$_2$ in which oxygen bridges are retained [111].

The *N*(*t*-butyldimethylsilyl)-3-buten-1-amine NH(SiMe$_2$-*t*-Bu)CH$_2$CH$_2$CHCH$_2$ reacts cleanly with 2 equiv. of *n*-BuLi to generate the 1-azapentadienyl lithium complex Li[N(SiMe$_2$-*t*-Bu)CHCHCHCH$_2$] [112].

The deprotonation of either 9-*N*(*t*-butylaminomethyl)-fluorene or the related 6-(*t*-butylamino)dibenzofulvene with butyllithium in diethyl ether yields the U-shaped η^5-azapentadienyllithium derivative described in Scheme 43. Under heating, this derivative showed a dynamic NMR spectra which was investigated by computational methods [88].

The regioselectivity of the reactions of heteroatom-stabilized allyl anions with electrophiles has been described in an extense review including *N*-allylimines [113]; and the preparation of



Scheme 44.

metalloenamines by deprotonation of *N*-alkenylimines has been reported after facile prototropic isomerization to *N*-allylic imines and α,β-unsaturated imines [114]. There is a comprehensive survey about the synthesis, characterization and reactivity of the main group and d- and f-block metal 1-azaallyl [115].

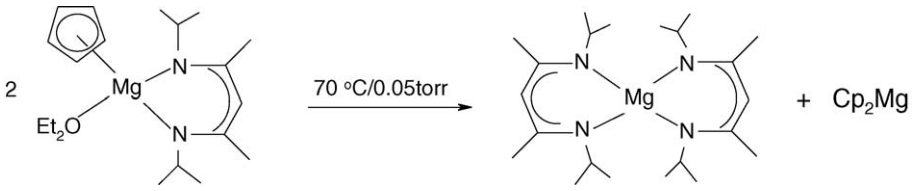
Recently, the synthesis and crystal structure (R′ = Ph) 1-azaallyls of type [Li{N(R)C(R′)C(H)(2-pyr)}]$_2$ [R = SiMe$_3$; R′ = Ph or *t*-Bu, 2-pyr = (C$_5$H$_3$N-2,6)] were reported, along with the versatile complexes [Li$_2$(tmen)][{N(SiMe$_3$)C(*t*-Bu)-CH}$_2$C$_5$H$_3$N-2,6] and [Li$_2$(tmen)$_2$][{N(SiMe$_3$)C(Ph)CH}$_2$C$_5$H$_3$N-2,6] as ligand transfer agents (Scheme 44) [116].

As example of group 2, treatment of CpMgMe(Et$_2$O)$_2$ with β-diketiminato ligands in diethyl ether gave compound CpMg[N(*i*-Pr)C(Me)CHC(Me)N(*i*-Pr)](OEt$_2$)$_2$ which slowly loss diethyl ether preventing its isolation. Attempts to sublime this complex afford a mixture of Cp$_2$Mg and Mg[N(*i*-Pr)C(Me)CHC(Me)N(*i*-Pr)]$_2$ as described in Scheme 45 [117]. Similar ligands have been used in small number of main group, transition and lanthanide metal complexes [117], as example, Scheme 82 in Section 3.5.

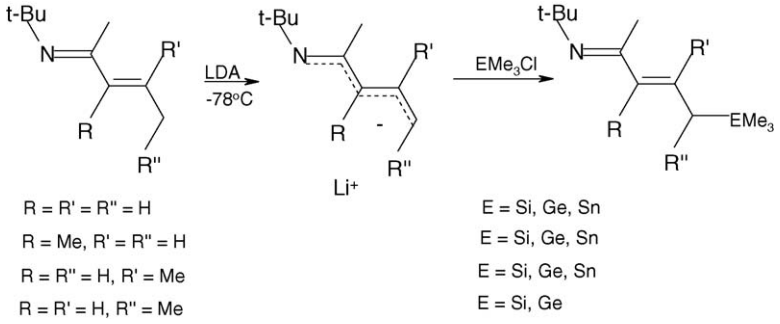
Finally and in contrast to anionic systems, the study of electrocyclization reactions of 1-aza- and 1-oxapentadienyl cations has been theoretically analyzed and discussed with respect to the corresponding experimental results [11]. Acyclic *O*- and *N*-substituted pentadienyl cations have also been theoretically and experimentally studied [118], and the synthesis of bis(pentadienylium) cations with bifunctional 1,4-phenylenediamine spacers leads to bis-cationic cyanine dyes with an enhanced delocalization pathway and original optical properties [119].

3.2. Azapentadienyl compounds with elements of group 14

The use of silylated and tin pentadienyl compounds is of increasing importance in synthetic chemistry because they are useful intermediates in organic synthesis, either as reagents for selective transformation or as intermediates for the creation of carbon–carbon bonds. In the latter case, the high selectivity of the tin–carbon bond cleavage involved in direct reactions, transmetallations or transition metal-catalyzed couplings is well established [120–127]. Pentadienyl anions are valuable precursors of pentadienylsilanes and stannanes, which are capable of converting ketones or aldehydes into dienyl alcohols [128].



Scheme 45.



Scheme 46.

The scope of the pentadienyl derivatives has now been extended considerably compared to the analogous chemistry for azapentadienyl derivatives from silicon [93–95,99] and related compounds [92,100,115,129–130], and only few reports involving the azapentadienyl derivatives from tin and germanium [106,131] have been published. A study of the 1-azapentadienides with different steric requirements along the chain was reported and extended to different elements from group 14, as it will be described here.

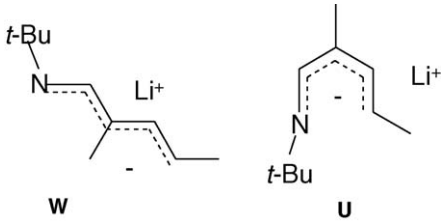
A series of lithium-1-azapentadienyls compounds Li[CHR″-C(R′)C(R)CHN-*t*-Bu] [R = R′ = R″ = H; R = Me, R′ = R″ = H; R = R″ = H, R′ = Me; R = R′ = H, R″ = Me; R = R″ = Me, R′ = H] show preference for the *exo* W-shaped isomer (Scheme 46), except for compound Li[CH(Me)CHC(Me)CHN(*t*-Bu)] which presents both W- and U-shaped structures in a 7:1 ratio (Scheme 47). Ab initio calculations predict that the W conformation will be more favorable than the U analogue by 4.7 kcal/mol [131].

The regio- and stereoselectivity of azapentadienyl compounds with organometallic electrophiles EMe_3^+ (E = Si, Ge, Sn) were studied. The reactions of the preferential *EE* isomers with these electrophiles generally gave the addition at the terminal carbon of the azapentadienyl moiety, which afforded the corresponding complexes $EMe_3CH_2CH{=}CHCH{=}N(t\text{-Bu})$ (E = Si, Ge, Sn); $Me_3ECH_2CH{=}C(Me)CH{=}N(t\text{-Bu})$ (E = Si, Ge, Sn) and the *EE* and *ZE* isomers $Me_3ECH_2C(Me){=}CHCH{=}N(t\text{-Bu})$ (E = Si, Ge, Sn), respectively (Scheme 48).

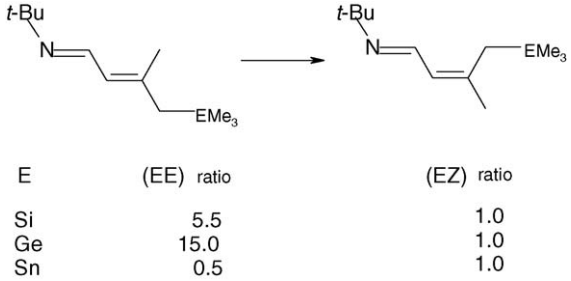
Compound Li[N(*t*-Bu)CHCHCHCH(Me)] reacts highly regioselectively with $SiMe_3Cl$ and affords the *EE* isomer $SiMe_3CH_2C(Me){=}CHCH{=}N(t\text{-Bu})$, but a diminished regioselectivity is observed with the corresponding Ge and Sn analogues. In contrast, an attack at the central carbon is observed for Li[(*t*-Bu)NCHC(Me)CHCH(Me)], which gives $CHMe{=}CH(EMe_3)C(Me)CH{=}N(t\text{-Bu})$ (E = Si, Ge) (Scheme 46). Although the regioselectivity remains for Si and Ge derivatives, a thermodynamic rearrangement occurs for the Sn isomer $SnMe_3CH(Me)CH{=}C(Me)CH{=}N(t\text{-Bu})$ which shows the addition of the $SnMe_3$ at the terminal carbon atom (Scheme 49) [131].

The study of the kinetic and thermodynamic products was established by ^1H, ^{13}C and ^{119}Sn NMR data, along with thermal isomerization studies. Condensed Fukui functions were derived from ab initio electronic structure calculations and they are useful reactivity indexes (better than conventional charges) to rationalize the observed Li[N(*t*-Bu)CHC(R)C(R′)CHR″] chemical derivation products with electrophiles [131].

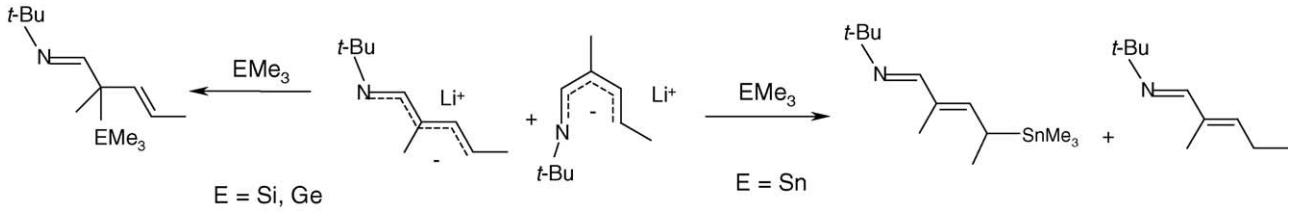
In successive electrophilic reactions with $SiMe_3Cl$, the regiochemistry of azapentadienides was controlled by steric



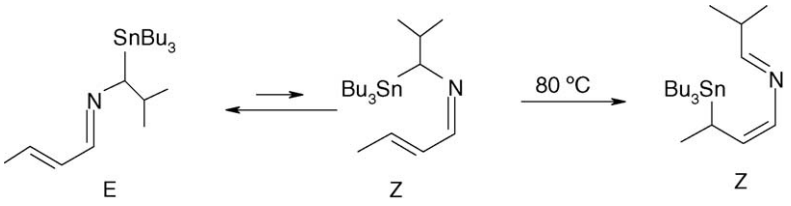
Scheme 47.



Scheme 48.



Scheme 49.



Scheme 50.

hindrance, as observed for N(*t*-Bu)CHCHCHMe and N(*t*-Bu)CHCHCMe$_2$ [93]. It has been observed that silylated azapentadienyl derivatives could suffer condensation with aldehydes in a γ-regioselective manner (at terminal carbon) to give useful polietilenic aldehydes in the synthesis of natural products [93–95], vide supra, Section 3.1. For stannyl imines isomers *E* and *Z* [(*i*-Pr)C(SnBu$_3$)N=CHCH=CH(Me)] are obtained in excellent yield, and there is evidence of [1,5]-sigmatropic rearrangement of the SnBu$_3$ group when the sample is heated (Scheme 50) [106].

3.3. Azapentadienyl compounds with transition metals

The manganese, iridium and ruthenium azadienyl chemistry has revealed some unique aspects.

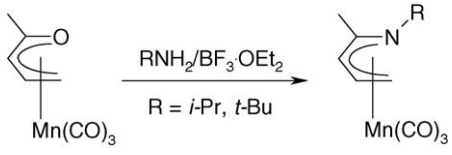
Apparently, η^5-azapentadienyl complexes have been prepared via the nucleophilic addition of RNH$_2$ (R = *t*-Bu, *i*-Pr) to the oxopentadienyl complex [Mn(CO)$_3$(η^5-CH$_2$CHCHCOMe)] (Section 2.2) in the presence of BF$_3$·OEt$_2$ (Scheme 51) [21].

The reaction mixture of MnBr(CO)$_5$ and the azapentadienyl tin derivative was monitored through the IR, and after 1 h of refluxing THF, compounds Mn(CO)$_3$[1-3,5-η-CH(R″)C(R′)C(R)CHN(R)] [R = *t*-Bu, R = R″ = H, R′ = Me; R = *t*-Bu, R = R″ = Me, R′ = H] and Mn(CO)$_3$[1,3-5-η-CH$_2$CHCHCHN(R)][R = *t*-Bu, *i*-Pr, Cy] were isolated as volatile yellow products (Scheme 52) [132,133].

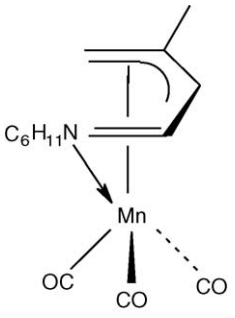
According to IR, ^{1}H and ^{13}C chemical shifts and coupling constants, the new azapentadienyl compounds are coordinated through the lone pair of the nitrogen atom (η^1-N) and the η^3-allyl moiety [132,133], instead of the full delocalized system η^5 proposed for the Mn(CO)$_3$[η^5-CH$_2$CHCHC(Me)NR] [R = *t*-Bu, *i*-Pr] (Scheme 53) [21].

The absence of planarity was clearly demonstrated with the crystallographic study of compound Mn(CO)$_3$[$\eta^{3,1}$-CH$_2$CHCHCHN(Cy)], in which the bond distance of Mn–C4 is 2.550(2) Å (Fig. 1) [133].

