Structure and Reactivity of Coordinatively Unsaturated Half-Sandwich Iron, Ruthenium and Osmium Complexes

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This review deals with the study of coordinatively unsaturated half-sandwich iron, ruthenium and osmium complexes, in particular those bearing bulky phosphane ligands. The synthesis, properties and structure of neutral complexes of the type $[(C_5R_5)MX(L)]$ and their cationic derivatives $[(C_5R_5)M(L)_2]^+$, are described here. We will also refer to related compounds containing hydrotris(pyrazolyl)borate (Tp) ligands, given the formal relationship existing between these and those containing cyclopentadienyl groups. In addition, we discuss the reactivity of these unsaturated species towards small molecules and alkynes.

1. Introduction

Organometallic derivatives that do not adhere to the 18-electron rule are also known as coordinatively unsaturated organometallics, and have been referred to as the interface between Werner-type complexes and 18-electron organometallic complexes.[1] Bulky ligands are known to play an important role in the stabilization of coordinatively unsaturated metal complexes, by the steric protection provided, against the entry of additional ligands which might eventually complete the electron count at the metal centre. Since such unsaturated compounds are potential catalysts, it is

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MICROREVIEWS: This feature introduces the readers to the author's research through a concise overview of the selected topic. Reference to important work from others in the field is included.

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desirable to understand the parameters that correlate structure with stability and reactivity. Our research group has been studying the chemistry of transition metal complexes containing bulky phosphane ligands, particularly those with the strong electron-releasing phosphane 1,2-bis(diisopropylphosphano)ethane (dippe).[2−11] We have focused on the isolation of coordinatively unsaturated complexes and the study of their reactivity towards small molecules and alkynes. We initially worked with the 16-electron hydride complex $[RuH(dippe)_2][BPh_4]$.[2−4] Studies on the reactivity of this material led us to report the first example of dioxygen activation at a dihydrogen-binding site unequivocally supported by the X-ray structure analysis of the hydridodioxygen derivative *trans*-$[RuH(O_2)(dippe)_2][BPh_4]$.[2,3] Some of these results were extended later to osmium,[12,13] but we were already interested in the chemistry of half-sandwich complexes prior to that.[7−10] $[(C_5R_5)MX(L)_2]$ (R = H, Me; M = Fe, Ru, Os; X = monoanionic ligand; L = neutral ligand) derivatives constitute a very extensive class of 18-electron compounds.[14,15] Ligand dissociation from these materials gives rise to two possible types of 16-electron complexes: a) neutral complexes $[(C_5R_5)MX(L)]$ generated by dissociation of one of the neutral ligands, and b) cationic complexes $[(C_5R_5)M(L)_2]^+$ generated by dissociation of the monoanionic ligand. Both types of complexes are considered as intermediates in ligand-exchange reactions which follow a dissociative mechanism. In general, these complexes are short-lived, highly reactive transient species that are difficult to isolate. However, with a proper combination of the steric bulk and the electron-donating abilities of the ligands, the isolation of such coordinatively unsaturated species has been possible in a number of cases. These compounds are stable enough to be handled allowing their study and, in some instances, even characterisation by X-ray structure analysis. However, consistent with their coordinatively unsaturated nature, these 16-electron species remain very reactive towards a large number of substrates, including rather inert molecules such as dinitrogen. In this review we discuss the synthesis, structure and reactivity of these stable, yet reactive 16-electron half-sandwich complexes of iron, ruthenium and osmium, with emphasis on those bearing bulky phosphane ligands. We will also refer to related compounds containing hydrotris(pyrazolyl)borate (Tp) ligands, given the formal relationship existing between these and those containing cyclopentadienyl groups.[16]

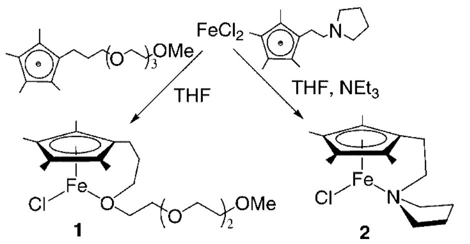
2 Neutral Complexes of the Type $[(C_5R_5)M(X)(L)]$

2.1 Iron Complexes

Compared to the heavier elements in its group, iron complexes that do not follow the 18-electron rule are in general more abundant since iron is a first-row transition metal.[1] However, 16-electron complexes of formula $[(C_5R_5)Fe(X)(L)]$ are rather scarce.

Based upon the magnetic properties the complex $[Cp^*Fe(acac)(PMe_3)]$ ($Cp^* = C_5Me_5$) is likely to have a 16-electron, spin triplet configuration with a monodentate acac ligand, or is in equilibrium with a paramagnetic product of phosphane dissociation.[17]

The reaction of $FeCl_2$ with $Li[C_5Me_4(CH_2)_2N(C_4H_8)]$ in THF/NEt_3[18] or with $Li[C_5Me_4(CH_2)_3(OCH_2CH_2)_3OMe]$ in THF[19] at low temperature yields the corresponding neutral 16-electron complexes, which appear stabilised by intramolecular coordination of the pendant amine or glycol ether moiety to iron.



Whereas **1** appears to be stable only in solution, where it was characterised by derivatization reactions,[19] **2** has been isolated in the crystalline state.[18]

Notably, the diamagnetic 14-electron complex $[Cp^*Fe\{N(SiMe_3)_2\}]$ has been reported.[20] This compound, prepared by reaction of $FeCl_2$ with one equivalent of $K[N(SiMe_3)_2]$ in THF and subsequent addition of LiCp*, has a "pogo-stick" structure unprecedented in the chemistry of open shell organometallics (Figure 1).

In contrast with this unique compound, which contains Cp*, there is a small but growing number of 14-electron complexes of the type $[Tp^RFeX]$ [Tp^R = hydrotris(3-*tert*-butylpyrazolyl)borate, hydrotris(3,5-diisopropylpyrazolyl)borate, hydrotris(3,4,5-trimethylpyrazolyl)borate; X = halide, alkyl, C≡CPh].[21,22] Several of these compounds have been structurally characterized by X-ray crystallography, and show a distorted tetrahedral geometry around the iron atom (Figure 2).

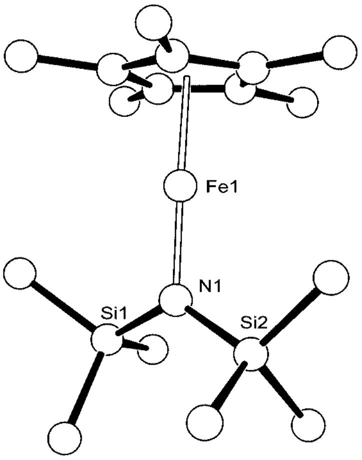


Figure 1. Molecular structure of $[Cp^*Fe\{N(SiMe_3)_2\}]$

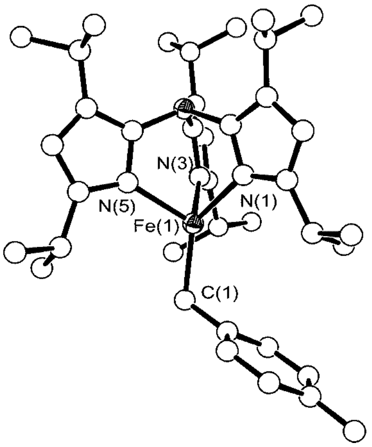
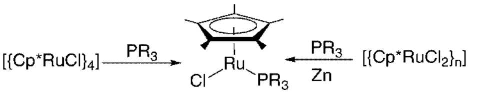


Figure 2. Molecular structure of the 14-electron complex [Tp*i*PrFeCH_2Tol]

[Tp^RFeX] derivatives, and in particular alkyl complexes such as [Tp*i*PrFeCH_2CH_3] [Tp*i*Pr = hydrotris(3,5-diisopropylpyrazolyl)borate],[22] appear to be remarkably stable despite the coordinative unsaturation, and do not undergo a β-elimination reaction. Besides, the reactions of the alkyl complexes [Tp*i*PrFeR] towards unsaturated organic substrates (olefins, acetylene) tend to be slow. This stability is attributed to the high-spin electronic configuration where four out of five frontier orbitals are singly occupied, as suggested by extended Hückel molecular orbitals (EHMO) calculations.[22]

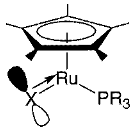
2.2 Ruthenium Complexes

Compounds of the type [Cp*RuCl(PR_3)] are well-established reactive intermediates in dissociative phosphane-exchange reactions.[23] If bulky phosphane ligands are used, the isolation of the 16-electron complexes [Cp*RuCl(PR_3)] becomes feasible. In 1988, Tilley and co-workers prepared the compounds [Cp*RuCl(PR_3)] (R = *i*Pr, Cy) by reaction of tetrameric, cubane-like [$(Cp^*RuCl)_4$][24] with one equivalent of the corresponding phosphane in dichloromethane.[25] Almost simultaneously, Chaudret and co-workers also reported the synthesis of these compounds by reduction of the Ru^{III} precursors [Cp*$RuCl_2$(PR_3)] (R = *i*Pr, Cy, *t*Bu), usually generated in situ by reaction of [Cp*$RuCl_2$]$_n$ with the appropriate amounts of phosphane and Zn in a variety of solvents.[26]

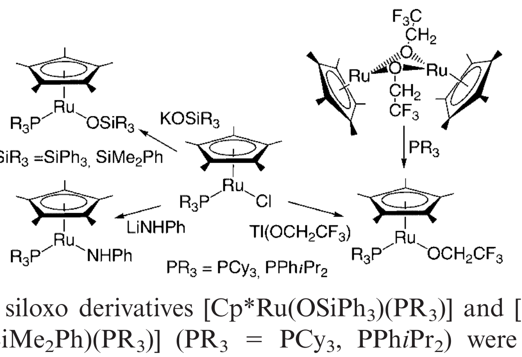


The complexes [Cp*RuCl(PMe*t*Bu_2)],[27] [Cp*RuCl(PPh*i*Pr_2)],[28] [Cp*RuCl(PMe*i*Pr_2)],[29] and [Cp*RuCl(η^1-(P)-$PCy_2CH_2CH_2OMe$)] (bearing a pendant ether group)[30] have also been synthesized by following any of the methods outlined above. Only bulky phosphanes with a sufficiently large cone angle allow the isolation of these 16-electron complexes. Smaller phosphanes, such as PMe_3 or PEt_3, readily form the corresponding 18-electron species [Cp*RuCl$(PR_3)_2$]. Furthermore, the reaction of [Cp*RuCl(PR_3)] (R = *i*Pr, Cy) with smaller cone angle phosphane ligands yielded complexes with filled coordination spheres. These reactions have been the subject of very detailed thermochemical investigations, which have shown that sterically demanding phosphane ligands exhibit the weakest Ru−PR_3 bonds.[31] There is an upper limit for the phosphane cone angle which allows the stabilization of [Cp*RuCl(PR_3)] species. If the cone angle is too large this results in an inefficient Ru−PR_3 interaction. Consistent with this, it has been noted that the reaction of [$(Cp^*RuCl)_4$] with bulkier phosphanes such as PPh*t*Bu_2 or P(*o*-toly)$_3$ gave the unreacted starting material [$(Cp^*RuCl)_4$] after 24 h at 25 °C in hexanes.[28] On the other hand, the phosphane PMe*i*Pr_2 defines a lower limit for the cone angle range, as both [Cp*RuCl(PMe*i*Pr_2)] and the 18-electron complex [Cp*RuCl(PMe*i*Pr_2)$_2$] are accesible depending on the phosphane to tetramer ratio.[29]

Another requirement for the stabilization of [Cp*RuX(PR_3)] complexes is the presence of π-electrons at the X ligand, since π-donation by lone pairs mitigates the coordinative unsaturation which would be present if the X ligand were a pure σ-donor. This is termed π-stabilized unsaturation. For this reason, these compounds have been referred to as *operationally* unsaturated, rather than *coordinatively* unsaturated.[28,32]



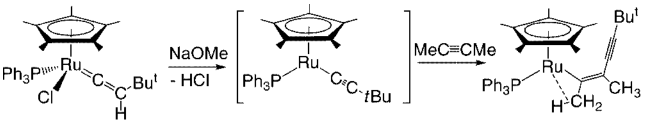
Following the initial report on the isolation of [Cp*RuCl(PR_3)] derivatives, the compounds of general formula [Cp*RuX(L)] (X = monoanionic ligand; L = neutral ligand) have become an important class of 16-electron complexes. Thus, alkoxo, siloxo and phenylimido complexes have been prepared. The alkoxo derivatives [Cp*Ru(OCH_2CF_3)(PR_3)] (PR_3 = PCy_3, PPh*i*Pr_2) were obtained either by reaction of the corresponding [Cp*RuCl(PR_3)] with Tl(OCH_2CF_3) in toluene or, alternatively, by addition of the appropriate amount of phosphane to the dimer [{Cp*Ru(μ-OCH_2CF_3)}$_2$].[28]



The siloxo derivatives [Cp*Ru($OSiPh_3$)(PR_3)] and [Cp*Ru($OSiMe_2Ph$)(PR_3)] (PR_3 = PCy_3, PPh*i*Pr_2) were prepared by reaction of [Cp*RuCl(PR_3)] with K[$OSiPh_3$] or K[$OSiMe_2Ph$] in toluene, whereas the phenylimido complexes [Cp*Ru(NHPh)(PR_3)] (PR_3 = PCy_3, PPh*i*Pr_2) were obtained in a similar fashion by reaction of [Cp*RuCl(PR_3)] with Li[NHPh].[28] All of these [Cp*RuX(PR_3)]

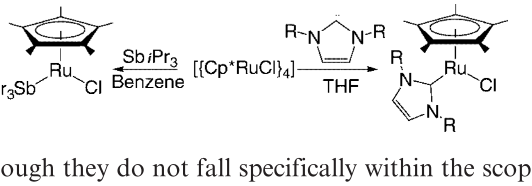
derivatives contain X ligands which bear electron lone pairs at the donor atom, and hence fall into the category of π-stabilized unsaturated complexes.

The complexes [Cp*Ru(C≡CR)(PPh$_3$)] (R = Ph, *t*Bu) are coordinatively unsaturated species considered to be key intermediates in the catalytic coupling of alkynes.[33,34] These intermediates are generated in situ by deprotonation of the corresponding neutral vinylidene complexes [Cp*-Ru=C=CHR(Cl)(PPh$_3$)], but they have never been isolated as such in stable form. However, the reaction of [Cp*Ru=C=CH*t*Bu(Cl)(PPh$_3$)] with MeC≡CMe and NaOMe in MeOH has made possible the isolation and characterization of the β-agostic enynyl complex [Cp*Ru{C(H-CH$_2$)=CMeC≡C*t*Bu}(PPh$_3$)].[33]

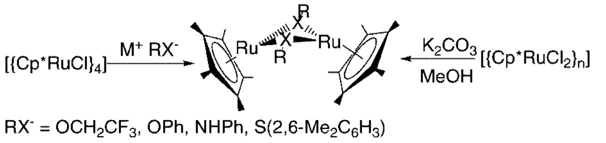


Whereas no stable compounds of the type [TpRu(X)(L)] are known, the involvement of 16-electron alkynyl species [TpRu(C≡CR)(PR$_3$)] in catalytic processes is well established.[35−37]

Non-phosphane ligands are also capable of stabilizing 16-electron complexes of the type [Cp*RuX(L)]. Thus, the triisopropylstibane complex [Cp*RuCl(Sb*i*Pr$_3$)] has been synthesized by reaction of [(Cp*RuCl)$_4$][24] with Sb*i*Pr$_3$ in benzene, or, alternatively, by reduction of [Cp*RuCl$_2$-(Sb*i*Pr$_3$)] with magnesium amalgam in THF albeit in poorer yields.[38] A series of carbene complexes of the type [Cp* RuCl(carbene)] {carbene = 1,3-R$_2$-imidazol-2-ylidene, R = mesityl (IMes), cyclohexyl (ICy), tolyl (ITol), 4-chlorophenyl (IpCl), adamantyl (IAd), diisopropylphenyl (IPr), (*R*)-(−)-1-cylohexylethyl [(−)ICMe], (1*S*,2*S*,3*S*,5*R*)-(+)-isopinocamphenyl [(+)I^{i}PCamp]; 1,3-dimesityl-4,5-dichloroimidazol-2-ylidene (IMesCl)} has been recently reported.[39−42] Many of these compounds have been structurally characterized, and all were prepared by reaction of the tetramer [{Cp*RuCl}$_4$][24] with the corresponding free carbene in THF.



Although they do not fall specifically within the scope of this review, we should mention here a number of binuclear 16-electron complexes of the type [(Cp*Ru)$_2$(μ-RX)$_2$] {RX = OMe,[43,44] OPh,[45] OCH$_2$CF$_3$,[28] PhNH,[46] S(2,6-Me$_2$C$_6$H$_3$)[47]}, which are useful precursors for the preparation of further unsaturated complexes. These compounds display "folded" structures in the solid state and have been prepared by reaction of [(Cp*RuCl)$_4$][24] with the corresponding M$^+$RX$^-$ salts or, in the case of [(Cp*Ru)$_2$(μ-OMe)$_2$], by reaction of [(Cp*RuCl$_2$)$_n$] with K$_2$CO$_3$ in MeOH.[43]



All [Cp*RuX(L)] derivatives structurally characterized display two-legged piano-stool structures, like [Cp*RuCl-(P*i*Pr$_3$)][25] represented in Figure 3.

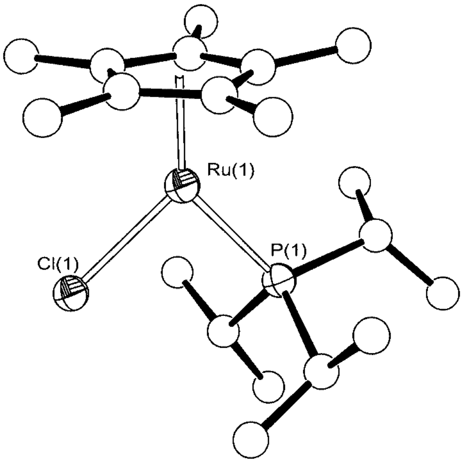


Figure 3. Molecular structure of [Cp*RuCl(P*i*Pr$_3$)]

Relevant bond lengths and angles for [Cp*MX(L)] (M = Ru, Os) compounds are summarized in Table 1.

The plane defined by the atoms X−Ru−L is almost perpendicular to the plane defined by the C$_5$ ring of Cp*. This is reflected in the pyramidalization angle α, which is the angle between the centroid of the Cp* ring, the metal atom and the centroid of the moiety X−M−L. The value of α is 170° or greater in most cases. EHMO calculations have shown the preference for a planar (non-pyramidalized, α = 180°) structure in the case of the model compounds [CpRuI-(PH$_3$)] and [CpRu(OH)(PH$_3$)], consistent with experimental data.[28] It can be said that the presence of a π-donor ligand increases the preference for a planar structure over a σ-donor ligand, whereas π-acceptor ligands favour a bent structure {α = 160° for [CpRu(CO)$_2$]$^+$}.[28]

In Table 1, we can see that the carbene complex [Cp*-RuCl(ICy)] has α = 143.1°. The reason for this is that this particular compound is an 18-electron chloride-bridged dimer, with a Ru−Ru separation of 3.968 Å, despite the fact that it was initially reported as a 16-electron monomer.[40] A packing diagram produced by ORTEP[48] (Figure 4) confirms the dimeric structure of [Cp*RuCl(ICy)].

A similar situation occurred for the complex [Cp*Ru-(acac)], which was initially reported as a monomer having a bent structure.[49] A packing diagram showed a 18-electron dimeric structure consisting of two independent molecules in the asymmetric unit, linked through an inversion centre, and each ruthenium bonded to the γ-carbon of the symmetry related acac group (Figure 5).[50]

Despite this, there is numerous spectral evidence in support of the coordinatively unsaturated nature of [Cp*Ru-(acac)] in solution.[51] Most likely [Cp*RuCl(ICy)] exists

Table 1. Relevant bond lengths and angles (°) for structurally characterized neutral complexes of the type [Cp*MX(L)] (M = Ru, Os)

Compound	M−X [Å]	M−L [Å]	M−Cp*(centroid) [Å]	X−M−L [°]	α [°][a]	Ref.
[Cp*RuCl(P*i*Pr$_3$)]	2.365	2.395	1.810	91.4	175.6	[25]
[Cp*RuCl(PMe*t*Bu$_2$)]	2.395	2.392	1.770	96.32	174.5	[27]
[Cp*RuI(PPh*i*Pr$_2$)]	2.664	2.377	1.781	94.9	172.2	[28]
[Cp*Ru(OCH$_2$CF$_3$)(PCy$_3$)]	1.992	2.418	1.790	81.6	174.1	[28]
[Cp*Ru(OSiPh$_3$)(PCy$_3$)]	2.028	2.396	1.774	85.0	176.1	[28]
[Cp*RuCl(PCy$_3$)]	2.378	2.383	1.771	91.2	175.5	[39]
[Cp*RuCl(IMes)]	2.376	2.105	1.766	90.6	170.3	[39]
[Cp*RuCl(ICy)][b]	2.524	2.071	1.658	93.7	143.1	[40]
[Cp*RuCl(ITol)]	2.340	2.068	1.755	96.0	176.5	[40]
[Cp*RuCl(IAd)][c]	2.438	2.154	1.778	87.9	166.0	[40]
[Cp*RuCl(IMesCl)]	2.375	2.074	1.765	89.94	169.2	[40]
[Cp*RuCl(IPr)]	2.376	2.105	1.766	90.6	–[d]	[41]
[Cp*RuCl{(−)ICMe}]	2.377	2.097	1.763	87.1	172.4	[42]
[Cp*RuCl{(+)I^{i}PCamp}]	2.371	2.113	1.768	90.4	172.3	[42]
[Cp*Ru{PhC(N*t*Bu)$_2$}]	2.073	2.073	1.782	64.4	178.8	[53]
[Cp*OsBr(P*i*Pr$_3$)]	2.479	2.349	1.790	93.5	174.4	[63]

[a] Pyramidalization angle α = C$_5$ ring (centroid)−M−X(L)(centroid). [b] Reported as a 16-electron monomeric complex, it is actually a 18-electron chloride-bridged complex. [c] Displays one agostic interaction with one of the hydrogen atoms of one adamantyl group. [d] 3D-coordinates not available for calculation in the CSD.