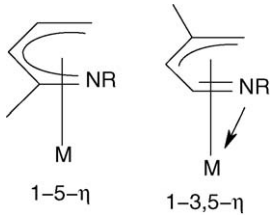
Half-open sandwich compounds have been developed recently with azapentadienyl ligands in a different coordination mode. They were obtained by the nucleophilic attack of primary amines (RNH$_2$) (R = Cy, *i*-Pr, *n*-Pr) to the oxopentadienyl complex [Cp*Ir(η^5-CH$_2$C(Me)CHC(Me)O)][PF$_6$]. A nucleophilic addition carried out on this cationic compound [Cp*Ir(η^5-CH$_2$C(Me)CHC(Me)O)][PF$_6$] with cyclohexylamine and isopropylamine affords a mixture of products [Cp*Ir(RNH$_2$)(η^3-CH$_2$C(Me)CHC(Me)O)][PF$_6$] and [Cp*Ir(1-3,5-η-CH$_2$C(Me)CHC(Me)NR)][PF$_6$] [R = Cy, *i*-Pr, *n*-Pr].



Scheme 51.



Scheme 52.



Scheme 53.

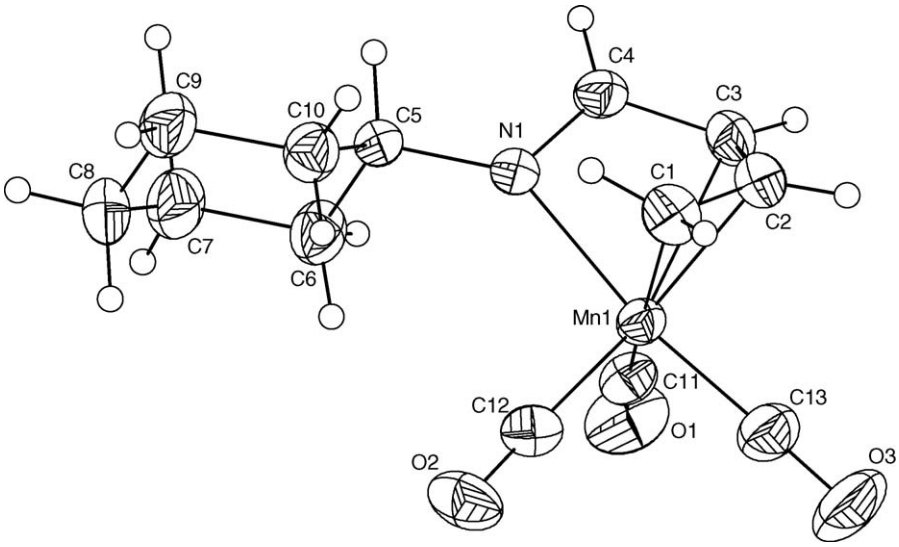
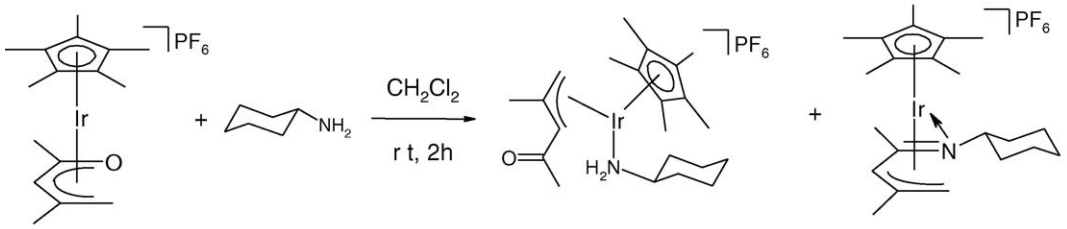


Fig. 1. Structure of $Mn(CO)_3[(\eta^{3,1}\text{-}CH_2CHCHCHN(Cy)]$.



Scheme 54.

Isolation of these mixtures is difficult, so they were studied only by ^1H and ^{13}C NMR, except for $[Cp^*Ir(CyNH_2)(\eta^3\text{-}CH_2C(Me)CHC(Me)O)][PF_6]$ which was fully characterized (Scheme 54) [134].

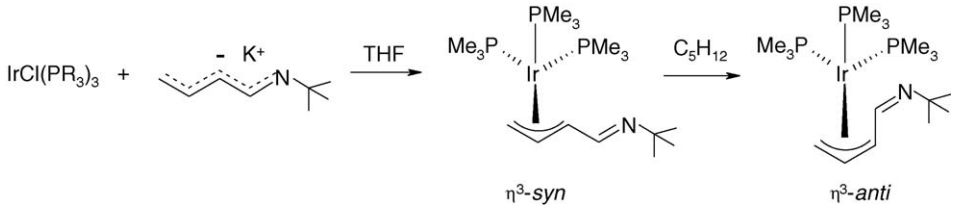
Some η^3-azapentadienyl complexes have been reported from the reaction of $ClIr(PMe_3)_3$ with potassium *tert*-butylazapentadienide (Scheme 55) [91].

The $Ir(PMe_3)_3[\eta^3\text{-}syn\text{-}CH_2CHCHCHN(t\text{-}Bu)]$ could isomerize to $Ir(PMe_3)_3[\eta^3\text{-}anti\text{-}CH_2CHCHCHN(t\text{-}Bu)]$. The absence of coordination of the nitrogen atom has been justified on the steric hindrance of the *tert*-butyl substituent. Relevant proton and carbon iminic chemical shifts of these *syn* and *anti* isomers are 7.41, 164.5 ppm and 7.11, 158.9 ppm, respectively. The reaction of these isomers in presence of triflic acid will be described in Section 3.4.

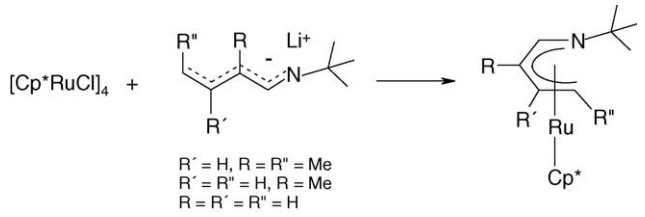
A successful synthesis of a nitrogen-containing half-open ruthenocenes was ultimately obtained from the azadienyl anions or through tin, germanium and silicon reagents, as described in Schemes 56 and 57, respectively.

The $[Cp^*RuCl]_4$ reacts readily with lithium *tert*-butylazapentadienide, which was prepared in situ at −78 °C from *tert*-butylazapentadiene and lithium diisopropylamine (LDA) in THF to afford the corresponding $Cp^*Ru(\eta^5$-azapentadienyl) compounds in high yield (Scheme 56). It is important to mention that the azapentadienide ion must be added to the tetramer in THF solution, otherwise $Cp^*Ru(\eta^5$-azapentadienyl) and Cp^*_2Ru in a 1:1 ratio will be formed [135].

An unexpected result was observed in the initial attempts to prepare the η^5-azapentadienyl compounds mixing directly the $[Cp^*RuCl]_4$ with an enimine in the presence of K_2CO_3: instead of the expected η^5-species, it lead to the formation of $Cp^*RuCl(\eta^4$-azapentadiene) compounds. Contrastingly, a similar synthetic procedure using aldehyde or ketone derivatives



Scheme 55.



Scheme 56.

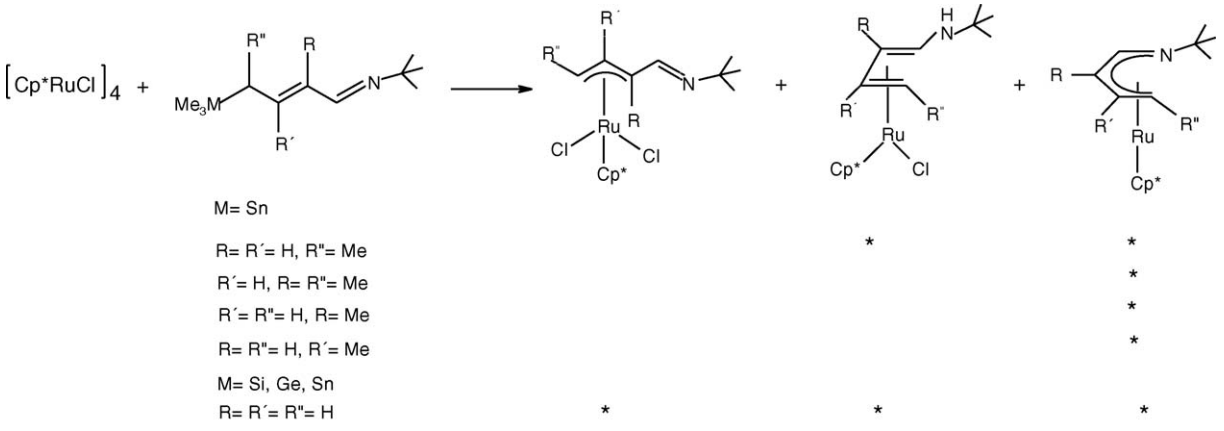
always afforded the corresponding $Cp^*Ru(\eta^5$-oxopentadienyl) compounds [23].

Group 14 enimine derivatives $Me_3MCH(R'')C(R')C(R)CHN(t\text{-Bu})$ (M = Si, Ge, Sn), were useful reagents to give, through transmetallation reaction with the ruthenium tetramer, compounds described in Scheme 57. The presence of methyl substituents on either R or R′ positions of group 14 enimine derivatives gives the formation of η^5 species; whereas in the absence of methyl substituents, treatment of $[Cp^*RuCl]_4$ afforded a mixture of η^4-, η^5-, and η^3-azapentadienyl ruthenium complexes (Scheme 57). The ratio of the species formed from reactions of $Me_3MCH_2CHCHCHN(t\text{-Bu})$ (M = Si, Ge, Sn) compounds and the ruthenium tetramer depended on the solvent. Reactions involving the Si derivative tended to favor the formation of an η^3 complex in THF, whereas the η^4 complex was formed almost exclusively in C_6D_6. The Ge derivatives led to the formation of η^3, η^4 and η^5 complexes with preferential formation of an η^4 complex in THF; whereas in C_6D_6 the η^5 complex dominated, followed by the η^4 species, and traces of the η^3 complex. In contrast, the Sn derivatives favored the formation of an η^5 complex in all cases [135]. It is clear from the comparative study between Si, Ge and Sn derivatives that the Si complexes react by a completely different mechanism than Ge and Sn; the reactivity of these derivatives correlates with the expected M–C bond polarity [136]. Another interesting η^4-butadien-α-imine compound $Cp^*RuCl[\eta^4\text{-}CH_2{=}CHCH{=}CHCH{=}N(t\text{-Bu})]$ was isolated in a very small yield, identify only by ^1H NMR, during the purification of the complex mixture of azapentadienyltin derivatives (Section 3.2) [132,135].

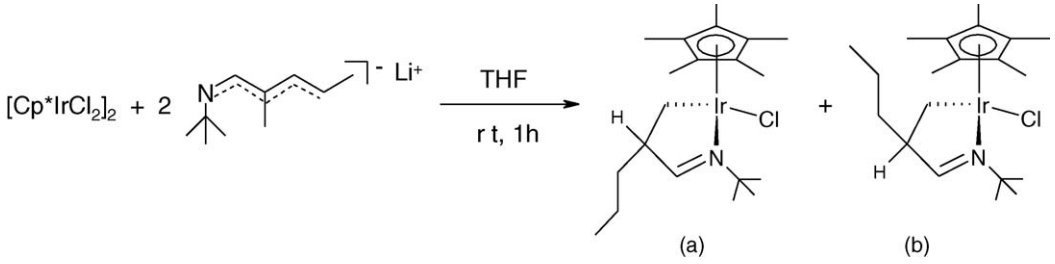
Crystal structures of different azapentadienyl iridium [91] and ruthenium [135] complexes are described in the literature. The photoelectron spectroscopy of the $Cp^*Ru[\eta^5\text{-}CH(Me)CHCH(Me)CHN(t\text{-Bu})]$ has been carried out and compared to the corresponding pentadienyl and oxopentadienyl analogues (Section 2.2) [39].

The chemistry displayed by the lithium azapentadienide in the formation of half-open η^5-aza-ruthenocenes (Scheme 56) was useful; therefore, analogous chemistry with the $[Cp^*IrCl_2]_2$ should also prove interesting.

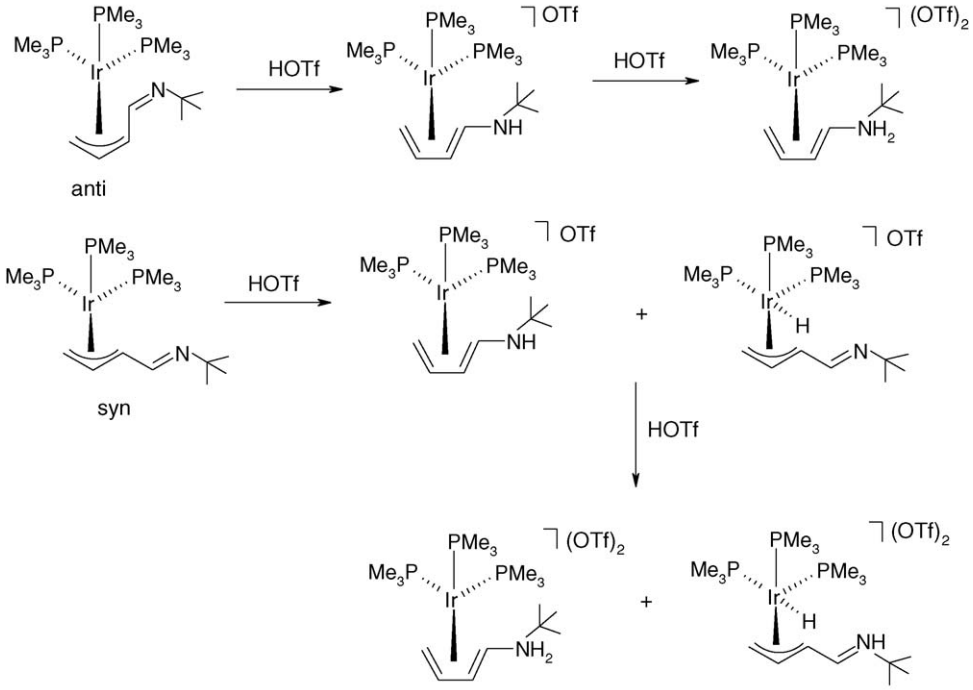
A reaction was indeed observed under similar conditions, but an entirely different course was followed (Scheme 58). A mixture of two azairidacyclopentene isomers was observed in a 2:1 ratio and the formation of these five-membered rings implies the C–H activation from one of the methyl groups. Crystallographic studies of $Cp^*IrCl[1,4\text{-}\eta\text{-}CH_2CH(Pr)CHN(t\text{-Bu})]$ (a) were carried out, and crystals from this isomer (a) in a solution of toluene-d_8 showed both isomers with the same 2:1 ratio, which suggests the presence of an equilibrium [134].