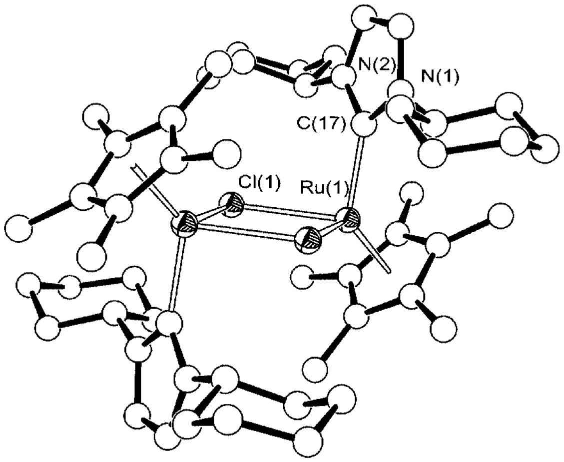


Figure 4. Molecular structure of the binuclear complex [{Cp*-Ru(ICy)}$_2$(μ-Cl)$_2$]

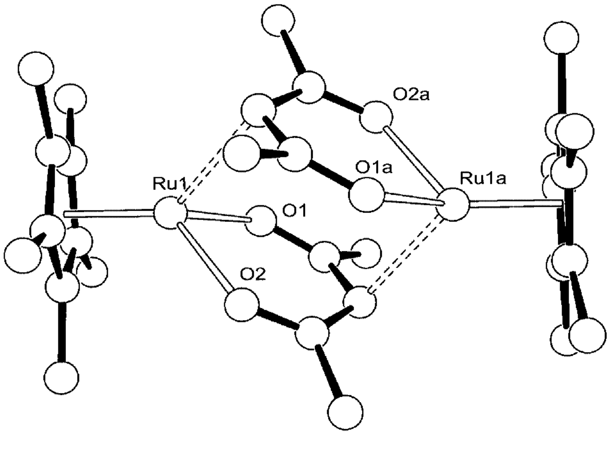


Figure 5. Molecular structure of the dimer [{Cp*Ru(acac)}$_2$]

also in solution as the monomeric species, presumably in equilibrium with its dimeric form, as has been observed for [Cp*RuCl(PMe*i*Pr$_2$)].[29]

The value of 166° found in the case of [Cp*RuCl(IAd)] is attributed to the presence of one agostic interaction with one hydrogen atom of one of the adamantyl groups (Figure 6).

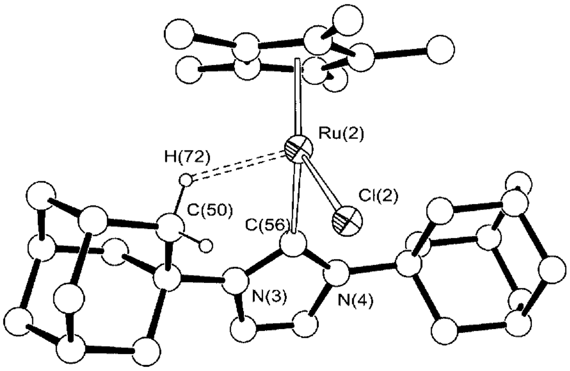


Figure 6. Molecular structure of the complex [Cp*RuCl(IAd)]; calculated average Ru···H^{agostic} 2.20 Å

The average Ru···C(H^{agostic}) distance of 2.89 Å (calculated average Ru···H^{agostic} 2.20 Å) compares well with the average value of 2.875 Å reported for the Ru···C separations in [RuPh(CO)(PMe*t*Bu$_2$)$_2$][BAr′$_4$], a complex which contains two strong agostic interactions with hydrogen atoms of the *t*Bu groups of the two phosphanes.[52]

Very recently, a series of π-stabilized complexes of the type [Cp*Ru{RC(NR′$_2$)}] (R = Me, Ph; R′ = *i*Pr, *t*Bu, Cy) has been reported.[53] In these compounds, the amidinate ligand is acting both as a σ- and π-donor to compensate coordinative unsaturation. The crystal structure of [Cp*-

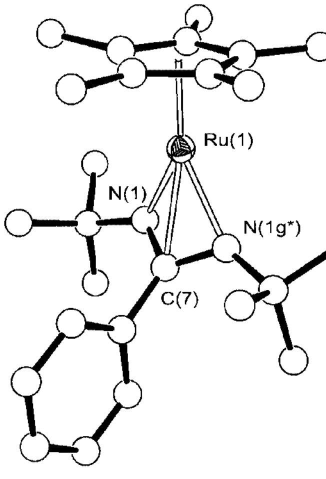
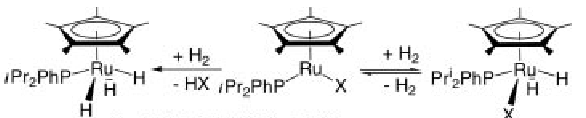


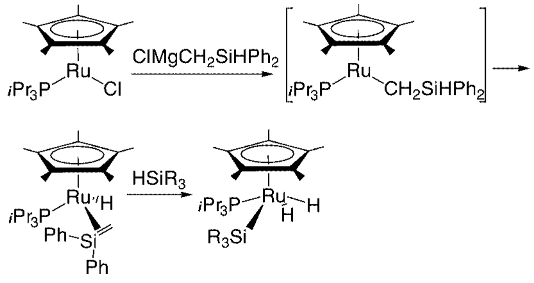
Figure 7. Molecular structure of the amidinate complex $[Cp^*Ru\{PhC(N\textit{t}Bu)_2\}]$

$Ru\{PhC(N\textit{t}Bu_2)\}]$ (Figure 7) shows an almost perfectly planar arrangement of the Cp* centroid and the RuN_2 moiety (α = 179°), but the NCN plane appears “folded”, with an angle of 48.9° and a Ru···C separation of 2.336 Å, in a fashion which resembles that of the allyl ligands.

All coordinatively unsaturated complexes of the type $[Cp^*Ru(X)(L)]$ are extremely air sensitive materials ranging in color from dark blue to purple. The blue or purple colour is actually very characteristic of these 16-electron systems, whereas complexes having filled coordination spheres tend to be yellow, orange or red. Consistent with their coordinatively unsaturated nature, and despite any partial electronic compensation coming from π-donor ligands, $[Cp^*Ru(X)(L)]$ derivatives are very reactive, with a strong tendency to add one ligand L (L = CO, olefins, pyridine) to attain the 18-electron configuration.[25−28] However, they are unreactive towards N_2 and are very reluctant to react with hydrogen. Thus, $[Cp^*RuCl(PPh\textit{i}Pr_2)]$ shows no evidence for reaction with 2 atm of H_2 at −80 °C in $[D_8]$toluene. However, within 5 min of exposure of $[Cp^*Ru(X)(PPh\textit{i}Pr_2)]$ (X = Br, I) to H_2 at 25 °C in $[D_8]$toluene, there is evidence for the formation of the labile adducts $[Cp^*RuH_2(X)(PPh\textit{i}Pr_2)]$ in equilibrium with $[Cp^*Ru(X)(PPh\textit{i}Pr_2)]$. A *cisoid* square pyramidal structure has been proposed for these Ru^{IV} species. The reaction of $[Cp^*Ru(X)(PPh\textit{i}Pr_2)]$ ($X = CF_3CH_2O$, NHPh, $OSiPh_3$) with H_2 under similar conditions involves Ru−X bond cleavage leading to $[Cp^*RuH_3(PPh\textit{i}Pr_2)]$ plus HX.[54]

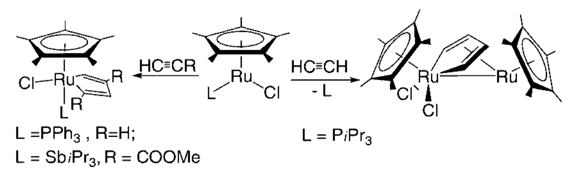


The reaction of $[Cp^*Ru(X)(PR_3)]$ derivatives with silicon-containing molecules has been thoroughly investigated. Intramolecular Si−H oxidative addition to ruthenium in $[Cp^*RuCH_2SiHPh_2(P\textit{i}Pr_3)]$, generated by reaction of $ClMgCH_2SiHPh_2$ with $[Cp^*RuCl(P\textit{i}Pr_3)]$, was used to produce the first isolated η^2-silene complex, $[Cp^*RuH(\eta^2\text{-}CH_2{=}SiPh_2)(P\textit{i}Pr_3)]$.[55] The reaction of this compound with hydrosilanes occurs via 16-electron alkyl or silyl derivatives produced by migration of the hydride back to the silene ligand, leading to Ru^{IV} silyl hydride complexes of the types $[Cp^*RuH_2(SiR_3)(P\textit{i}Pr_3)]$ and $[Cp^*RuH(SiR_3)_2(P\textit{i}Pr_3)]$.[56]

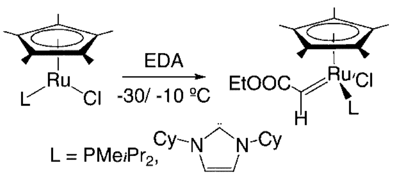


The derivatives $[Cp^*RuH_2(SiR_3)(PPh\textit{i}Pr_2)]$ were generated by reaction of $[Cp^*Ru(OCH_2CF_3)(PPh\textit{i}Pr_2)]$ with tertiary silanes $HSiR_3$ in pentane, whereas the reaction with the secondary silane SiH_2Ph_2 led to a mixture of $[Cp^*RuH_2(SiHPh_2)(PPh\textit{i}Pr_2)]$ and $[Cp^*RuH_2\{Si(OCH_2CF_3)HPh_2\}(PPh\textit{i}Pr_2)]$.[54]

$[Cp^*RuCl(P\textit{i}Pr_3)]$ reacts with acetylene to yield the binuclear ruthenacyclopentadiene $[Cp^*RuCl_2\{\kappa^2(C,C)\text{-}\mu\text{-}C_4H_4\}RuCp^*]$,[57] whereas the reaction of the stibane homologue $[Cp^*RuCl(Sb\textit{i}Pr_3)]$ with HC≡CCOOMe generates the mononuclear ruthenacyclopentadiene complex $[Cp^*RuCl\{\kappa^2(C,C)\text{-}C(COOMe){=}CHC(COOMe){=}CH\}(Sb\textit{i}Pr_3)]$.[38] The reaction of acetylene with $[Cp^*RuCl(PPh_3)_2]$ also leads to the ruthenacyclopentadiene complex $[Cp^*RuCl\{\kappa^2(C,C)\text{-}CH{=}CHCH{=}CH\}(PPh_3)]$ by intermediacy of the 16-electron species $[Cp^*RuCl(PPh_3)]$ generated in situ.[58]



Diazo compounds add to $[Cp^*RuCl(PMe\textit{i}Pr_2)]$ complexes furnishing the unstable carbene complexes $[Cp^*Ru{=}CHR(Cl)(PMe\textit{i}Pr_2)]$ (R = COOEt, $SiMe_3$).[59] In analogous fashion, the bis(carbene) derivative $[Cp^*Ru{=}CHCOOEt(Cl)(ICy)]$ is accesible by reaction of the corresponding unsaturated carbene complexes $[Cp^*RuCl(ICy)]$ with $N_2CHCOOEt$ (EDA) in toluene at −10 °C.[60]



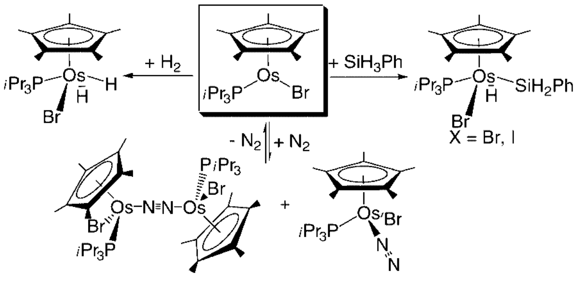
The unsaturated carbene complexes $[Cp^*RuCl(L)]$ (L = ICy, IMes) have been shown to be efficient catalysts for 1-alkyne dimerization. The conversion and selectivity of these reactions are strongly dependent on the alkyne as well as the *N*-heterocyclic carbene substituents.[61]

[Cp*RuCl(PCy$_3$)] has recently shown to be an effective catalyst, in conjunction with Al(O*i*Pr)$_3$, for the living radical polymerization of methylmethacrylate. Although this is a versatile system which gives very narrow molecular weight distributions, the polymerizations are slow and need over 100 h for completion.[62]

2.3 Osmium Complexes

Whereas [Cp*RuCl(P*i*Pr$_3$)] was reported in 1988,[25–26] the osmium complex [Cp*OsBr(P*i*Pr$_3$)] has only been prepared very recently.[63] One possible reason for this is the unavailability of the complex [Cp*OsCl]$_4$, the homologue of [Cp*RuCl]$_4$,[24] which could serve as the starting material for the preparation of [Cp*OsCl(L)] derivatives as in the ruthenium case. Alternatively, Girolami and co-workers have described the synthesis and crystal structure of the Os^{III} dimeric complex [(Cp*OsBr)$_2$(μ-Br)$_2$],[64] providing a useful and versatile starting compound for the entry into Cp*Os chemistry. Hence, the Os^{III} phosphane complex [Cp*OsBr$_2$(P*i*Pr$_3$)] was obtained by reaction of [(Cp*OsBr)$_2$(μ-Br)$_2$] with two equivalents of P*i*Pr$_3$ in CH$_2$Cl$_2$. Reduction of [Cp*OsBr$_2$(P*i*Pr$_3$)] with Na/Hg amalgam (0.3%, one equivalent) in THF followed by workup afforded purple-black crystals of the 16-electron complex [Cp*OsBr(P*i*Pr$_3$)].[63] This is the only stable compound of the type [Cp*Os(X)(L)] isolated so far. X-ray crystallography showed a planar two-legged piano stool structure for this compound, just as its ruthenium congeners (Table 1).

[Cp*OsBr(P*i*Pr$_3$)] reversibly binds N$_2$ at low temperature to give the terminal and bridging dinitrogen complexes [Cp*OsBr(N$_2$)(P*i*Pr$_3$)] [ν(N$_2$) 2074 cm^{-1}] and [{Cp*OsBr(P*i*Pr$_3$)}$_2$(μ-N$_2$)], which were characterized by ^{15}N NMR spectroscopy. Reaction with H$_2$ affords the Os^{IV} dihydrido complex [Cp*OsBrH$_2$(P*i*Pr$_3$)], whereas reaction with PhSiH$_3$ yielded the silylhydrido derivative [Cp*OsHBr(SiH$_2$Ph)(P*i*Pr$_3$)].[63]

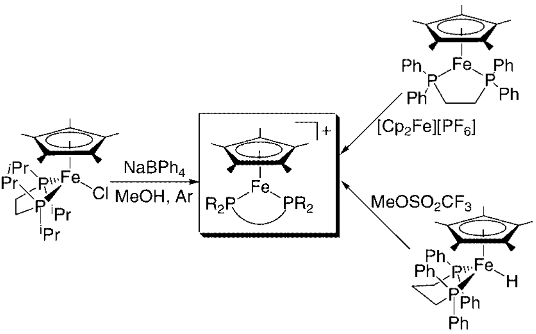


The complex [CpOsCl(P*i*Pr$_3$)$_2$] dissociates one P*i*Pr$_3$ ligand very easily in solution generating the unsaturated complex [CpOsCl(P*i*Pr$_3$)] in situ, which reacts rapidly with P(OMe)$_3$, olefins and internal alkynes furnishing 18-electron complexes of the type [CpOsCl(L)(P*i*Pr$_3$)] [L = P(OMe)$_3$, methylacrilate, bis(carboxymethyl)acetylene].[65] Besides, [CpOsCl(P*i*Pr$_3$)] is capable of H−X activation (X = H, C, Si, Ge, Sn).[66] In a similar fashion, thermolysis of the alkyl complexes [(C$_5$R$_5$)OsCH$_2$SiMe$_3$(PR$_3$)$_2$] (R = H, Me; PR$_3$ = PPh$_3$, PMe$_3$) also generates the corresponding highly reactive 16-electron complexes [(C$_5$R$_5$)OsCH$_2$SiMe$_3$(PR$_3$)] in situ, which easily undergo C−H activation processes leading to alkyl, silyl and hydridosilyl derivatives.[67]

3. Cationic Complexes of the Type [(C$_5$R$_5$)M(L)$_2$]$^+$

3.1 Iron Complexes

Although not strictly a half-sandwich complex, the 16-electron pentadienyl derivative [(η^5-pentadienyl)Fe(PEt$_3$)$_2$][PF$_6$] was reported in 1990. It was prepared by reaction of [Fe(η^5-pentadienyl)(η^3-pentadienyl)(PEt$_3$)] with Ag[PF$_6$] and PEt$_3$ in dichloromethane, or, alternatively, by addition of [HPEt$_3$][PF$_6$] to the former iron complex.[68] The first 16-electron half-sandwich complexes of iron isolated and unequivocally characterized were [(C$_5$R$_5$)Fe(dippe)][BPh$_4$] (R = H, Me).[7] These yellow-brown compounds were prepared by halide abstraction from the corresponding chloro complexes [(C$_5$R$_5$)FeCl(dippe)][6] in MeOH under argon, using NaBPh$_4$ as a chloride scavenger. The complex [Cp*Fe(dppe)][PF$_6$], prepared by oxidation of the 17-electron radical complex [Cp*Fe(dppe)] using [Cp$_2$Fe][PF$_6$], was reported shortly afterwards.[69] The related derivative [Cp*Fe(dppp)][CF$_3$SO$_3$] [dppp = 1,3-bis(diphenylphosphano)propane] has been described recently.[70] This compound was obtained by hydride abstraction from [Cp*FeH(dppp)] using MeOSO$_2$CF$_3$ as a hydride scavenger.



All compounds [(C$_5$R$_5$)Fe(P)$_2$]$^+$ reported to date, as well as [(η^5-pentadienyl)Fe(PEt$_3$)$_2$]$^+$, are paramagnetic species with magnetic moments ranging from 2.93 to 3.8 μ$_B$. These values for the magnetic moment are consistent with the presence of two unpaired electrons, and hence have a triplet state electron configuration. The structure of these coordinatively unsaturated two-legged piano-stool complexes has been analyzed using both extended Hückel methodology[71] and density functional theory (DFT).[71–72] Detailed DFT calculations performed on the complex [Cp*Fe(dppe)]$^+$ found a triplet ground state with a small singlet-triplet separation. Geometry optimization has shown that the structure of the compounds [(C$_5$R$_5$)Fe(PR′$_2$CH$_2$CH$_2$PR′$_2$)]$^+$ (R = H, Me; R′ = H, Ph) is planar in the triplet state (α = 177° to 180°), whereas in the singlet state it is pyramidalized, with the angle α between 145° and 162°.[72] The question of the spin state, geometry and structural dynamics of these systems has been explained in terms of the second-order Jahn−Teller instability of their planar (non-pyramidalized) geometry.[72] The through-space coupling (TSC) concept has also been applied to the study of the geometry of $[Cp'ML_2]$ systems (Cp′ = cyclopentadienyl or a derivative, M = Fe^{II}, Ru^{II}, L = P- or N-donor co-ligands). This concept is the molecular orbital representation of van der Waals-like repulsive-attractive forces between the ligands in addition to the interactions with the metal centre.[73] According to this, the combination of both determines whether a planar or a pyramidal structure is adopted and also whether the complex is diamagnetic or paramagnetic.[73]

The theoretical findings are supported by the experimental solid-state structures of $[Cp^*Fe(dippe)][BPh_4]$ (Figure 8),[7] $[Cp^*Fe(dppe)][PF_6]$,[69] and $[Cp^*Fe(dppp)][CF_3SO_3]$.[70] All of these compounds were determined by X-ray crystallography.

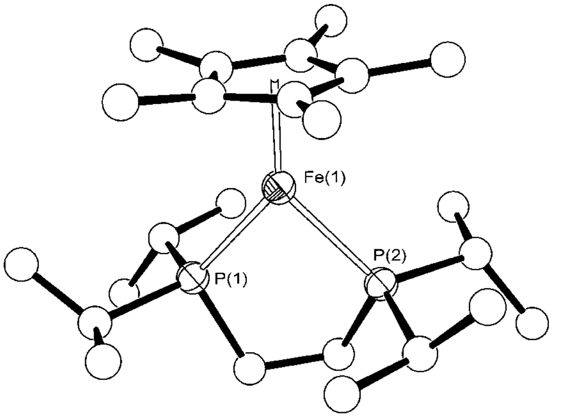


Figure 8. Molecular structure of the cation $[Cp^*Fe(dippe)]^+$

These compounds display planar two-legged piano-stool structures, and their most significant dimensions are summarized in Table 2.

There are two basic reactivity patterns for these $[(C_5R_5)Fe(P)_2]^+$ unsaturated complexes: a) addition of the ligand L to form the corresponding 18-electron complex $[(C_5R_5)Fe(L)(P)_2]^+$; and b) oxidation reactions to Fe^{III} complexes.