Scheme 57.



Scheme 58.



Scheme 59.

3.4. Reaction of the azapentadienyl ligands with transition metals

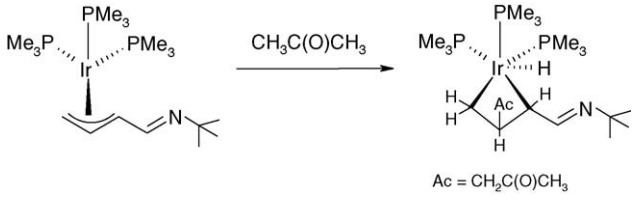
The reaction of $Ir(PMe_3)_3[\eta^3$-*anti*-$CH_2CHCHCHN(t$-$Bu)]$ with HOTf gives the protonation on the nitrogen atom, which affords an η^4-azapentadiene compound $[Ir(PMe_3)_3\{\eta^4$-$CH_2CHCHCHNH(t$-$Bu)\}][OTf]$; while isomer $Ir(PMe_3)_3[\eta^3$-*syn*-$CH_2CHCHCHN(t$-$Bu)]$ gives the formation of a hydride-iridium compound $[IrH(PMe_3)_3\{\eta^3$-$CH_2CHCHCHN(t$-$Bu)\}][OTf]$ (Scheme 59) [91].

The addition of a second equiv of triflic acid afforded, in both cases, dicationic species, with the double protonation on the nitrogen $[Ir(PMe_3)_3\{\eta^4$-$CH_2CHCHCHNH_2(t$-$Bu)\}][OTf]_2$ and the iridium and nitrogen protonation $[IrH(PMe_3)_3\{\eta^3$-$CH_2CHCHCHNH(t$-$Bu)\}][OTf]_2$ for the *syn* and *anti* derivatives, respectively (Scheme 59). It is interesting to mention that the reaction between compound $Ir(PMe_3)_3[\eta^3$-*syn*-$CH_2CHCHCHN(t$-$Bu)]$ and a molecule of acetone gives the formation of the adduct $IrH(PMe_3)_3[\eta^3$-*syn*-$CH_2CH(Ac)CHCHN(t$-$Bu)]$ [Ac = $CH_2C(O)Me$], probably as a result of the attack of the ketone or due to the enolic form, at the central carbon atom, of the azapentadienyl ligand (Scheme 60) [91].

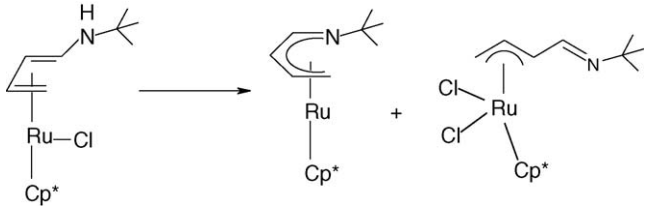
The transformation of compound $Cp^*RuCl[\eta^4$-$CH_2{=}CHCH{=}CHNH(t$-$Bu)]$, into a C_6D_6 solution, afforded compounds $Cp^*Ru[\eta^5$-$CH_2CHCHCHN(t$-$Bu)]$ and $Cp^*Ru[\eta^3$-$CH_2CHCHCHN(t$-$Bu)](Cl)_2$ after 4 days at room temperature (Scheme 61) [135].

A similar reaction has been observed for $Cp^*RuCl(\eta^4$-$CH_2{=}CHCH{=}CHOSiMe_3)$ which gives the corresponding $Cp^*Ru(\eta^5$-$CH_2CHCHCHO)$ and $Cp^*Ru(\eta^3$-$CH_2CHCHCHO)(Cl)_2$ along with crotonaldehyde, Me_3SiCl, Me_3SiOH and $(Me_3Si)_2O$ [28]. The apparent instability of $Cp^*Ru(\eta^3$-$CH_2CHCHCHN(t$-$Bu))(Cl)_2$ [135] contrasts with the analogous $Cp^*Ru(\eta^3$-$CH_2C(R)CHC(R)O)(Cl)_2$ (R = H [28], Me [25]) and $Cp^*Ru(\eta^3$-$CH_2C(Me)CHC(Me)CH_2)(Cl)_2$ [25]. Compound $Cp^*Ru(\eta^3$-$CH_2CHCHCHN(t$-$Bu))(Cl)_2$ can exist as *syn-cis* and *syn-trans*, which corresponds to the kinetic and thermodynamic isomers, respectively (Scheme 62) [135].

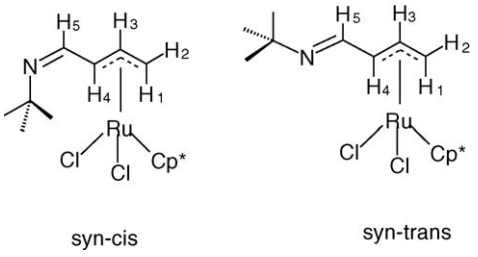
The addition of AgOTf to compound $Cp^*RuCl[\eta^4$-$CH(Me){=}CHC(Me){=}CHNH(t$-$Bu)]$ lead to a new product $Cp^*Ru[1$-2,5-η-$CH(Me)CHC(CH_2)CHN(t$-$Bu)]$ along with the expected η^5 complex $Cp^*Ru[\eta^5$-$CH(Me)CHC(Me)CHN(t$-$Bu)]$. The unexpected product (1-2,5-η) has a double bond and a nitrogen atom coordinated to ruthenium, and presents



Scheme 60.



Scheme 61.



Scheme 62.

an unusual mode of coordination of the enimine (Scheme 63) [135].

Reaction of the azapentadienyl complex $Cp^*Ru[\eta^5$-$CH_2CHC(Me)CHN(t$-Bu)] with diphenylacetylene affords the azadienyl/alkyne coupling product $Cp^*Ru[\eta^5$-N(*t*-Bu)CHC(Me)CHCH{C(Ph)CH(Ph)}] (Scheme 64) [137].

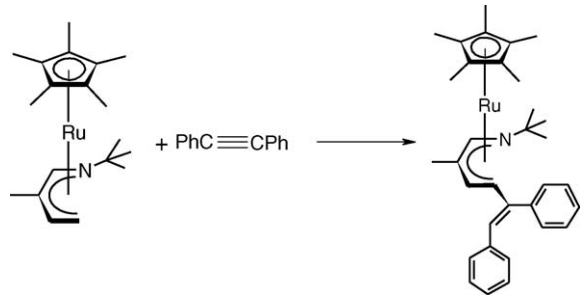
3.5. Related compounds with azaallyl, azadienyl and azadiene ligands

Reactions of primary and secondary amines with (η^5-pentadienyl)tricarbonylmanganese have been investigated and spectroscopic characterization proved that the nitrogen has been added stereoselectively to the terminal carbon atom on the pentadienyl ligand and it also coordinates to the manganese atom. A single proton abstraction from the NH or NH_2 groups occurs with the formation of the neutral substituted aminopentenyl derivatives, which gives evidence of the cyclohexylamino isomers of the kinetic and thermodynamic products, respectively (Scheme 65) [138,139].

The molecular structure for the kinetic intermediate, cyclohexylamino-pentenyl tricarbonylmanganese complex Mn[1-3,5-η-$CHMeCHCHCH_2N(RR')](CO)_3$, as well as those for the thermodynamic products, including pyrrolidyl, piperidyl, isopropyl and *tert*-butyl derivatives Mn[2-4,5-η-CH_2MeCH-$CHCHN(RR')](CO)_3$ have been published [138,139].

Reactivity of Mn[2-4,5-η-$CH_2MeCHCHCHN(RR')](CO)_3$ towards PMe_2Ph affords Mn[2-4-η-$CH_2(Me)CHCHCH$-$(NRR')](CO)_3(PMe_2Ph)$, which suggests the labile Mn–N coordinate bond in some complexes [138]. Contrastingly, the reaction of equimolar primary amine derivative Mn[HN(*i*-Pr)(η^3-$CHCHCHCH_2Me)](CO)_3$ and PMe_2Ph afforded essentially starting materials [139].

Mixtures of regioisomers are obtained from the reaction with (1-methyl-η^5-pentadienyl)tricarbonylmanganese and *iso*-propyl and *tert*-butyl-amines (Scheme 66) [138].



Scheme 64.

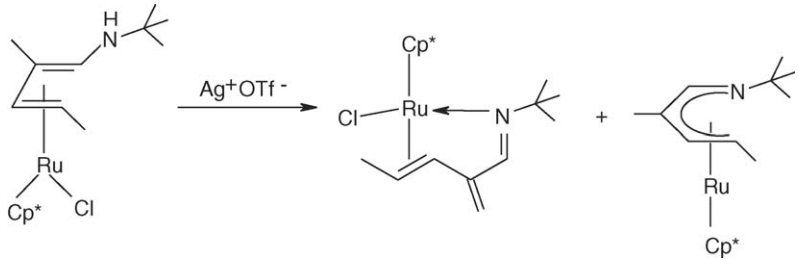
Reaction of $PHCH_2Mn(CO)_5$ with 1,4-diaryl-1-aza-1,3-butadienes gives substituted pyrrolinolyl rings which are η^4-coordinated to a $Mn(CO)_3$ moiety. The formation of these compounds is proposed by intramolecular CO insertion into a non-isolated cyclomanganated intermediate, followed by cyclization. Other unsaturated reagents, such as phenylacetylene and methyl acrylate, can suffer a coupling to the azabutadiene through C4 to give a [tri-aryl-η^5-azacyclohexadienyl-$Mn(CO)_3$] and the disubstituted methyl-7-azahepta-3,6-dien-2-yloate ligand coordinated to a $Mn(CO)_3$ fragment via an η^3-allyl interaction with the remaining two electrons coming from the N atom (Scheme 67) [140].

Terminal alkynes react with an alkyl hydride η^1-acetone complex *trans*-$[IrH(OCMe_2)(CH_2NMePy)(PPh_3)_2]BF_4$ to afford a coupled η^3-allyl complex via a proposed pathway that involves C–C bond formation by $C(sp^3)$–$C(sp^2)$ reductive elimination (Scheme 68) [141].

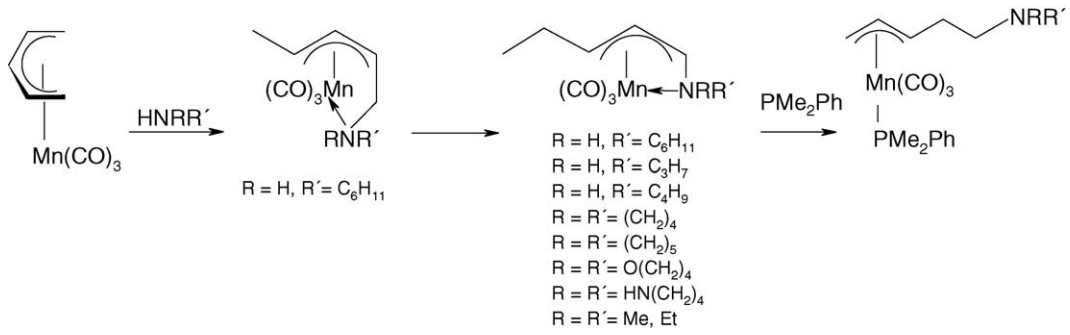
The synthesis of azametallacycles has been poorly explored, being the main efforts related to organic synthesis. Azametallacycles can be formed by insertion of organitriles or isocyanides in metal–ligand bonds [142,143], insertion of organoazides between Ni–C bonds [144], oxidative addition of haloaromatic-amino species on Pd(0) [145], cycloaddition of imido compounds with Ti, Zr, or Os with alkenes, alkynes and organoazides [146–148].

The reaction of 1-chloro-2,2-dicyanovinyl complexes $CpM(CO)_3[C(Cl)C(CN)_2]$ [M = Mo, W] under hydrolysis (in presence of alumina or triethylamine) or alcoholysis (in presence of methanol or ethanol and the corresponding sodium alkoxide) gives different kinds of metallacycles $CpM(CO)_2$[1,4-η-$C(R'')C(R')C(R)NH$] [R″ = H or CO_2R, R′ = CN, R = OH or OR] (Scheme 69) [149].