Complexes $[(C_5R_5)Fe(P)_2]^+$ react with a range of neutral donors such as H_2O, acetone, MeCN or CO affording the corresponding saturated complexes.[7,69,70] The resulting $[(C_5R_5)Fe(L)(P)_2]^+$ derivatives can be either diamagnetic or paramagnetic. In particular, those adducts containing oxygen-donor ligands such as acetone, H_2O or $[CF_3SO_3]^-$ in combination with Cp* as a co-ligand, all exhibit paramagnetic behaviour.[72] The complex $[Cp^*Fe(MeCN)(dippe)]^+$ is also paramagnetic at variance with its Cp counterpart, which is diamagnetic.[7] DFT has been used in an attempt to account for the unusual magnetic behaviour of these complexes.[72]

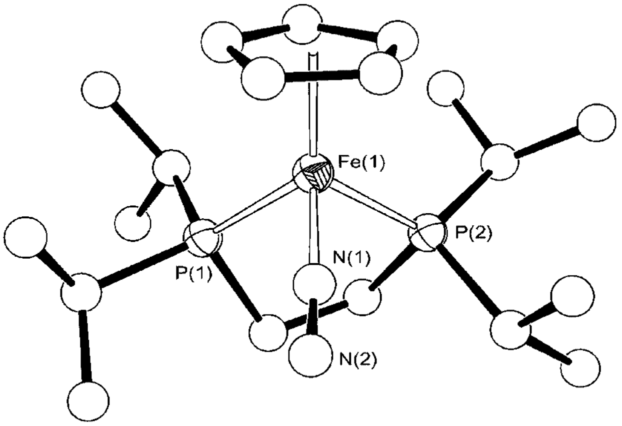
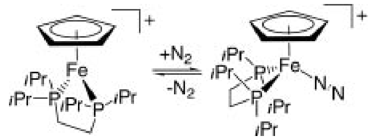


Figure 9. Molecular structure of the cationic dinitrogen complex $[CpFe(N_2)(dippe)]^+$

The complex $[CpFe(dippe)][BPh_4]$ binds N_2 reversibly, furnishing the diamagnetic terminal dinitrogen complex $[CpFe(N_2)(dippe)][BPh_4]$ [ν(N_2) 2112 cm^{-1}], which was structurally characterized (Figure 9).[7]

This dinitrogen complex exists in equilibrium with $[CpFe(dippe)][BPh_4]$ in acetone under dinitrogen. The study of this equilibrium allowed the calculation of $\Delta H°$ and $\Delta S°$ for this process (18.2 ± 0.5 kJ·mol^{-1} and 68 ± 2 J·mol^{-1} K^{-1}, respectively).



Thus, the dissociation process is entropy driven and addition of N_2 may be favoured by lowering the temperature. Poli has pointed out that the actual strength of the $Fe-N_2$ bond in this complex is greater because part of the energy spent in breaking this bond is regained as a result of the spin-state change from singlet to triplet in $[CpFe(dippe)]^+$.[1]

3.2 Ruthenium Complexes

Cationic complexes of the type $[(C_5R_5)Ru(P)_2]^+$ are readily generated in situ by reaction of the corresponding halide

Table 2. Relevant bond lengths (Å) and angles (°) for structurally characterized cationic complexes of the type $[Cp^*Fe(P)_2]^+$

Compound	M−L [Å]	M−L [Å]	M−Cp*(centroid) [Å]	X−M−L [°]	α [°][a]	Ref.
$[Cp^*Fe(dippe)][BPh_4]$	2.290	2.291	1.80	87.0	176	[7]
$[Cp^*Fe(dppe)][PF_6]$	2.232	2.260	1.77	86.5	174	[69]
$[Cp^*Fe(dppp)][CF_3SO_3]$	2.266	2.274	1.79	95.6	178	[70]

[a] Pyramidalization angle α = C_5 ring (centroid)−M−X(L)(centroid).

complex $[(C_5R_5)RuX(P)_2]$ (X = Cl, Br, I) with a suitable halide scavenger, such as Ag^+ or Tl^+ salts. However, the resulting unsaturated cations $[(C_5R_5)Ru(P)_2]^+$ are in most cases too reactive to be isolated, and react with any suitable donor molecule in the reaction mixture to give 18-electron complexes. The donor can be a solvent molecule, particularly if it is coordinating, or, alternatively, the counterion may also act as a ligand. Hence, reports claiming the synthesis of the supposedly 16-electron complexes such as $[CpRu(dcpe)][CF_3SO_3]$ [dcpe = 1,2-bis(dicyclohexylphosphano)ethane][74] or $[Cp^*Ru(dppe)][CF_3SO_3]$[75] as orange solids which were characterized by NMR spectroscopy and microanalysis, might actually correspond to the 18-electron species $[CpRu(\eta^1\text{-}(O)\text{-}CF_3SO_3)(dcpe)]$ or $[Cp^*Ru(\eta^1\text{-}(O)\text{-}CF_3SO_3)(dppe)]$, respectively. Even counterions such as $[BPh_4]^-$ are known to bind in an η^6-fashion to ruthenium.[10] The introduction of the bulky, non-coordinating anion $[BAr'_4]^-$ {Ar′ = 3,5-$[(CF_3)_2C_6H_3]$}[76] and its use as a halide scavenger opens up new possibilities to generate and stabilize cationic, highly electrophilic 16-electron species. Thus, halide abstraction from $[Cp^*RuCl(TMEDA)]$ (TMEDA = $Me_2NCH_2CH_2NMe_2$) using $NaBAr'_4$ in Et_2O affords the blue cationic 16-electron complex $[Cp^*Ru(TMEDA)][BAr'_4]$ in 92% isolated yield.[77] In a similar fashion, the reaction of $[(Cp^*RuCl)_4]$ with the diamines $Me_2NCH_2CH_2NR_2$ [R_2 = iBu$_2$, $(CH_2CH_2)_2O$] and $NaBAr'_4$ in Et_2O afforded the corresponding unsaturated cationic complexes $[Cp^*Ru(Me_2NCH_2CH_2NR_2)][BAr'_4]$ in high yields. However, when the diamine $Me_2NCH_2CH_2NMePh$ was used, the 18-electron η^6-arene complex $[Cp^*Ru\{\eta^6\text{-}C_6H_5N(Me)CH_2CH_2NMe_2\}][BAr'_4]$ was obtained.[78] The complex $[CpRu(TMEDA)][BAr'_4]$ has also been synthesized following a a similar procedure, and structurally characterized (Figure 10).[79]

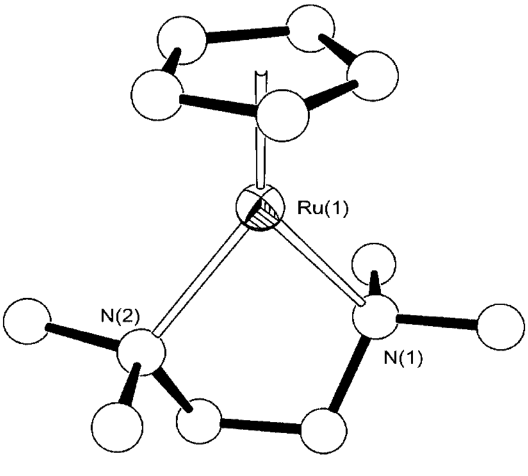
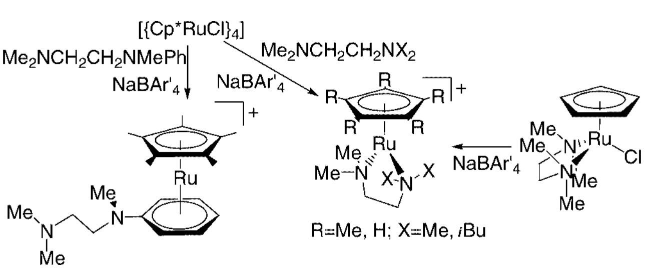
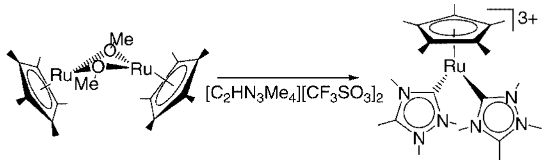


Figure 10. Molecular structure of the cation $[CpRu(TMEDA)]^+$



By addition of one equivalent of the dicationic carbene precursor 1,2,3,4-tetramethyl-1,2,4-triazolium bis(triflate) $[C_2HN_3Me_4][CF_3SO_3]_2$ to the dimer $[\{Cp^*Ru\}_2(\mu\text{-}OMe)_2]$,[43] the remarkably stable tricationic bis(carbene) complex $[Cp^*Ru(C_2N_3Me_4)_2][CF_3SO_3]_3$ was isolated in moderate yield.[80]



The rather long Ru−C(carbene) bond lengths in this complex (Figure 11) are in agreement with two datively bound carbenes acting as two-electron donors, and therefore the cation $[Cp^*Ru(C_2N_3Me_4)_2]^{3+}$ should be considered as a 16-electron species.

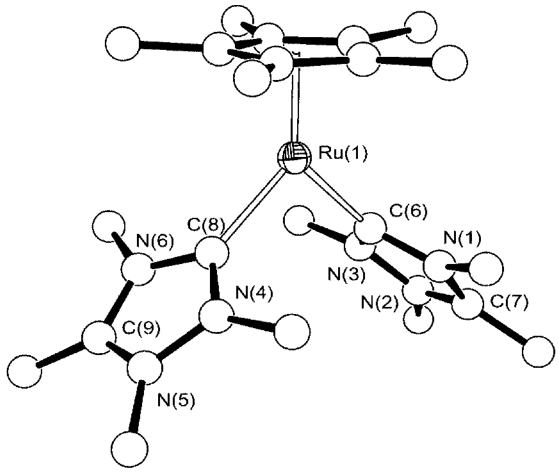


Figure 11. Molecular structure of the tricationic complex $[Cp^*\text{-}Ru(C_2N_3Me_4)_2]^{3+}$

The first stable compounds of the type $[Cp^*Ru(P)_2]^+$ were unequivocally characterized and recently reported by our research group.[81,82] The complex $[Cp^*Ru(PMe\textit{i}Pr_2)_2][BAr'_4]$ (Figure 12) was prepared by reaction of $[Cp^*RuCl(PMe\textit{i}Pr_2)]$[29] with $NaBAr'_4$ in fluorobenzene under argon in the presence of PMeiPr$_2$, whereas the derivatives $[Cp^*Ru(dippe)][BAr'_4]$ (Figure 13) and $[Cp^*Ru(PEt_3)_2][BAr'_4]$ were similarly obtained by chloride abstraction from either $[Cp^*RuCl(dippe)]$[9] or $[Cp^*RuCl(PEt_3)_2]$[83] using $NaBAr'_4$ in fluorobenzene under argon.

Although this seems to be a general reaction for the preparation of cationic 16-electron half-sandwich ruthenium complexes, the range of stable compounds of this type amenable to isolation is in fact very limited. Scheme 1 summarizes the variety of products which may result from the halide abstraction reaction of $[(C_5R_5)RuCl(P)_2]$ complexes using $NaBAr'_4$ in fluorobenzene under argon.

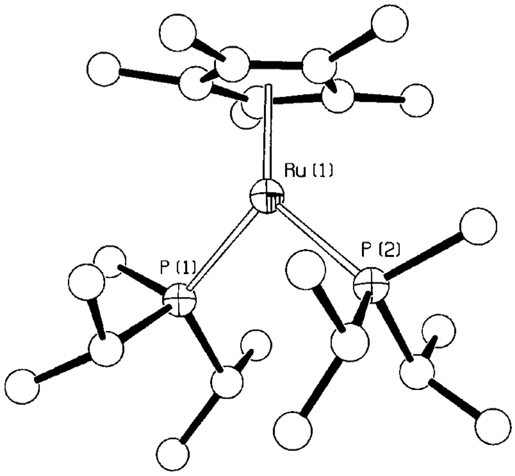


Figure 12. Molecular structure of the cation $[Cp^*Ru(PMe\textit{i}Pr_2)_2]^+$

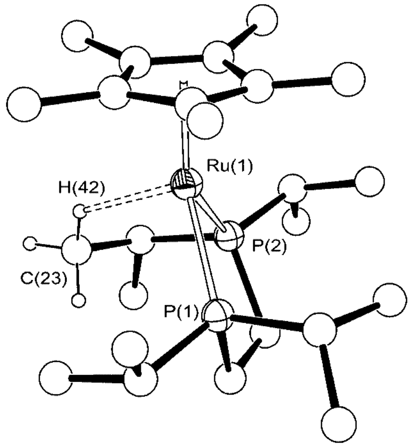
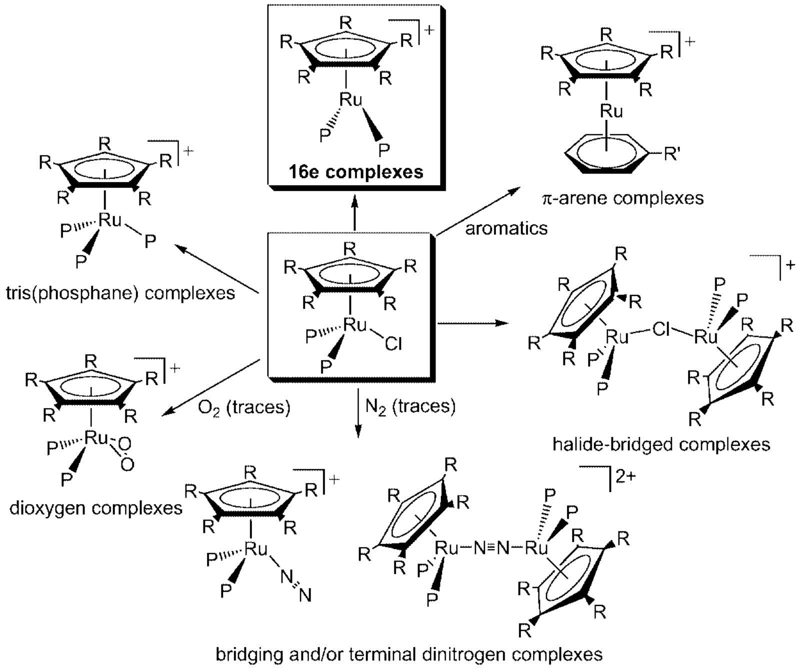


Figure 13. Molecular structure of the cation $[Cp^*Ru(dippe)]^+$; calculated $Ru\cdots H^{agostic}$ 2.262 Å

Thus, with phosphanes other than $PMe\textit{i}Pr_2$, dippe or PEt_3, a variety of 18-electron compounds have been isolated. Even a non-coordinating solvent such as fluorobenzene might become a good ligand under these conditions, and hence the sandwich complex $[Cp^*Ru(\eta^6\text{-}FPh)][BAr'_4]$ has been isolated from the reactions of $[Cp^*RuCl(PR_3)]$ (PR_3 = $P\textit{i}Pr_3$, PCy_3) with $NaBAr'_4$ in fluorobenzene under argon in the presence of PR_3 in an attempt to prepare the corresponding unsaturated complexes.[82] Halide abstraction from $[Cp^*RuCl(PMe_3)_2]$ in fluorobenzene results in ligand redistribution and a mixture of $[Cp^*Ru(\eta^6\text{-}FPh)][BAr'_4]$ and the tris(phosphane) complex $[Cp^*Ru(PMe_3)_3][BAr'_4]$ is obtained. If aromatic substituents are present on the phosphane ligand, the ultimate product from the halide abstraction reaction is usually the corresponding sandwich derivative $[Cp^*Ru(\eta^6\text{-}C_6H_5PR_2)][BAr'_4]$ (R = *i*Pr, Ph).[82] Another way to attain the 18-electron configuration for these systems is the formation of halide bridges. When the halide ligand is abstracted and the 16-electron fragment is generated, it can react with the remaining halo complex furnishing a cationic 18-electron halide-bridged binuclear complex. This happens in the course of the reaction of $[Cp^*RuCl(dppm)]$ with $NaBAr'_4$ in fluorobenzene under argon, and the resulting binuclear compound undergoes phosphane rearrangement yielding $[\{Cp^*Ru\}_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2][BAr'_4]$.[84] In a similar fashion, halide abstraction from $[Cp^*RuCl(CO)(PR_3)]$ (PR_3 = PEt_3, $PMe\textit{i}Pr_2$) also leads to halide-bridged binuclear complexes $[\{Cp^*Ru(CO)(PR_3)\}_2(\mu\text{-}Cl)][BAr'_4]$.[85]

The use of Cp* instead of Cp as the co-ligand is also very important for the stabilization of cationic half-sandwich 16-electron species of the type $[(C_5R_5)Ru(P)_2]^+$. Thus, when halide abstraction from $[CpRuCl(P)_2]$ $[(P)_2$ = dippe, PEt_3, $PMe\textit{i}Pr_2]$ using $NaBAr'_4$ in fluorobenzene under argon was



Scheme 1. Variety of products which may result from the halide abstraction reaction of $[(C_5R_5)RuCl(P)_2]$ using $NaBAr'_4$/FPh

attempted, the resulting 16-electron species generated in this way are potentially so reactive that they scavenge trace amounts of dinitrogen present even in high-purity argon, giving dinitrogen-bridged complexes $[\{CpRu(P)_2\}_2(\mu\text{-}N_2)][BAr'_4]_2$ (Figure 14).[86]

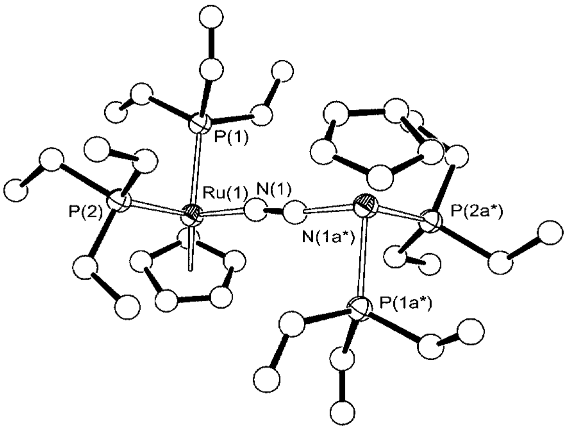


Figure 14. Molecular structure of the dicationic dinitrogen-bridged complex $[\{CpRu(PEt_3)_2\}_2(\mu\text{-}N_2)]^{2+}$

Chloride abstraction from $[CpRuCl(PMe\mathit{i}Pr_2)(PPh_3)]$ under argon afforded a compound of formula $[CpRu(PMe\mathit{i}Pr_2)(PPh_3)][BAr'_4]$. However, this compound is not a genuine 16-electron species, since the vacant coordination position is occupied by one of the C=C bonds of a phenyl substituent of the PPh_3 ligand (Figure 15). Hence in this case, the PPh_3 ligand adopts a very rare η^3-coordination mode[87] and the system attains the 18-electron configuration in this way.[86]

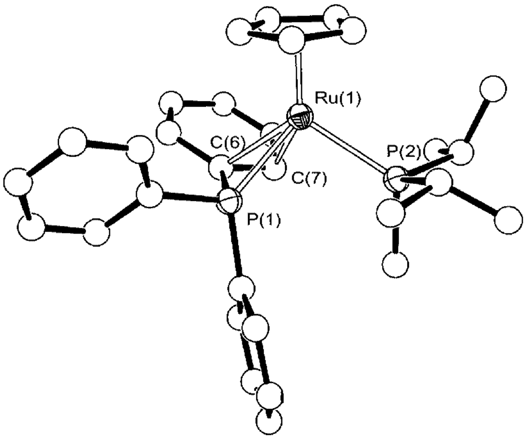


Figure 15. Molecular structure of the cation $[CpRu(\eta^3\text{-}PPh_3)(PMe\mathit{i}Pr_2)]^+$

In a similar fashion, the complexes [CpRu{(*R*)-(BINAP)}]$[CF_3SO_3]$[88,89] [BINAP = 2,2′-bis(diphenylphosphano)-1,1′-binaphthyl] and [CpRu(MeO-BIPHEP)]-$[BF_4]$[89] {MeO-BIPHEP = (6,6′-dimethoxybiphenyl-2,2′-diyl)bis[bis(3,5-di-*tert*-butylphenyl)phosphane]} contain chelating phosphane ligands acting as six-electron donors through coordination of one of the biaryl double bonds to ruthenium, also attaining the 18-electron configuration (Figure 16).

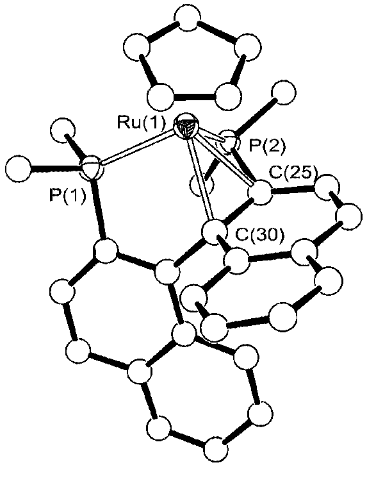


Figure 16. Molecular structure of the cation [CpRu[(*R*)-BINAP)]$^+$; only the *ipso*-carbon atoms of the phenyl rings of the BINAP ligand are represented

All cationic compounds $[(C_5R_5)Ru(L)_2]^+$ structurally characterized display two-legged piano-stool structures (Table 3). The pyramidalization angle α falls between 170° and 180° in most cases, indicative of non-pyramidalized structures.

The angle of 160° found for $[Cp^*Ru(dippe)]^+$ is due to the presence of an agostic interaction with one of the hydrogen atoms of an isopropyl group [Figure 13; $Ru\cdots C(H^{agostic})$ distance of 2.953(4) Å, calculated $Ru\cdots H^{agostic}$ 2.262 Å].[81,82] Complexes stabilized by bonding to C=C bonds of either aryl or biarylphosphane group (Figure 15 and 16) display pyramidalization angles of 155−157°, consistent with their coordinatively saturated character. Extended Hückel[73,78,79] and DFT[73,82] calculations have been performed on several model systems $[CpRu(L)_2]^+$ $[(L)_2 = (NH_3)_2, NH_2CH_2CH_2NH_2, (PH_3)_2, PH_2CH_2CH_2PH_2]$ (Figure 17). The TSC concept has also been applied recently to the MO analysis of $[CpRu(L)_2]^+$ complexes.[73]

The calculated ground-state structure of the model phosphane complexes is strongly pyramidalized (α = 149−152°), with an energy difference of ca. 6 kcal mol^{-1} between the ideally planar (α = 180°) and the pyramidal geometry. In contrast, the model amine complexes adopt essentially planar structures (α = 171−179°), with an almost flat inversion barrier.[82] It must be noted, however, that bending is hampered by bulky L_2 ligands, and the reactivity of the fragment is modified accordingly. Amine ligands participate much less than phosphane ligands in the LUMO, and this participation is further increased on bending. This is reflected in the observed agostic interaction in $[Cp^*Ru(dippe)]^+$.