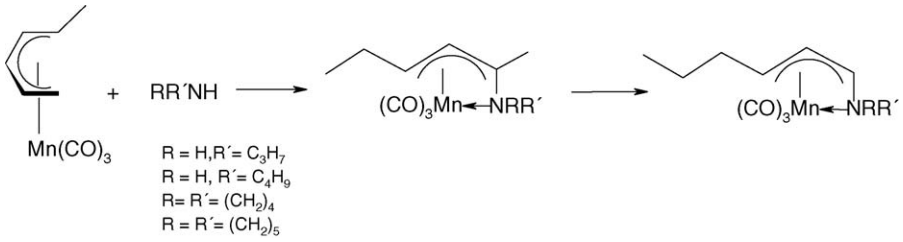
The synthesis in high yields of 1-azabuta-1,3-dienes was achieved by imine condensation of arylamines with cinnamalde-



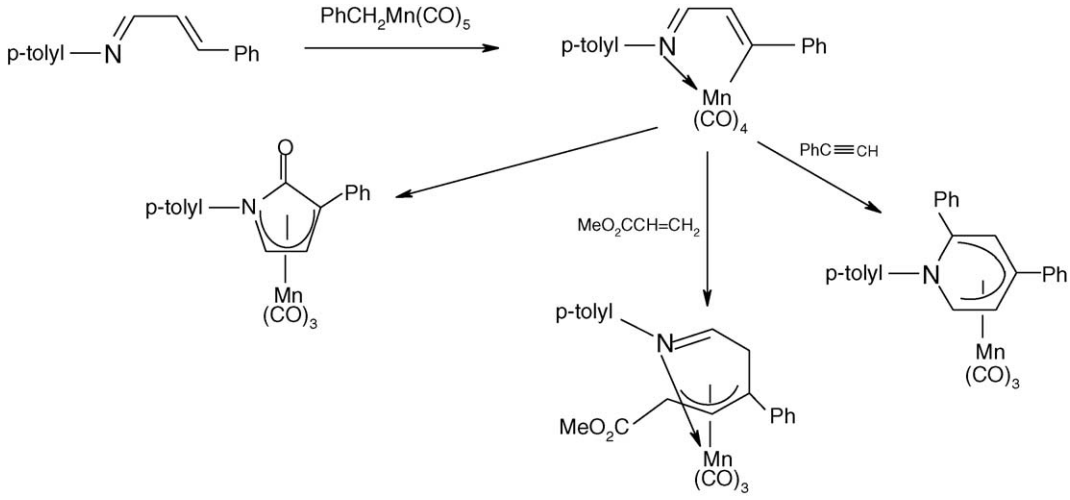
Scheme 63.



Scheme 65.



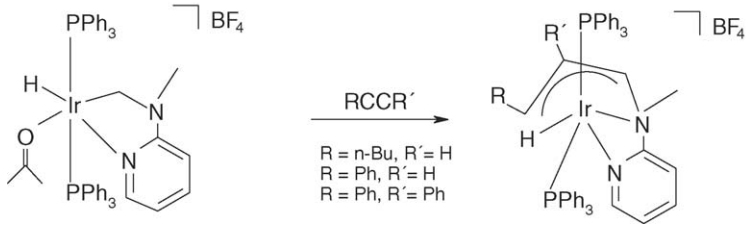
Scheme 66.



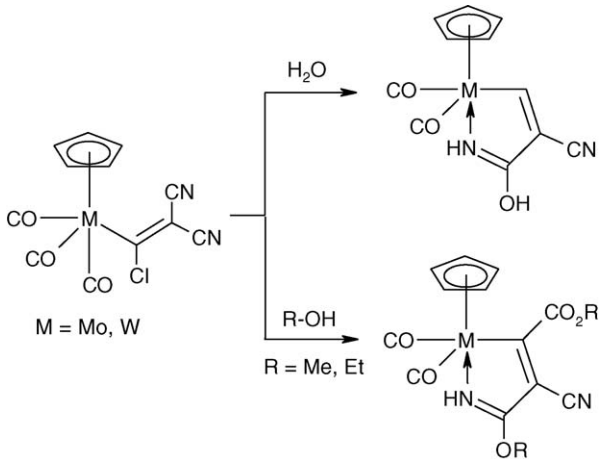
Scheme 67.

hydes. The electron density at the nitrogen of the 1-azabuta-1,3-dienes is crucial for the efficiency of the tricarbonyliron fragment using nonacarbonyldiiron or pentacarbonyliron. The ultrasound technique was found to be superior to the thermal one, particularly in the complexation of chiral 1-azabuta-1,3-dienes (Scheme 70) [150].

An optically pure 1-azabuta-1,3-diene adduct of iron (0) $Fe[N(CHMePh)CHCHCH(Ph)](CO)_2(PPh_3)$ has been reported [151]. Overviews of synthetic and structural aspects of 1-azabuta-1,3-diene complexes of iron are given and the reactivity of these complexes is discussed with regard to fluxional behaviour and inorganic, organometallic,



Scheme 68.



Scheme 69.

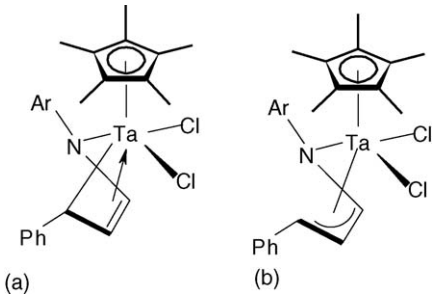
organic and stereochemical aspects of their chemistry [152].

The intramolecular C–C coupling of an alkyne with the acetymidoyle in tantalum compounds of general formula CpTa(Me)[η^2-C(Ar)C(Ar)][η^2-C(Me)N(*t*-Bu)] gives the azametallacyclopentatriene CpTa(Me)[1,4-η-C(Ar)C(Ar)C(Me)N(*t*-Bu)] (Scheme 71) [153].

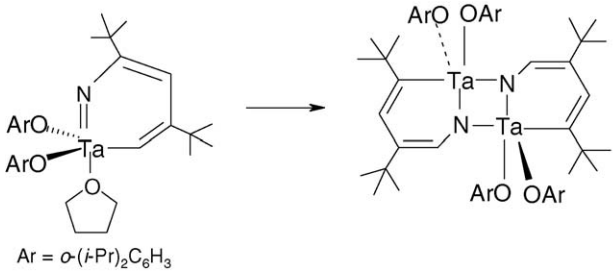
The treatment of a dimeric complex $[Cp^*TaCl_2]_2$ with (1,4-diphenyl)- or (1-*p*-methoxyphenyl-4-phenyl)-1-aza-1,3-butadiene affords half-metallocene complexes $Cp^*Ta(Cl)_2$(1,2-3,4-η-CH(Ph)CHCHN(Ar)) [Ar = Ph, *p*-(MeO)C_6H_4]. Compound with substituent Ar = Ph (Scheme 72a) proves to have a significant contribution of a [η^1-*N*-η^3-allyl, (1-3,4-η)] canonical form (Scheme 72b) [154].

Heating a solution of the THF adduct of [Ta{NC(*t*-Bu)CHC(*t*-Bu)CH(OAr)$_2$}(THF)] with Me_3SiI results in the formation of $Me_3SiOCH_2CH_2CH_2CH_2I$ and the dimer [Ta(μ-NC(*t*-Bu)CHC(*t*-Bu)CH(OAr)$_2$)]$_2$ as described in Scheme 73 [155].

The condensation of aromatic amines ($ArNH_2$, Ar = Ph, *p*-tolyl) with the oxaplatinacycle PtCl(CO)[1,4-η-C(Ph)CHC(Me)O] gives the corresponding azaplatinacycle PtCl(CO)[1,4-η-C(Ph)CHC(Me)N(Ar)] (Scheme 74) [156].



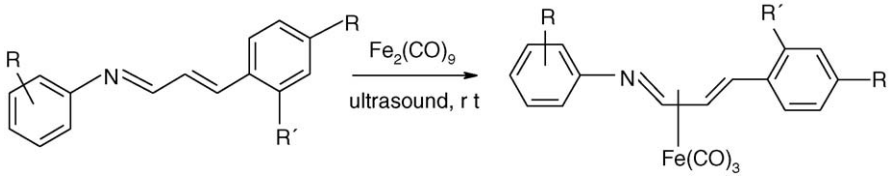
Scheme 72.



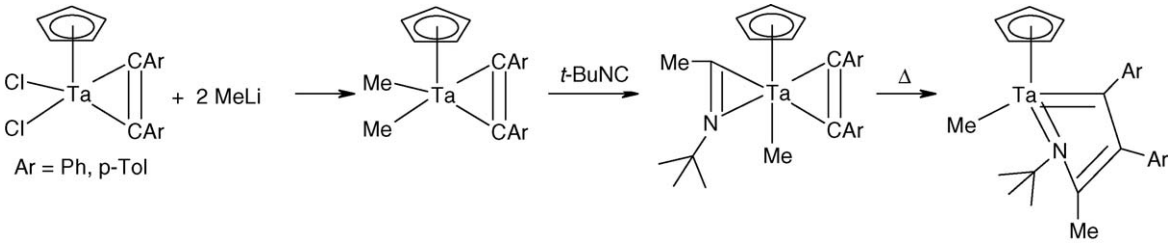
Scheme 73.

Both heterometallacycles have also been studied in presence of 1 and 2 equiv. of PPh_3, which forms PtCl(PPh_3)[1,4-η-C(Ph)CHC(Me)X] [X = O, NAr] via substitution of CO by the first PPh_3, and then, the descoordination of the heteroatom affords the corresponding species PtCl(PPh_3)$_2$[η^1-C(Ph)CHC(Me)X] [X = O, NAr] (Scheme 75) [156].

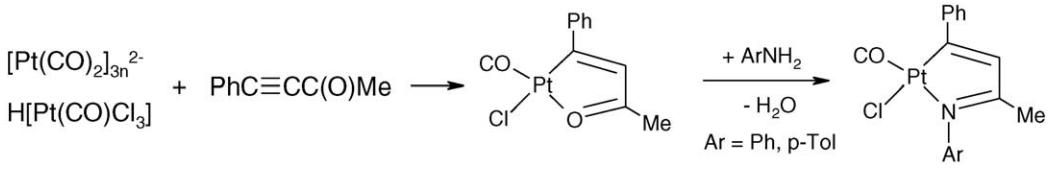
Azametallacycles were obtained by the regiospecific and stereoselective addition of HCl and $P(OMe)_3$ to RhCl(CO)[1-2,5-η-$CH_2C(R)CH_2CH(CO_2R')NH_2$], which is obtained from the $[Rh(CO)_2Cl_2]_2$ with allyl allylglycinates. The monomeric intermediates $RhCl_2(CO)P(OMe)_3$[1,4-η-C(Me)(R)$CH_2CH(CO_2R')NH_2$] are transformed in dimeric



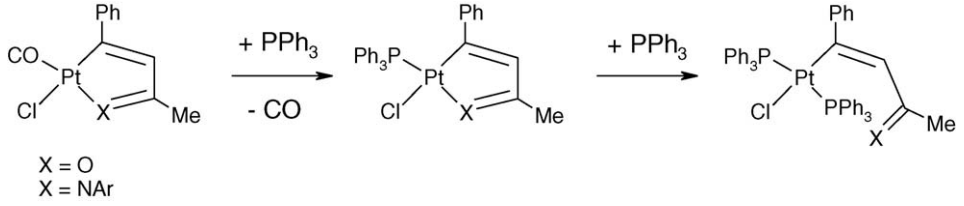
Scheme 70.



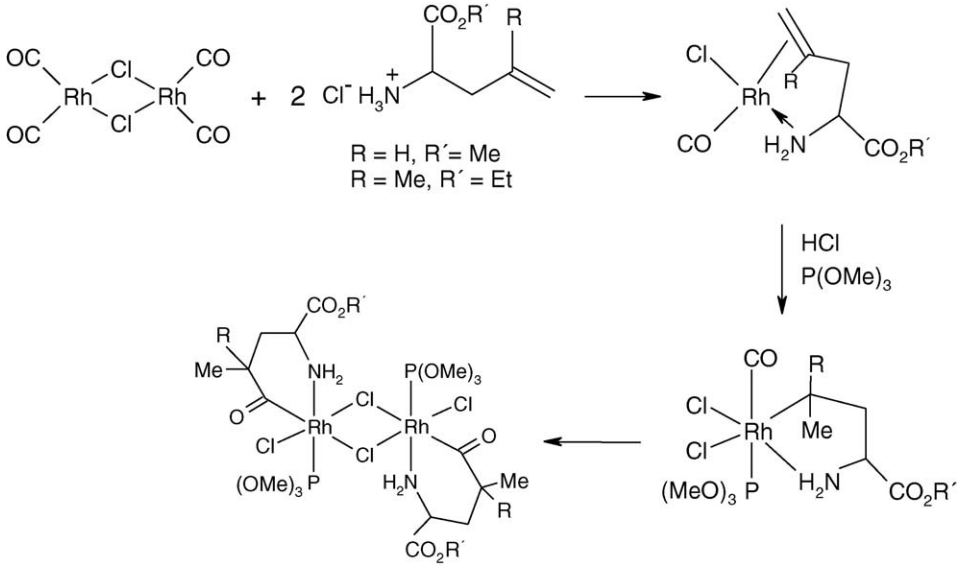
Scheme 71.



Scheme 74.



Scheme 75.

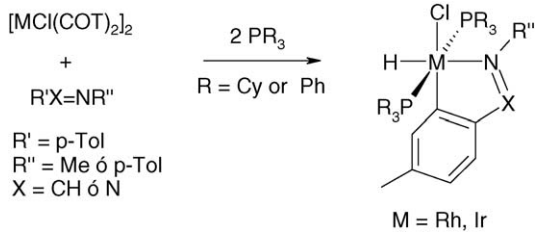


Scheme 76.

compounds of general formula $[RhCl_2P(OMe)_3\{1,5\text{-}\eta\text{-}C(O)C(Me)(R)CH_2CH(CO_2R')NH_2\}]_2$ (Scheme 76) [157].

Five-membered ring azametallacycles have been reported as a consequence of the reaction of $[MCl(COT)_2]_2$ [M = Rh, Ir] with R′X=NR″ (X = N or CH, R′ = *p*-tolyl, R″ = Me or *p*-tolyl) and PR_3 (R = Cy or Ph), which gives the cyclometallated products $MHCl(PR_3)_2(R'X{=}NR'')$ (Scheme 77) [158].

The complicated chemistry of the cluster $Ru_3(CO)_{12}$ with enimines $R_1CH{=}CHCH{=}NR_2$ gives a wide number of derivatives from which the di- and tetranuclear species predominate. A detailed study of the individual reactivity, as well as their interconversions has been carried out by Elsevier et al. [159]. The C–H activations and migration of hydrogens give preferentially five-membered ring azaruthenacycles (Scheme 78).

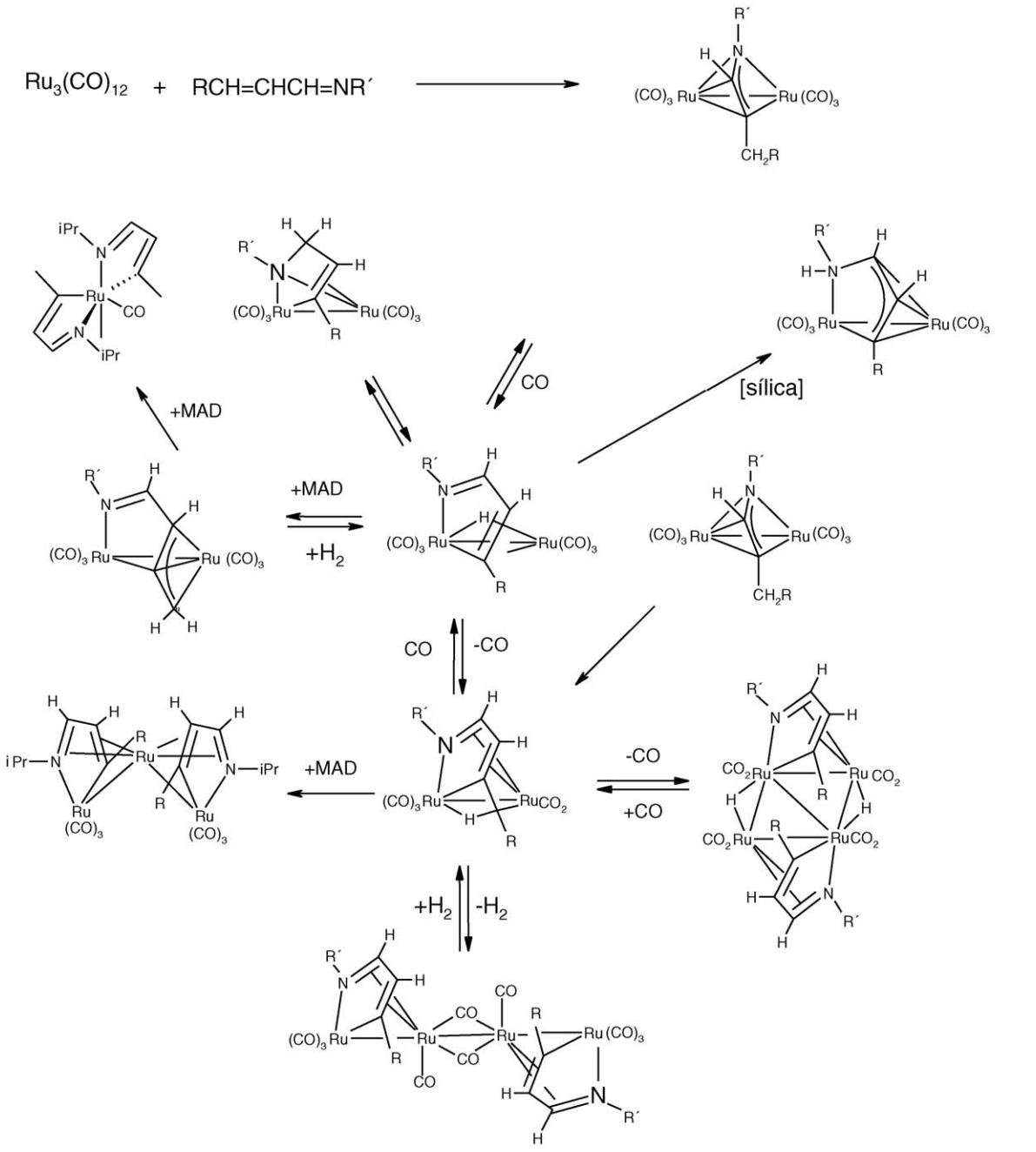


Scheme 77.

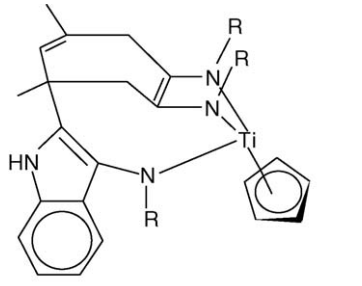
The reactions of $CpTi(2,4\text{-dimethyl-}\eta^5\text{-pentadienyl})(PEt_3)$ with isocyanides form a seven-carbon-atom ring with a coordinated diazabutadiene ligand or an unusual indole which is attached to the former pentadienyl ligand and to an amide coordinated to the metal center (Scheme 79) [160].

In contrast to the results for isocyanides, the nitrile and imine couplings are quite different (Scheme 80) [160,161].

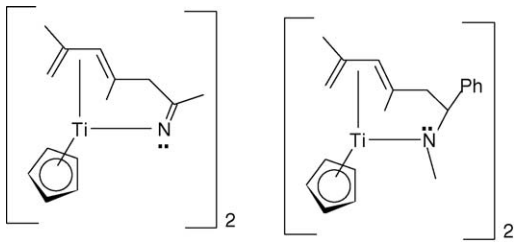
The β-diketimine zirconium complexes $Zr(Cl)_n[\eta^5\text{-}N(Ar)C(Me)CHC(Me)N(Ar)]_m$ ($n=3$, $m=1$; $n=2$, $m=2$) and $CpZr(Cl)_2[\eta^5\text{-}N(Ar)C(Me)CHC(Me)N(Ar)]$ were prepared and ethylene polymerizations were conducted, being the cyclopentadienyl derivative more active than others (Scheme 81) [162,163]. Interesting magnesium η^2-complexes with β-diketiminato ligands have been described in Section 3.1.



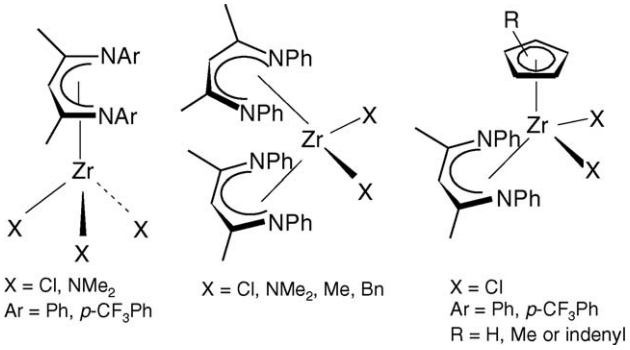
Scheme 78.



Scheme 79.



Scheme 80.



Scheme 81.

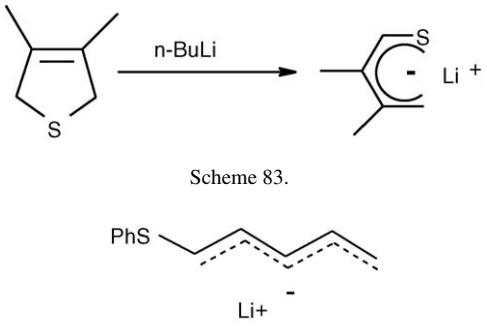
4. Thiapentadienyl compounds

4.1. Thiapentadienyl anions with alkaline metals

The chemistry of the thiapentadienyl anion [9] and its corresponding oxidized derivatives, such as the sulfinylpentadienyl [164] and the butadienesulfone [9,165] anions, is scarce compared to the chemistry of pentadienyl [1,65–79], oxopentadienyl [6–10] and azapentadienyl anions [80–110].

An extensive review of anionic heteroallylic compounds [113] reports the synthesis of allylic-SR, -S(O)R and -SO_2R and their reactivity with electrophiles, but only a few synthetic procedures are reported for the extended sulfurdienyl analogues [9], some of them with inconsistent results [166]. Recently, alternative methods for the synthesis of the following acyclic salts: M(CH_2CHCHCHS) [M = K, Na, Li,], M(CH_2CHCHCHSO) [M = K, Na], M(CH_2CHCHCHSO_2) [M = K, Na, Li,], M(CH(Me)CHC(Me)CHSO_2) [Me5-*syn*, M = K, Na, Li], M(CH(Me)CHCHC(Me)S) [Me5-*syn*, M = K, Na; Me5-*anti*, M = K, Na] have been reported as described in Scheme 82.These salts are the result of the activation of C–S bond in dihydrothiophenes by deprotonation with different bases [166].

The stability of these compounds depends on the size of the cation, the greater size, the greater stability.



Scheme 83.

Scheme 84.

A systematic theoretical study of the electronic and geometric properties of thiapentadienyl, sulfinylpentadienyl and butadienesulfonyl anions and their corresponding metal salts has been carried out [166].

The ring opening of the dimethyldihydrothiophene allowed the formation of the lithium dimethylated thiapentadienide, a useful reagent in the synthesis of six-membered metallacycles, vide infra, Section 4.3 (Scheme 83) [167].

Phenylthiopentadienyllithium was readily prepared by lithiation with *n*-BuLi of (*z*)-phenylpentadienylsulfide (Scheme 84) [168].

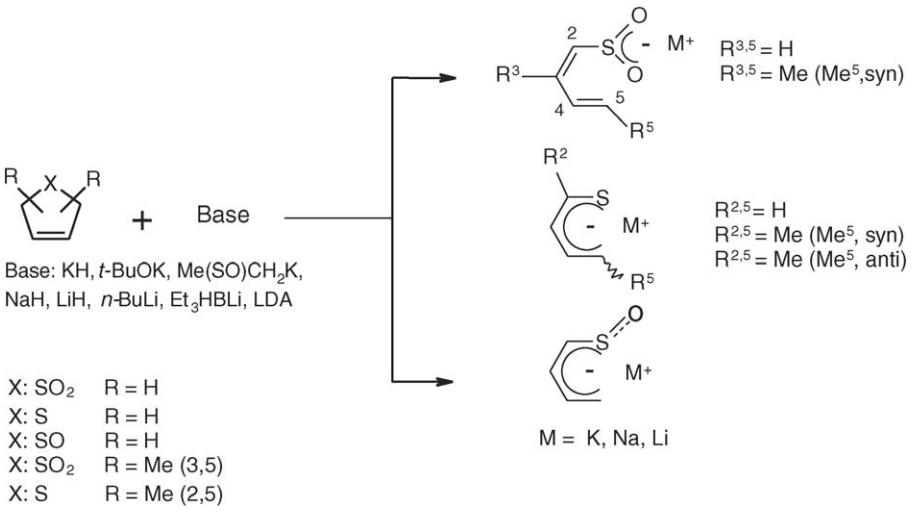
4.2. Thiapentadienyl compounds with transition metals

The chemistry of the thiapentadienyl compounds with transition metals has been developed based on basically two different kinds of ligands.

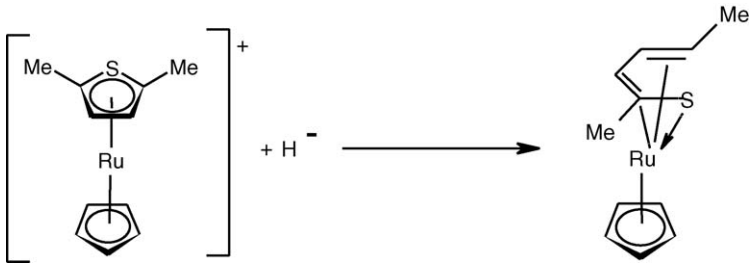
4.2.1. Thiophenes

Thiophenes, that once coordinated with transition metals result in the activation of the heterocycle to nucleophilic attack by a variety of anions, including hydride donors. This gives the corresponding ring-opened butadienethiolate coordinated ligands, which result from cleavage of a C–S bond [169–171].

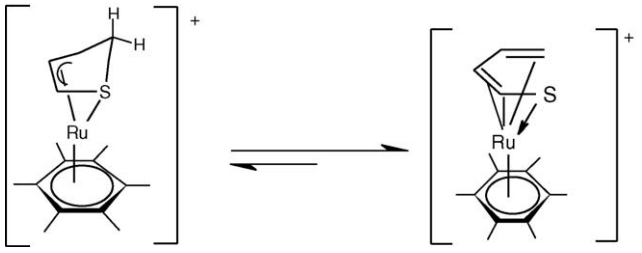
The thiophenes [172–174] and butadienethiolate ligands are known to coordinate to single metal centers through the sulfur



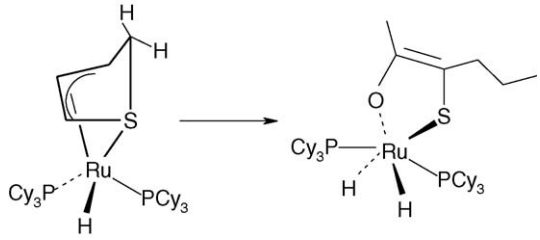
Scheme 82.



Scheme 85.



Scheme 86.



Scheme 87.

(η^1-S), through one, two, three or four carbon atoms (η^1, η^2, η^3, η^4, respectively) and through all five atoms (η^5) (Scheme 85). A proton-induced C–S scission and its reverse allows a complete determination of the key mechanistic details in [(η^6-C_6Me_6)Ru(η^4-C_4H_4S)]$^+$ which undergoes spontaneous C–S bond cleavage to the ring-opened product [(η^6-C_6Me_6)Ru(η^5-$CH_2CHCHCHS$)]$^+$, in solution as well as in solid state [175] (Scheme 86).

The thioallyl complex Ru[η^4-SCHCHCHCH$_2$](H)(PCy_3)$_2$ results from the activation of thiophene, whereas C–S cleavage occurs with 2-acetylthiophene, to afford the metallacycle Ru[SC(*n*-Pr)C(Me)O](H)$_2$(PCy_3)$_2$ (Scheme 87) [176].