Complexes $[(C_5R_5)Ru(L)_2]^+$ are highly electrophilic, as expected, although their reactivity depends strongly on the nature of both the C_5R_5 and L ligands. Thus, Cp complexes are more reactive than their Cp* homologues. For example, $[CpRu(TMEDA)]^+$ adds dihydrogen affording $[CpRu(H_2)(TMEDA)]^+$, whereas $[Cp^*Ru(TMEDA)]^+$ is unreactive

Table 3. Relevant bond lengths (Å) and angles (°) for structurally characterized cationic complexes of the type $[(C_5R_5)Ru(L)_2]^+$

Compound	M–L [Å]	M–L [Å]	M–Cp*(centroid) [Å]	X–M–L [°]	α [°][a]	Ref.
$[Cp^*Ru(TMEDA)][BAr'_4]$	2.184	2.181	1.77	80.3	179	[77]
$[Cp^*Ru(Me_2NCH_2CH_2\mathit{i}Bu_2)][BAr'_4]$	2.18	2.21	1.74	78.1	168	[78]
$[CpRu(TMEDA)][BAr'_4]$	2.143	2.164	1.71	80.9	180	[79]
$[Cp^*Ru(C_2N_3Me_4)_2][CF_3SO_3]_3$	2.081	2.071	1.79	93.7	180	[80]
$[Cp^*Ru(dippe)][BAr'_4]$[b]	2.331	2.356	1.84	83.1	160	[81,82]
$[Cp^*Ru(PMe\mathit{i}Pr_2)_2][BAr'_4]$	2.393	2.395	1.83	101.4	173	[81,82]
$[Cp^*Ru(PEt_3)_2][BAr'_4]$	2.28	2.36	1.85	99.3	170	[82]
$[CpRu(PMe\mathit{i}Pr_2)(PPh_3)][BAr'_4]$[c]	2.295	2.372	1.84	96.8	155	[86]
$[CpRu(BINAP)][BAr'_4]$[d]	2.332	2.327	1.90	90.6	155	[88]
$[CpRu(MeO\text{-}BIPHEP)][BF_4]$[d]	2.273	2.317	1.86	93.5	157	[89]

[a] Pyramidalization angle α = C_5 ring (centroid)–M–X(L)(centroid). [b] Contains one agostic interaction with a hydrogen atom of an isopropyl group. [c] Attains 18-electron configuration by coordination of one C=C bond of a Ph substituent of the PPh_3 ligand. [d] Attains 18-electron configuration by coordination of one of the biaryl bonds.

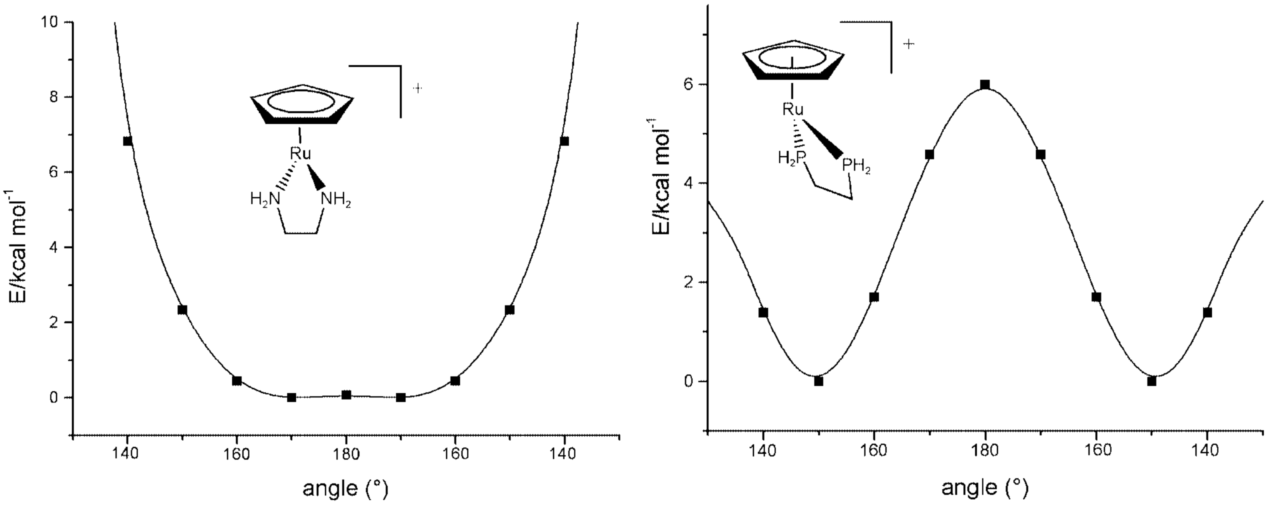
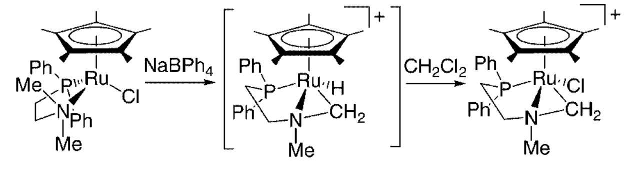


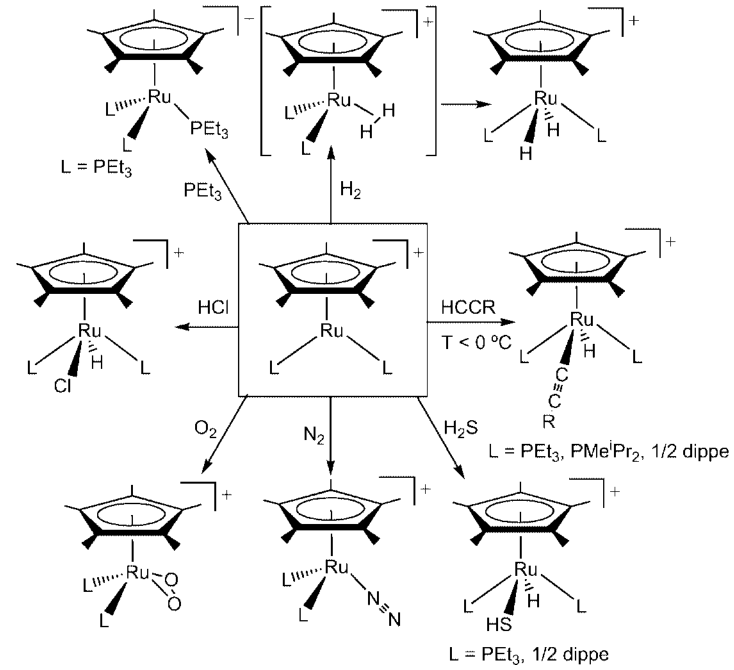
Figure 17. Energies of optimized $[CpRu(NH_2CH_2CH_2NH_2)]^+$ and $[CpRu(PH_2CH_2CH_2PH_2)]^+$ as a function of the pyramidalization angle α (°)

towards H_2.[79] In general, the transformation into the 18-electron configuration can be attained in three different ways, namely (a) direct ligand addition, (b) oxidative addition, and (c) degradation to other stable 18-electron species, such as the $[(C_5R_5)Ru(\eta^6\text{-arene})]^+$ complexes. The general reactivity patterns of $[(C_5R_5)Ru(L)_2]^+$ are summarized in Scheme 2.

All compounds $[(C_5R_5)Ru(L)_2]^+$ exhibit different degrees of affinity for an additional ligand. Whereas some compounds scavenge traces of N_2 present in argon to yield dinitrogen-bridged complexes such as $[\{CpRu(P)_2\}_2(\mu\text{-}N_2)][BAr'_4]_2$,[86] other systems {i.e. $[Cp^*Ru(TMEDA)]^+$ and $[Cp^*Ru(PMe\mathit{i}Pr_2)_2]^+$} are unreactive towards dinitrogen. However, most of them form terminal dinitrogen complexes $[(C_5R_5)Ru(N_2)(L)_2]^+$ {R = H, $(L)_2$ = TMEDA,[79] dippe, $(PMe\mathit{i}Pr_2)_2$, $(PMe\mathit{i}Pr_2)(PPh_3)$;[86] R = Me, $(L)_2$ = dippe,[10] dppe, dppm,[84] $(PEt_3)_2$[29]}. The reaction with oxygen often leads to the formation of stable dioxygen complexes $[(C_5R_5)Ru(O_2)(L)_2]^+$ {R = H, $(L)_2$ = TMEDA;[79] R = Me, $(L)_2$ = dppe,[75] dippe,[9] dppm,[90] $(PEt_3)_2$[29]}. All compounds of the type $[(C_5R_5)Ru(P)_2]^+$ add H_2 oxidatively furnishing the corresponding Ru^{IV} dihydride complexes $[(C_5R_5)RuH_2(P)_2]^+$. In many cases, the corresponding dihydrogen $[(C_5R_5)Ru(H_2)(P)_2]^+$ complexes have also been characterized in solution at low temperatures by NMR spectroscopy.[10,29,82]

With the exception of the reaction with HCl, the amine complexes $[(C_5R_5)Ru(TMEDA)][BAr'_4]$ (R = H, Me) are reluctant to undergo oxidative addition reactions, at variance with $[Cp^*Ru(P)_2]^+$ $[(P)_2$ = dippe, PEt_3, $PMe\mathit{i}Pr_2]$ derivatives. One particular case is the chelate-assisted methyl C–H activation that takes place in the course of the reaction of $[Cp^*RuCl(PPh_2CH_2CH_2NMe_2)]$ with $NaBPh_4$ in CH_2Cl_2 to yield the unstable hydrido complex $[Cp^*RuH\{\kappa^3(\mathit{P,N,C})\text{-}PPh_2CH_2CH_2N(=CH_2)Me\}]^+$, which is readily converted into $[Cp^*RuCl\{\kappa^3(\mathit{P,N,C})\text{-}PPh_2CH_2CH_2N(=CH_2)Me\}]^+$.[91]

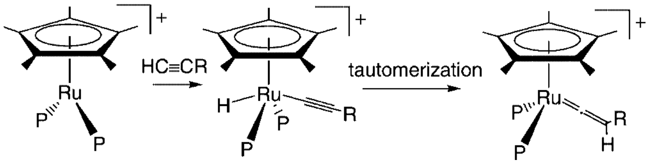




Scheme 2. General reactivity patterns of $[(C_5R_5)Ru(L)_2]^+$ complexes $[(L)_2$ = set of (NN) or (PP) ligands]