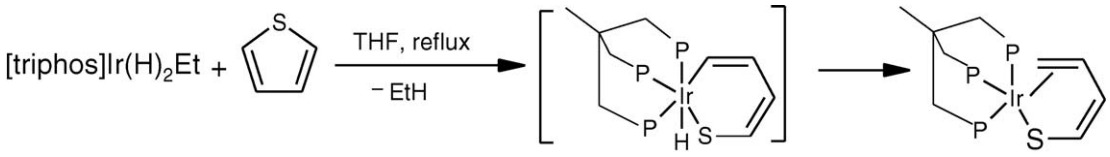
The reactive 16-electron fragment (triphos)IrH [triphos = MeC(CH_2PPh_2)$_3$] produced by reductive elimination of ethane has been found to insert a wide variety of thiophene C–S bond, such as the one described in Scheme 88, to afford finally, the thiapentadienyl ligand coordinated (1-2,5-η) through the terminal double bond and the sulfur to iridium [177] or rhodium [178] (Scheme 88).

The analogous fragment (triphos)RhH, generated in situ by thermolysis of the (triphos)Rh(H)$_3$ in refluxing THF, reacts with a variety of substituted thiophenes to give C–S insertion products of general formula (triphos)Rh(1-2,5-η-CH_2=CHCR′=CRS) (R′ = H, R = Me, Et, COMe, CO_2Et; R = H, R′ = Me, OMe, COMe), which are analogues of those described in Scheme 88. The steric control for these insertion products is determinant [178,179]. Treatment of these butadienethiolate complexes with MeI followed by a metathetical reaction with $NaBPh_4$ affords complexes of 1-methylthio-buta-1,3-diene with the formula [(triphos)Rh(1-2,5-η-CH_2=CHC(R′)=C(R)SMe)][BPh_4] (R′ = H, R = Me, COMe, CO_2Et, thienyl; R = H, R′ = Me, COMe, OMe). The rhodium thioether complex reacts with CO in THF to give free butadienyl methyl sulfides (*z*)-MeSCR=CR′CH=CH_2 and, quantitatively, the dicarbonyl complex [(triphos)Rh(CO)$_2$][BPh_4] [180].

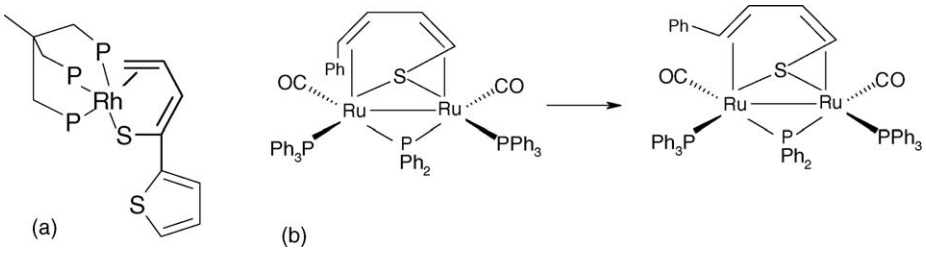
The butadienethiolate complex [(triphos)Rh(1-2,5-η-CH_2=CHCH=C(thienyl)S)] has been prepared by reaction of (triphos)Rh(H)$_3$ with 2,2′-bithiophene in refluxing THF (Scheme 89a) [180].

The reaction of $RuH_2CO(PPh_3)_3$ with thiophene in presence of styrene gives the diruthenium complex Ru[(μ-(1*z*,3*z*)-CH(Ph)=CHCH=CHS)CO(PPh_3)(μ-PPh_2)RuCO(PPh_3)] with a bridging 4-phenyl-1,3-butadienethiolate moiety made up of the 1-thiapenta-2,4-dien-1,5-diyl and phenyl group, which is derived from the thiophene and triphenylphosphine, respectively. The isomerization of the bridging moiety to (1*z*,3*z*) occurs on a preparative thin-layer chromatography plate of alumina or silica gel as described in Scheme 89b [181].

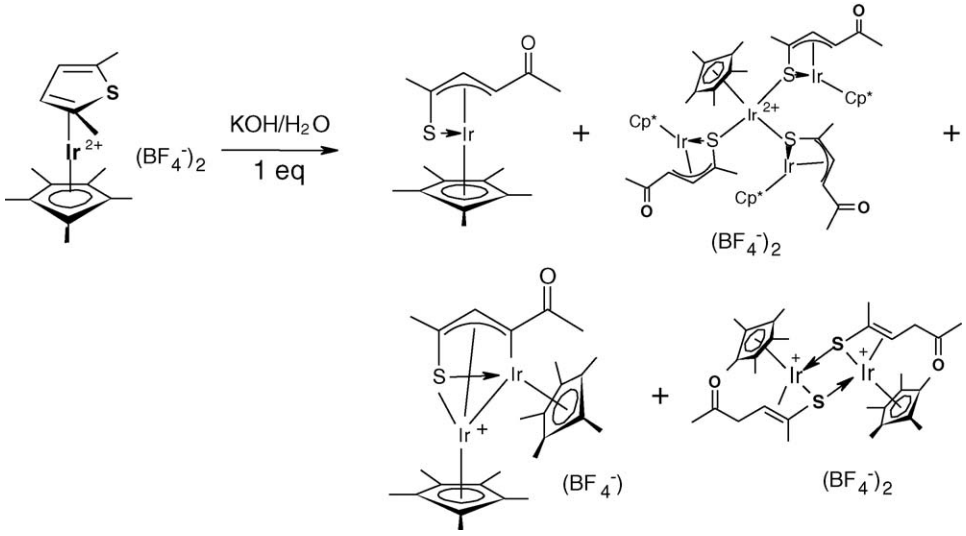
Reactions of aqueous base with the dicationic iridium and rhodium thiophene complexes [Cp^*Ir(2,5-dimethyl-η^5-thiophene)][X]$_2$ (X = BF_4, OTf) and [Cp^*Rh(2,5-dimethyl-η^5-thiophene)][BF_4]$_2$ and the acid/base reactivity of these products have been studied [182]. The reaction of the iridium tetrafluoroborate salt with one equiv of aqueous KOH (0.01 M) affords a mixture of mono-, di- and tetranuclear



Scheme 88.



Scheme 89.



Scheme 90.

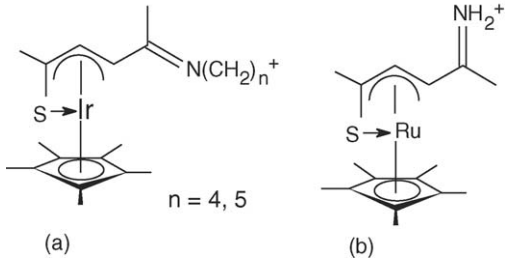
compounds [Cp*Ir(η4-SC(Me)CHCHC(O)Me)], (Cp*Ir) [Cp*Ir(η4-SC(Me)CHCHC(O)Me)]3(BF4)2, [(Cp*Ir)2(μ2,η4-SC(Me)CHCC(O)Me)](BF4) and [Cp*Ir(μ2,η3-SC(Me)CHCH2C(O)Me)]2(BF4)2. The mononuclear acylthiolate complex [Cp*Ir(η4-SC(Me)CHCHC(O)Me)] was also reported from the reaction of [Cp*Ir(2,5-dimethyl-η5-thiophene)][BF4]2 with PhLi in THF [183] or (*n*-Bu)4N+OH− in MeCN [183]. The complexes with higher nuclearity are formed by a complex series of reactions that begin with the displacement of the 2,5-dimethylthiophene ligand from the dicationic iridium salt and the reaction of the resulting "[Cp*Ir]2+" fragment with the neutral mononuclear acylthiolate compound (Scheme 90) [182].

The rhodium analogue [Cp*Rh(2,5-dimethyl-η5-thiophene)][BF4]2 reacts with D2O and MeOH to give the dinuclear complex [(Cp*Rh)2(μ2,η4-SC(Me)CHCC(O)Me)][BF4], without evidence of the other products observed in the analogous reactions with the iridium atom [182]. Meanwhile the studies on the base hydrolysis of the tetramethylated [Cp*Rh(η5-SC4Me4)][BF4]2 give an acylthiolate Cp*Rh(η4-SC(Me)C(Me)C(Me)C(O)Me) and there is no evidence of compounds with higher nuclearity [184].

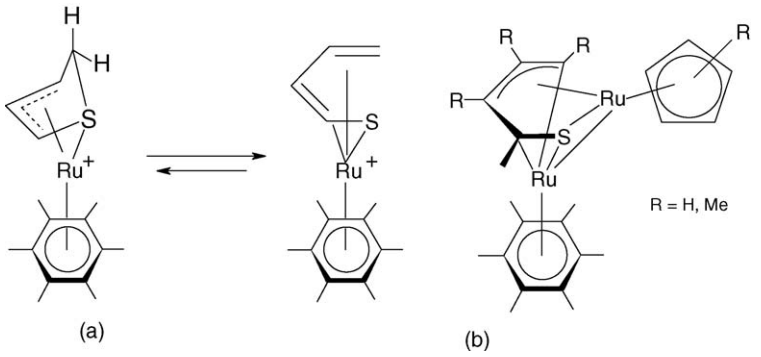
The dicationic thiophene complex [Cp*Ir(2,5-dimethyl-η5-thiophene)][BF4]2 readily add secondary amines, which have the highest efficient transformation if cyclic amines are used (Scheme 91a) [185]. Studies of aminolysis of similar dicationic ruthenium thiophene complexes show that the C–S cleavage produce iminium-thiolato derivatives, as the example described in Scheme 91b [186].

Hydrolysis of [Os(η6-*p*-cymene)(2,5-dimethyl-η5-thiophene)][OTf] gives the corresponding acylthiolate osmium complex [Os(η6-*p*-cymene)(2,5-dimethyl-η4-acylthiolate)] [187], closely related to ruthenium analogues, which also coordinates tetramethylthiophene to give the corresponding methyl substituted acylthiolates. Compound Ru(η6-*p*-cymene)(2,5-dimethyl-η4-acylthiolate) generates, by protonation, the dimerization product [Ru(η6-*p*-cymene)(μ2,η3-SC(Me)CHCH2C(O)Me)]2[BF4]2, which is formed by simple detachment of a carbon upon deprotonation of the methylene group. This reaction is analogous to the iridium dicationic dimer described in Scheme 90 [188].

The influence of the methyl substituents in thiophenes is important, as observed from the protonation of the thiophene



Scheme 91.



Scheme 92.

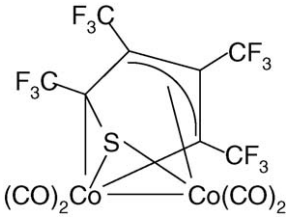
complex [Ru(η^6-C_6Me_6)(η^4-SC_4H_4)] giving [Ru(η^6-C_6Me_6)(η^4-SC_4H_5)]$^+$, which reversible undergoes C–S scission to give a thiapentadienyl complex [Ru(η^6-C_6Me_6)(η^5-SC_4H_5)] (Scheme 92a) [189]. However, the protonation does not promote the cleavage C–S bonds with complexes of 2,5-dimethylthiophene or tetramethylthiophene ligands [189,190]. The presence of methyl substituents in the coordinated thiophenes is also important in the nuclearity adopted by this sort of compounds [180–184]. The crystal structure of [(η^5-C_5H_5)(η^6-C_6Me_6)Ru_2(SC_4Me_4)][PF_6] is an example of a dinuclear compound obtained after treatment of (η^6-C_6Me_6)Ru(SC_4Me_4) with [(η^5-C_5H_5)Ru(NCMe)$_3$][PF_6] (Scheme 92b)[189].

Hexafluoro-2-butyne reacts with hexacarbonyltetrakis(pentafluorobenzenethiolato)dicobalt to give several complexes, one of which has the composition $Co_2(CO)_4[C_4(CF_3)_4S]$, according to the X-ray crystallographic studies (Scheme 93) [191,192].

There is an excellent review concerned to patterns of reactivity of thiophenes in organotransition metal chemistry. It organizes reactions to emphasize patterns of reactivity of thiophenes, such as metal insertion into C–S bonds, reactions of η^5-thiophene compounds with nucleophiles, reduction of η^5-thiophene compounds, reactions of η^4-thiophene compounds with electrophiles and nucleophiles and reactions of η^1(S)- and η^2-thiophene compounds with electrophiles and bases [172].

The ring opening reactions of thiophene with metal complexes have also been widely studied, paying special interest on subsequent hydrogenation and desulfurization [193], and several reviews of various aspects of hydrodesulfurization (HDS) studies have been published [178,194–199].

In contrast with the coordinated thiophene compounds, not many studies have been done directly on the thiapentadienyl ligand per se; they will be discussed in the following section.



Scheme 93.

4.2.2. Acyclic thiapentadienyl anions

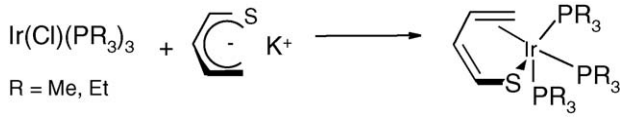
Acyclic thiapentadienyl anions, established with different alkaline metal cations, such as lithium [166,167], potassium [166,200,201] or sodium [166], have been described in Section 4.1. Initial studies by Bleeke et al. focused on electron-rich thiapentadienyl-iridium-phosphine compounds involving chloro-iridium-phosphine precursors and the potassium thiapentadienide to give (1,2,5-η-thiapentadienyl)Ir(PR_3)$_3$ (R = Me, Et) (Scheme 94) [201]. The tris(PEt_3)$_3$ derivative undergoes intramolecular C–H bond activation upon stirring in THF at room temperature (vide supra, Section 4.3) [167].

The reactions of RhCl(PR_3)$_3$ (R = Me, Et) with the lithium 2,3-dimethyl-5-thiapentadienide have been recently investigated. The tris(trimethylphosphine) derivative shows a structure similar to the one described for iridium in Scheme 94, and it is also closely related to the iridium complexes obtained via thiophene C–S bond cleavage, which are described in Section 4.2.1 (Scheme 88). The crystal structure of Rh[(1,2,5-η)-2,3-dimethyl-5-thiapentadienyl](PMe_3)$_3$ has been solved [202] and the reactivity of this compound will be described in Section 4.3.

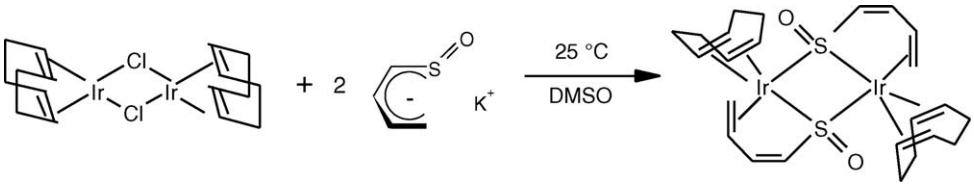
A new approach to the synthesis of analogous thiapentadienyl metal compounds has recently been carried out with the corresponding sulfinylpentadienyl $(CH_2CHCHCHSO)^-$ [166] and the butadienesulfinate $(CH_2{=}CHCH{=}CHSO_2)^-$ [166] anions, which are described in Section 4.1.

Treatment of [IrCl(η^4-COD)]$_2$ with potassium sulfinylpentadienyl produces the dimer [Ir(μ_2-)(1-2,5-η-CH_2=CHCH=CHSO)(COD)]$_2$ (Scheme 95) [203,204], whereas the metathesis reaction of [Cp^*IrCl_2]$_2$ with butadienesulfinate lithium affords the dinuclear compounds [Cp^*Ir(Cl)$_2${(5-η-CH(R)=CHC(R)=$CHSO_2$)}(Li)(THF)]$_2$ (R = H, Me) which easily break to afford compounds Cp^*IrCl[1,2,5-η-CH(R)=CHC(R)=$CHSO_2$] (R = H, Me) upon displacement of THF and LiCl (Scheme 96) [204].

It is interesting to observe that the preferred coordination mode in the chemistry of thiapentadienyl-iridium or rhodium



Scheme 94.



Scheme 95.

compounds is (1-2,5-η) (Schemes 94, 88, 89a, 98 and 100–103). This type of bonding has been previously observed for several iridium [172,177,178,200,201,204–207] and rhodium compounds, analogues to those described in Schemes 88 and 89a [179,180,208].

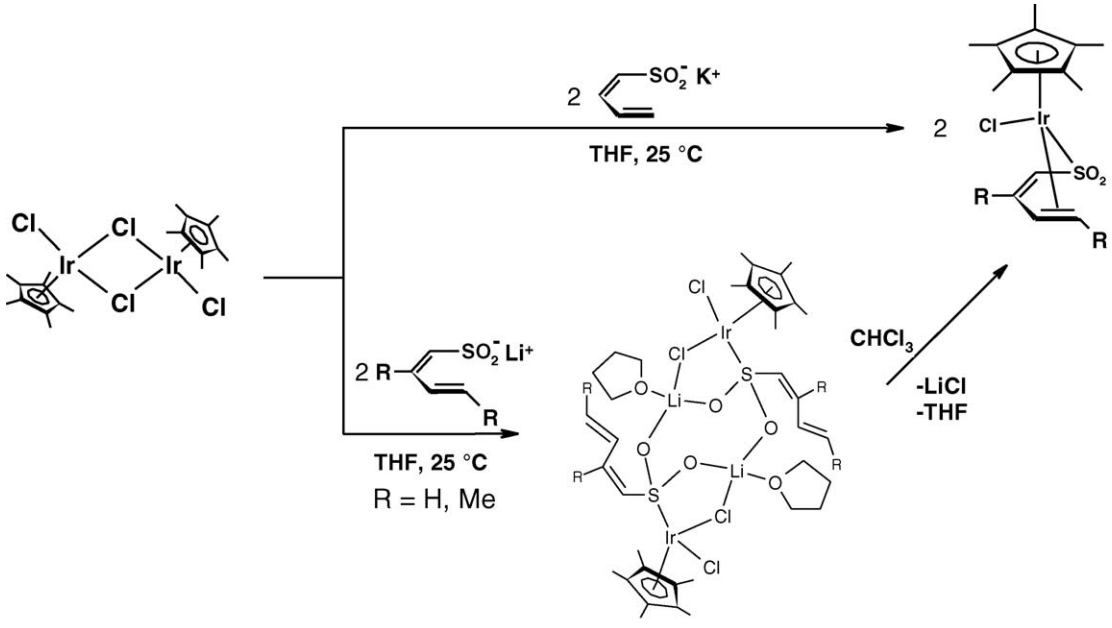
The corresponding oxidative derivatives of the thiapentadienyl ligand also show a bonding mode that involves a localized iridium–sulfur and iridium–olefin coordination, as described in Schemes 95 and 96 for the thermodynamic products. Contrastingly, the dinuclear intermediates described in Scheme 96 showed η^1 coordination of the sulfinate ligand through the sulfur to the iridium atom. A similar complex has also been isolated for rhodium [209]. Until now, there is no evidence of an isolated η^5 mode for iridium or rhodium complexes. Only compounds $[Cp^*Rh(\eta^5\text{-hydroxybutadienethiolate})]^+$ [210] and $Rh[(\eta^5\text{-}CH_2C(Me)C(Me)CHS)(PMe_3)_2]$ (vide infra, Scheme 103) [202] have been proposed as intermediates. In contrast, ruthenium compounds have shown η^5 bonding modes in butadienethiolate ligands, as described in Schemes 85, 86, 92a and 106.

4.3. Reactions of thiapentadienyl ligands with transition metals

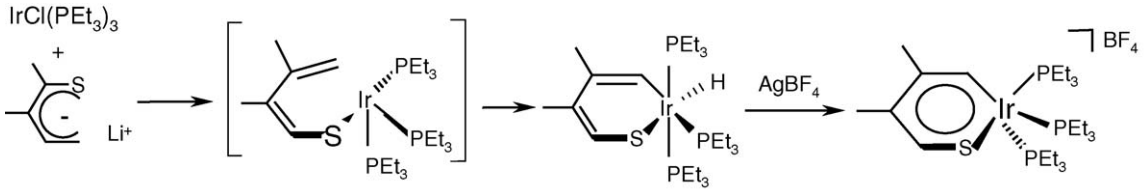
Interesting metallathiabenzene molecules have been obtained by Bleeke et al. [167,211] using acyclic thiapentadienide salts as precursors (Scheme 97); while other metallathiabenzenes have been obtained by the thiophene C–S bond activation [172,177,212,213]. The lithium 2,3-dimethyl-5-thiapentadienide reagent (Scheme 83, Section 4.1) leads to the formation of the six-membered metallacycle, and iridathiacyclohexa-1,3-diene, via C–H bond activation (Scheme 97) [167,214].

The presence of both methyl groups prevent the C–H bond activation and formation of five-membered metallacycles [167,200,201], such as the iridathiacyclopentenes described in Scheme 98.

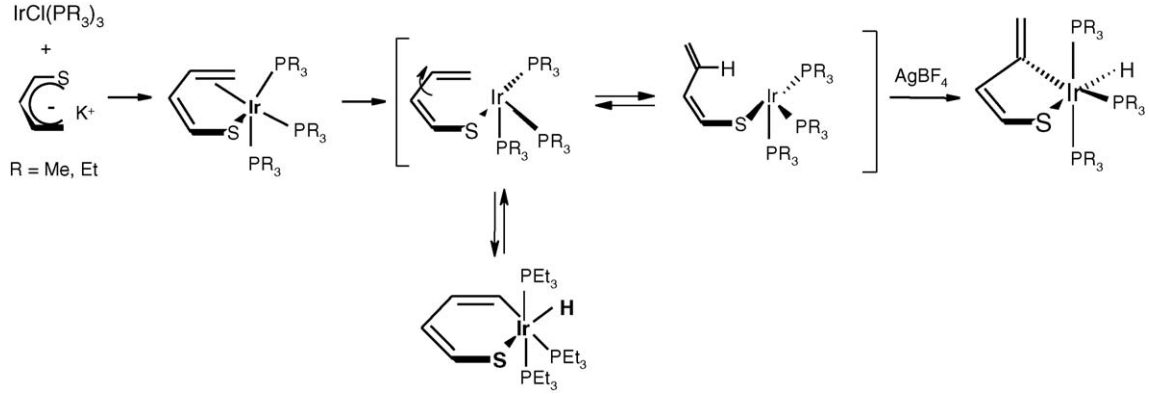
The reaction between potassium thiapentadienide with $IrCl(PR_3)_3$ gives Ir(1,2,5-η-thiapentadienyl)$(PR_3)_3$ (R = Me, Et), from which both compounds can be isolated and crystallized in pure form. Their reactivity is quite different: while the trimethylphosphine derivative, upon heating in toluene at reflux, undergoes intramolecular C–H bond activation and generates the five-membered iridathiacycle; the triethylphosphine derivative is less robust thermally and undergoes intramolecular C–H bond activation at room temperature, which produces a mixture of six- and five-membered ring iridathiacyclohexadiene and iridathiacyclopentene, respectively. There is a thermodynamic preference for the five-membered ring product over the six-membered ring product, as observed from the fact that the iridathiacyclohexadiene gradually converts to the iridathiacycle with an exocyclic double bond. This preference can be understood by considering the ring strain in each iridathiacycle. The



Scheme 96.



Scheme 97.



Scheme 98.

iridathiacyclohexadiene was only observed for the triethylphosphine complex [200,201].

Reaction of the iridathiacyclopentene complex with electrophiles, in presence of strong acids such as HBF_4 or HO_3SCF_3, gives the first example of a transition-metal-containing an analogue of thiophene, and in presence of methylating agents, such as Me_3OBF_4 or MeO_3SCF_3, it affords the methylation of the sulfur atom. The reactivity pattern suggests that the exocyclic carbon center is the most basic site in the molecule; therefore it gives an "iridathiophene", while sulfur, due to its greater polarizability and accessibility, is the best nucleophile [201,215] which produces a cationic complex (Scheme 99).

Examples of the solid state structures of tetrafluoroborate iridathiophene [201,215] iridathiacyclopentene [200,201] and the non-aromatic methyl-sulfur triflate derivative [201] have been published.

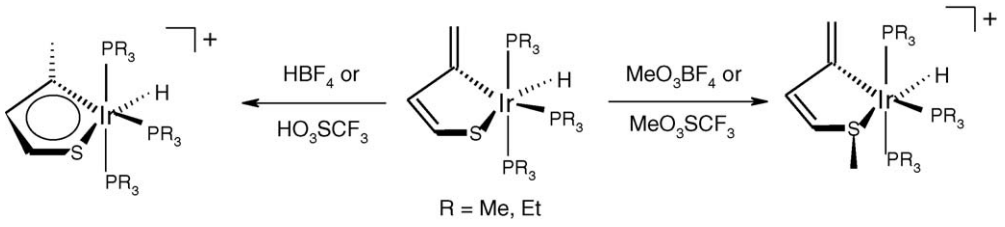
Treatment of compound Ir(1-2,5-η-thiapentadienyl)$(PMe_3)_3$ (Schemes 94 and 98) with the electrophile $HBF_4{\cdot}OEt_2$ gives [Ir(2-5-η-thiapentadiene)$(PMe_3)_3$][BF_4] [201] which, after heating in refluxing acetone, is converted to the corresponding less-hindered *anti*-isomer with the same η^4-thiapentadiene structure, except for the position of the terminal methyl group (Scheme 100).

The same complex reacts with methyl triflate which leads to a methyl attack at sulfur and the formation of [Ir{(1,2,5-η)-5-methyl-5-thiapentadienyl}$(PMe_3)_3$]OTf. There is an isomerization to [Ir{(1-4-η)-5-methyl-5-thiapentadiene}$(PMe_3)_3$]OTf upon stirring in tetrahydrofuran at room temperature (Scheme 101) [201].

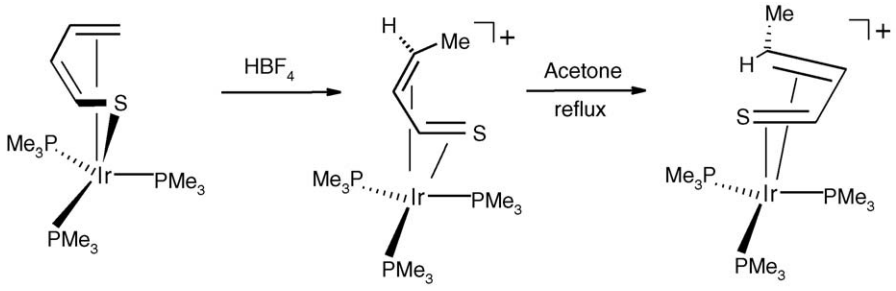
The chemistry of Rh[(1,2,5-η)-2,3-dimethyl-5-thiapentadienyl]$(PMe_3)_3$ has shown a rapid solution-phase dynamic process in which the double bond C1–C2, at the terminal position, undergoes dissociation from the rhodium center and reassociation (Scheme 102). The 16 e^- dissociated intermediate can be trapped by exposing it to air, which affords an interesting peroxo Rh[(5-η)-2,3-dimethyl-5-thiapentadienyl](O)$_2(PMe_3)_3$ [202].

There is a gradual isomerization from Rh[(1,2,5-η)-2,3-dimethyl-5-thiapentadienyl]$(PMe_3)_3$ to Rh[(1,4,5-η)-2,3-dimethyl-5-thiapentadienyl]$(PMe_3)_3$ in which the thiapentadienyl ligand is σ-bonded to rhodium through the carbon end of the chain (C1) and π-bound through the sulfur end. This isomer is not fluxional at room temperature, and its formation suggests an η^5-thiapentadienyl intermediate as described in Scheme 103 [202].