The Ru^{IV} hydridometallothiol complexes $[Cp^*RuH(SH)(P)_2]^+$ $[(P)_2$ = dippe, $PEt_3]$[83,92] result from the oxidative addition of H_2S to either $[Cp^*Ru(dippe)]^+$ or $[Cp^*Ru(PEt_3)_2]^+$. Interestingly, the addition of thiophenol yields the thiol adduct $[Cp^*Ru(HSPh)(dippe)]^+$ rather than the oxidative addition product.[92]

One of our research group contributions has been the isolation and characterization of the metastable Ru^{IV} alkynyl and hydroxyalkynyl hydrido complexes $[Cp^*RuH(C{\equiv}CR)(P)_2]^+$ $[(P)_2$ = dippe, PEt_3, $PMe\textit{i}Pr_2]$[8,93–97] as intermediates in the alkyne to vinylidene tautomerization process. This process takes place both in solution and in the solid state.[98]



Since the initial EHMO calculations by Silvestre and Hoffmann on the alkyne to vinylidene rearrangement,[99] most theoretical studies had concluded that the intermediacy of alkynyl hydrido complexes generated by oxidative addition of the alkyne to a d^6 metal centre is too high in energy, and an alternative reaction pathway, namely a 1,2-H shift, is preferred. Recent DFT studies performed on $[CpRu(HC{\equiv}CH)(PMe_3)_2]^+$ have shown that in this particular case the energy barriers for the 1,2-H shift and the oxidative addition are almost similar, so that the latter process might become competitive.[100] Further theoretical support for the involvement of alkynyl hydrido complexes in the alkyne to vinylidene tautomerization process has been found recently, when Cp* instead of Cp is introduced in the model system for computation using a combination of DFT and quantum mechanics/molecular mechanics calculations.[97]

Whereas the solid-state structures determined by X-ray crystallography for several alkynyl hydrido complexes show a *transoid* disposition of alkynyl and hydrido ligands (Figure 18), we have spectral evidence in the case of the complexes $[Cp^*RuH(C{\equiv}CR)(PMe\textit{i}Pr_2)_2]^+$ [R = Ph, COOMe, *t*Bu, $CH_2(OH)$, CMeH(OH), $CMe_2(OH)$, CMePh(OH), CHPh(OH), $CPh_2(OH)$, CCy(OH)] are consistent with the occurrence of a rapid equilibrium between the *cisoid* and *transoid* isomers in solution.[96]

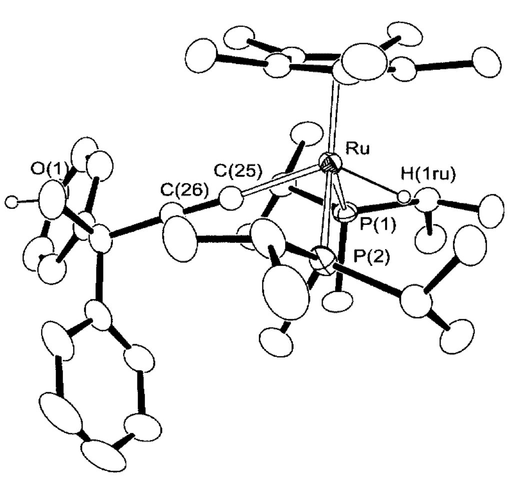
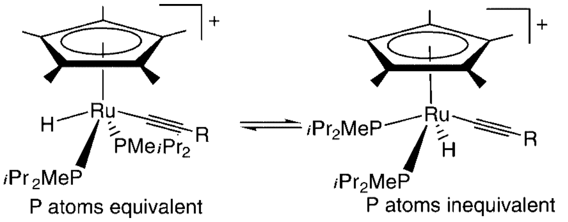


Figure 18. Molecular structure of the hydroxyalkynyl hydrido complex $[Cp^*RuH(C{\equiv}CC(OH)Ph_2(PMe\textit{i}Pr_2)_2]^+$



The halide abstraction reactions from hydridotris(pyrazolyl)borate $[TpRuX(L)_2]$ (L = PPh_3, dppe, dippe, PEt_3, $PMe\textit{i}Pr_2$, $PPh_2CH_2CH_2NMe_2$) has so far not allowed the isolation of stable 16-electron species formally analogous to their Cp*Ru counterparts.[101−105] The resulting coordinatively unsaturated fragments $[TpRu(L)_2]^+$ are extremely reactive, being trapped by any donor molecule L′ (i.e. counterion, solvent, N_2, H_2O) present in the reaction mixture to give the corresponding 18-electron complexes $[TpRu(L')(L)_2]^+$. Aquo complexes $[TpRu(H_2O)(L)_2]^+$ are often the final products isolated from halide abstraction reactions.[101,104,105] In the case of $[Tp\textit{i}PrRu(H_2O)(dppe)][CF_3SO_3]$, the H_2O ligand is labile and can be removed by means of molecular sieves (4 Å) affording the coordinatively unsaturated species $[Tp\textit{i}PrRu(dppe)][CF_3SO_3]$. This compound is stabilized by means of an agostic interaction with a hydrogen atom of one of the isopropyl groups of the Tp*i*Pr ligand, as revealed by X-ray crystallography [Figure 19; $Ru\cdots C(H^{agostic})$ 2.627(6) Å, $Ru\cdots H^{agostic}$ 1.83(6) Å].[106] There is spectral evidence for the formation of analogous species in the cases of $[Tp\textit{i}PrRu(dppm)]^+$ and $[Tp\textit{i}PrRu(Ph_2PCH{=}CHPPh_2)]^+$, but these are too unstable to be isolated.[106]

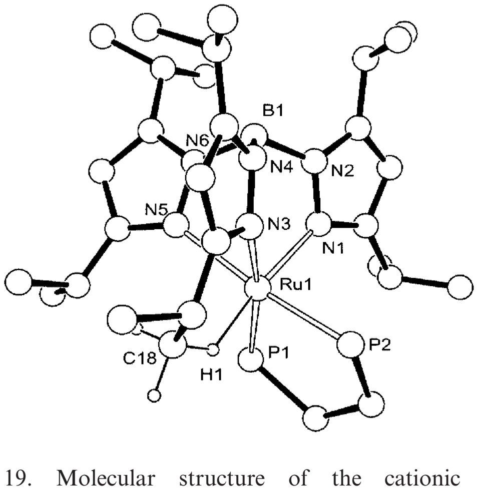


Figure 19. Molecular structure of the cationic complex $[Tp\textit{i}PrRu(dppe)]^+$; the phenyl rings of the dppe ligand have been omitted; the distance $Ru\cdots H^{agosti}$ is 1.83(6) Å.

3.3 Osmium Complexes

To date, no stable compound of the type $[(C_5R_5)Os(L)_2]^+$ has been reported. Phosphane complexes $[(C_5R_5)Os(P)_2]^+$ can be generated in situ, but these are extremely reactive and easily undergo metallation reactions furnishing 18-electron organoosmium(IV) species. Thus, $[CpOsCl(P\textit{i}Pr_3)(PR_3)]$ (PR_3 = $P\textit{i}Pr_3$, PPh_3) dissociates its chloride ligand in methanol or acetone, and the resulting unsaturated metallic fragment is capable of activating a methyl or phenyl C−H bond of a phosphane ligand to afford either $[CpOsH\{CH_2CH(CH_3)P\textit{i}Pr_2\}(P\textit{i}Pr_3)]^+$,[65] or $[CpOsH\{(C_6H_4)PPh_2\}(P\textit{i}Pr_3)]^+$.[107] The X-ray crystal structure of $[CpOsH\{(C_6H_4)PPh_2\}(P\textit{i}Pr_3)][PF_6]$ has been determined (Figure 20).[107]

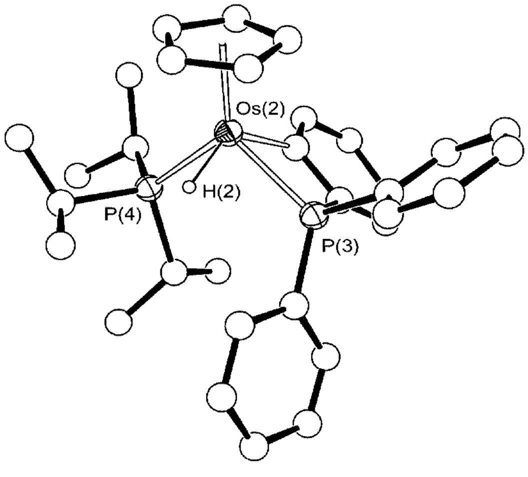


Figure 20. Molecular structure of the Os^{IV} metallated complex $[CpOsH(C_6H_4PPh_2)(P\textit{i}Pr_3)]^+$

In a similar fashion, the labile triflate complex $[CpOs(\eta^1\text{-}(O)\text{-}CF_3SO_3)(PPh_3)_2]$, generated by reaction of $[CpOsBr(PPh_3)_2]$ with $AgCF_3SO_3$ in toluene, undergoes spontaneous metallation both in solution and in the solid state furnishing the Os^{IV} derivative $[CpOsH\{(C_6H_4)PPh_2\}(PPh_3)][CF_3SO_3]$.[67]

Further proof of the extreme reactivity of the moieties $[(C_5R_5)Os(P)_2]^+$ comes from the fact that the fragment $\{[Cp^*Os(dmpm)]^+\}$ [dmpm = 1,2-bis(dimethylphosphano)methane], generated in situ, has been shown to bind CH_4. The authors claimed a σ-bound methane molecule as an intermediate for hydrogen scrambling of the hydride into the methyl group in $[Cp^*OsH(CH_3)(dmpm)]^+$.[108]

Given the strong tendency displayed by the fragments $\{[(C_5R_5)Os(P)_2]^+\}$ to undergo oxidative addition reactions, the formation of Os^{IV} alkynylhydrido complexes is much easier than in ruthenium complexes. Thus, the reaction of $[CpOsCl(P\textit{i}Pr_3)_2]$ with $TlPF_6$ and the appropriate alkyne or alkynol in acetone/dichloromethane yields the alkynylhydrido derivatives $[CpOsH(C{\equiv}CR)(P\textit{i}Pr_3)_2][PF_6]$ [R = Ph, Cy, C(OH)MePh, $C(OH)Ph_2$].[109] However, at variance with their ruthenium homologues, these Os^{IV} alkynylhydrido complexes are stable species which do not rearrange into their vinylidene isomers.

4. Conclusion

Coordinatively unsaturated half-sandwich complexes of Fe, Ru and Os are very reactive species. However, with the proper combination of electron donating capabilities and steric protection of the co-ligands, the isolation of 16-electron complexes of type $[(C_5R_5)MX(L)]$ or $[(C_5R_5)M(L)_2]^+$ is possible in some cases. These species display two-legged piano-stool structures which exhibit different degrees of pyramidalization. These structures have been rationalised by means of several theoretical approaches, namely EHMO, TSC and DFT. The reactivity patterns of the unsaturated complexes change steadily from iron to osmium through ruthenium, with an increase in the tendency to undergo oxidative addition reactions to attain 18-electron configuration. From the knowledge of the correlations structure-reactivity of these species it should be possible in the future to develop new catalytic applications in C−C bond formation reactions such as alkyne oligomerisation or olefin polymerisation.

Acknowledgments

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