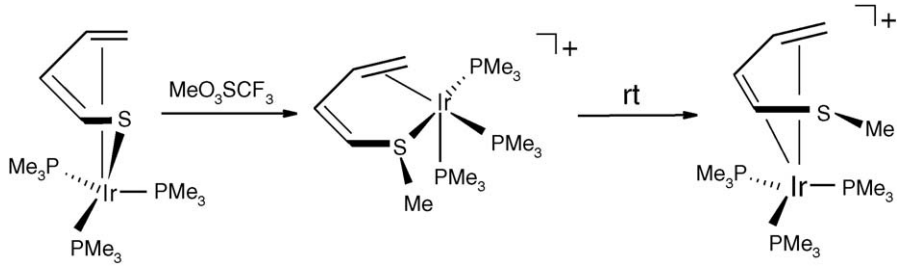
Contrastingly, when $RhCl(PEt_3)_3$ is treated with lithium 2,3-dimethyl-5-thiapentadienide, the product obtained is



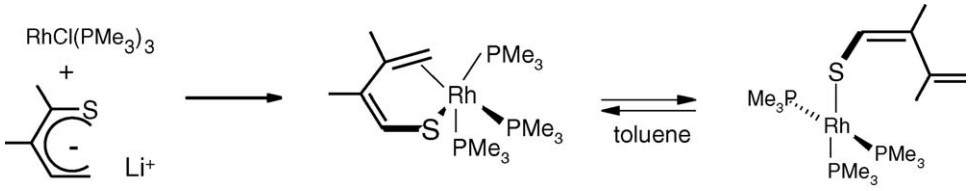
Scheme 99.



Scheme 100.



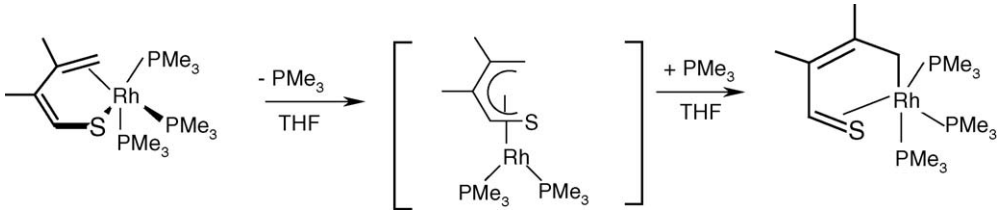
Scheme 101.



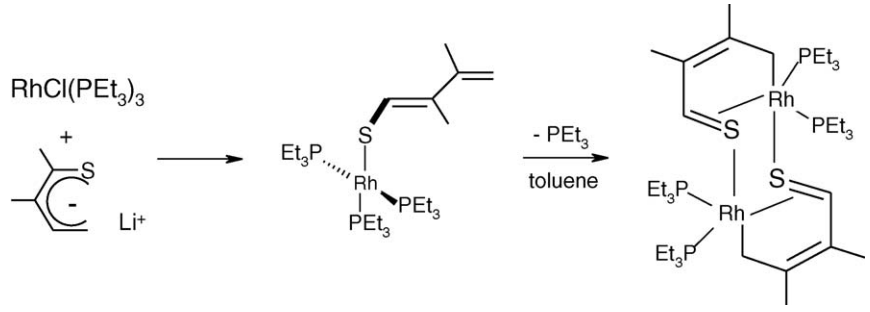
Scheme 102.

the η^1-thiapentadienyl compound Rh[(5-η)-2,3-dimethyl-5-thiapentadienyl](PEt$_3$)$_3$. This complex can be transformed into a sulfur-bridged dimer stirring in toluene at room temperature. The difference in chemistry between the trimethyl- and triethylphosphine derivatives is attributed to the corresponding steric effects (Scheme 104) [202].

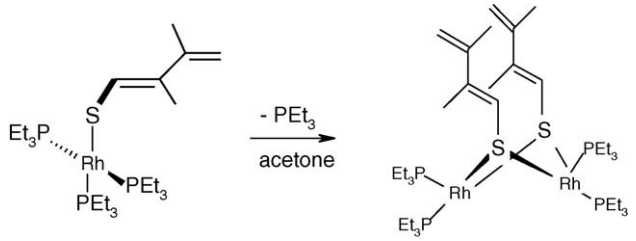
When compound Rh[(5-η)-2,3-dimethyl-5-thiapentadienyl](PEt$_3$)$_3$ is stirred in acetone, another dimeric product,



Scheme 103.



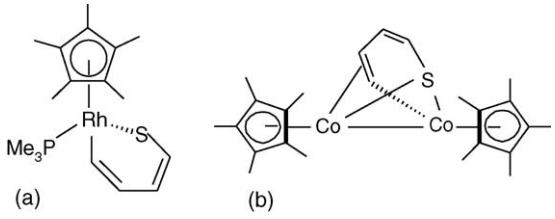
Scheme 104.



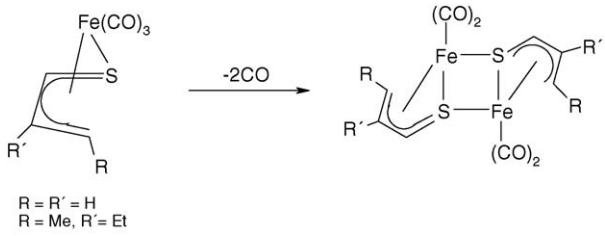
Scheme 105.

which contains bridging S-bound η^1-thiapentadienyl ligands, is isolated, as described in Scheme 105 [202].

Reactions of the CpRu(η^5-thiapentadienyl) with phosphines or carbon monoxide slowly displaced the butadiene fragment of the butadienethiolate or thiapentadienyl ligand from the metal to give compounds CpRu(η^1-thiapentadienyl)L_2 (L = CO, PMePh$_2$) without evidence of the CpRu(η^3-thiapentadienyl)L. Crystal structures of CpRu[1,2-3,4-5-η-CH(Me)CHCHC(Me)S] (with disorder) [171], and CpRu[5-η-CH(Me)=CHCH=C(Me)S](PMePh$_2$)$_2$ [169] have been established by X-ray diffraction studies. The reactivity of CpRu(η^5-thiapentadienyl) with electrophiles, such as $(Me_3O)BF_4$ affords the corresponding thioether compounds [CpRu(η^5-CH(R)CHCHC(R)S(Me))]BF_4 (R = H, Me). The addition of PMePh$_2$ affords [CpRu{1-3-η-CH(R)CHCHC(R)S(Me)}(PMePh$_2$)]BF_4, and when R = Me the analysis of the crystal structure was carried out [169]. The formation of compound CpRu(η^3-butadiene-thioether)(PMePh$_2$) is contrasted with the direct yield of CpRu(η^1-thiapentadienyl)(PMePh$_2$)$_2$ (vide supra) [169]. Other CpRu[*cis*,*trans*-η^1-SC(R)CHCHCH(Nu)L_2] [R = H, Me; Nu = OMe, SEt; L = dppe; L_2 = PMePh$_2$] have also been studied (Scheme 106) [169].



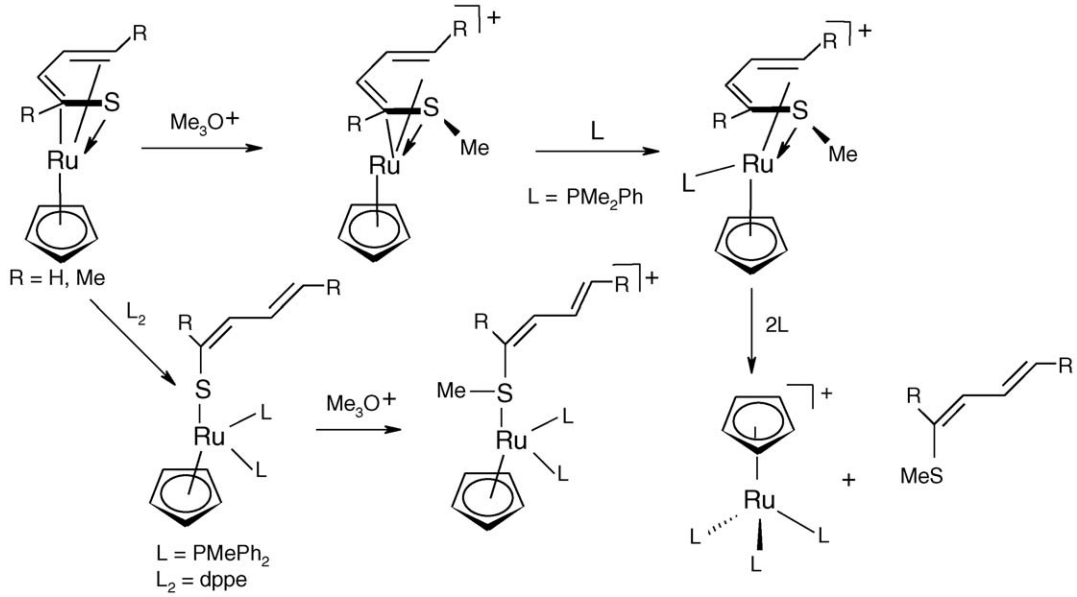
Scheme 107.



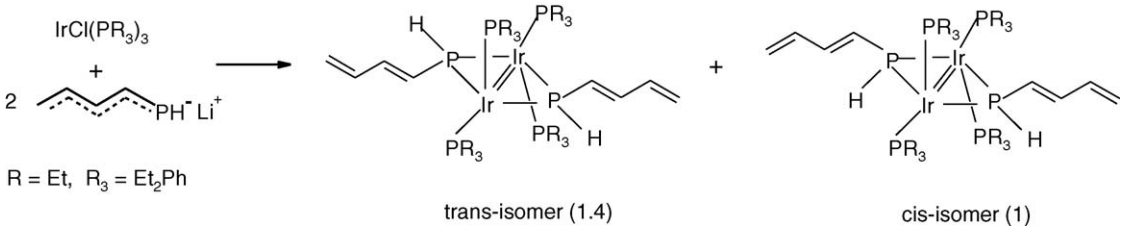
Scheme 108.

4.4. Related compounds with thiadienyl ligands

The reaction of Cp*Rh(Ph)(H)(PMe$_3$) with thiophene affords Cp*Rh(SC$_4$H$_4$)(PMe$_3$) by reductive elimination of benzene. The C–S bond cleavage and the oxidative addition occur by initial coordination of the thiophene, followed by migration of the α-carbon to the metal center, thereby producing the six-membered metallathiahexadiene ring (Scheme 107a) [190,216]. While the cobalt complex Cp*Co(H$_2$C=CH$_2$)$_2$ reacts with excess of thiophene to give the dinuclear complex [Cp*Co]$_2$(SC$_4$H$_4$), in which the cobalt has been inserted into the thiophene C–S bond to form a "cobalthiahexadiene" that is chelated to a second Cp*Co moiety (Scheme 107b) [217].



Scheme 106.



Scheme 109.

Treatment of thiacyclobutenes with several iron or cobalt carbonyls yields complexes of thioacroleins, and from them dimeric structures containing an essentially square FeS_2 array were obtained together with their corresponding S-oxides on mild oxidation with peracids or oxygen (Scheme 108) [218]. Some bond distances and angles of the dimer (R = Me, R′ = Et) are included in the article and the crystal structure of the mononuclear $Fe(CO)_2(PPh_3)(\eta^4\text{-}SC_4H_4)$ is reported separately [219].

5. Phosphapentadienyl compounds

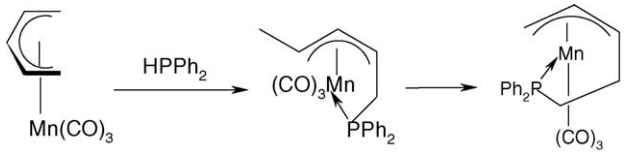
5.1. Lithium phosphapentadienide and phosphapentadienyl-iridium-phosphine dimers

Bleeke et al. published the first example of an anionic phosphapentadienide reagent obtained by treatment of butadienylphosphine, $H_2PCH{=}CHCH{=}CH_2$ [220] with *n*-BuLi which generates lithium phosphapentadienide in 95% yield as a tetrahydrofuran soluble solid [221]. The analogue 2,4-dimethylphosphapentadienide has also been reported in high yield (92%) [222]. The reactivity of these lithium phosphapentadienides in presence of $IrCl(PEt_3)_3$ affords the corresponding phosphapentadienyl-iridium-phosphine dimers $(\mu\text{-}\eta^1\text{-phosphapentadienyl})_2Ir_2(PEt_3)_4$ [221] and $(2,4\text{-dimethyl-}\mu\text{-}\eta^1\text{-phosphapentadienyl})_2Ir_2(PEt_3)_4$ [222] as equilibrium mixtures of *trans* and *cis* isomers in a 1.4:1 and 8:1 ratio, respectively. There are X-ray diffraction studies of the *trans* isomers of these primary phosphido-iridium dimers (Scheme 109) [221,222].

The analogous reaction involving $IrCl(PEt_2Ph)_3$ produced $[(\mu\text{-}\eta^1\text{-phosphapentadienyl})Ir(PEt_2Ph)_2]_2$, in a similar 1.4:1 ratio to those for $(PEt)_3$ derivatives [222].

5.2. Related compounds with phosphadienyl ligands

Diphenylphosphine reacts with $(\eta^5\text{-pentadienyl})$tricarbonylmanganese to give isomers $Mn[1\text{-}3,5\text{-}\eta\text{-}CH(Me)CHCHCH_2P(Ph)_2](CO)_3$ and $Mn[1\text{-}3\text{-}\eta\text{-}CH_2CHCHCH_2CH_2P(Ph)_2]$ $(CO)_3$. The phosphorous is added stereoselectively to the terminal carbon atom (Scheme 110) [223].



Scheme 110.

6. Concluding remarks

In this review we have illustrated the richness of the heterodienyl ligands which have many interesting features that make them unique and potentially useful in many different fields. Here the discussion has been focused on their syntheses, structure and reactivity. However, they have many characteristics which need to be studied in deeper detail, such as their electronic, theoretical, electrochemical, conformational and other spectroscopical aspects. The research in this field is just beginning, but based on the results until now it looks very promising. Further studies will provide a more unified understanding of heterodienyl complexes.

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