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Rhodium- and iridium-trispyrazolylborate complexes C–H activation and coordination chemistry

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Abstract

This review deals with rhodium and iridium complexes of the hydridotris(pyrazolyl)borate (Tp′) ligands. In addition to outlining the synthesis of precursor compounds, an overview of the coordination modes of the Tp′ ligands is given. Recent developments in the chemistry of some important families of compounds (carbonyls, isonitriles, classical and non-classical polyhydrides) are discussed. Particular attention is given to C–H activation reactions with these compounds. Over 100 references are covered, of which approximately half stem from the last 3 years.

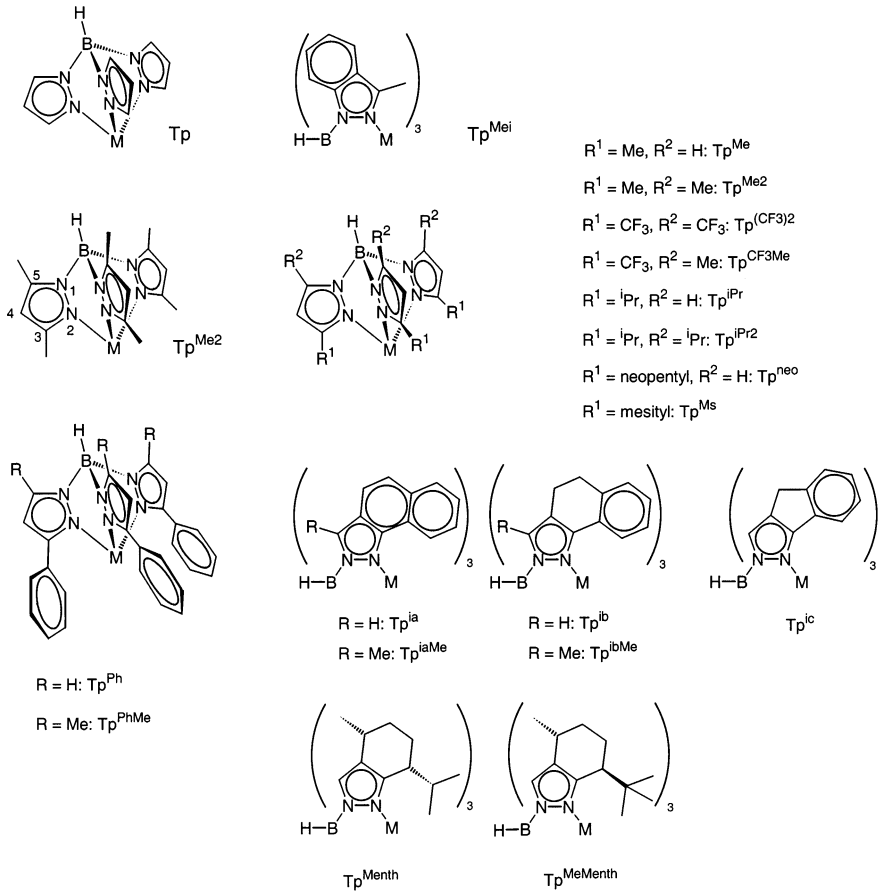
Keywords: Rhodium; Iridium; Hydrotris(pyrazolyl)borate; Coordination chemistry; C–H activation

1. Introduction

The tris(pyrazolyl)borate anion (Tp) was introduced as a ligand in coordination chemistry by Trofimenko in 1966 [1]. Since then, Tp and many of its derivatives (Scheme 1), most notably the 3,5-dimethylpyrazolyl substituted, Tp^{Me_2} (sometimes represented by Tp*) have found increasing applications as auxiliary ligands in main group and in transition metal coordination and organometallic chemistry [2,3]. This article reviews recent advances in the chemistry of Rh and Ir complexes of these ligands. Different families of compounds (e.g. alkene complexes, polyhydrides, etc.) are discussed and even though we focus on C–H bond activation reactions other important transformations are also considered. There is an increasing evidence that the Tp′ ligands may act as more than simple spectators in the course of chemical reactions experienced by their compounds, and have an important influence on their reactivity by means of temporary changes of denticity. The extensive studies of this behavior that have been undertaken, mainly with the purpose of gaining further mechanistic insights on the C–H bond activation reactions, are also discussed here. A related review dealing with RuTp′-chemistry has appeared recently in this journal [4].

At the early stages of their applications in transition metal chemistry, the Tp′ ligands were considered analogous to the ubiquitous cyclopentadienyls, Cp′. Both Cp′ and Tp′ are formally monoanionic and occupy three of the metal coordination sites, i.e. they are L_2X-type ligands. For electron-counting purposes, they act as 5-electron, or 6-electron donors, in the covalent or ionic models, respectively [5]. However, important differences between the two families of ligands actually exist, these dissimilarities being responsible for the diverse chemical behavior of their compounds, which has become apparent in the last years. The Tp′ ligands are bulkier than the Cp′ (some cone angles are Tp, 262°; Tp^{Me_2}, 276°; Cp, 150°; Cp*, 182° [2,3,6,79]) and their steric properties can be readily tuned. They are hard N-donors, as opposed to the soft Cp′ ligands, their donor ability changing in the order $Tp < Tp^{Me_2} \leq Cp < Cp^*$ [7,8]. It is worth to pointing out in this regard that within the Tp′ ligand series, modifying the nature of the pyrazolyl substituents at the 3- and 5-position have relatively little influence in the donor properties, although as expected, the extent of electron density donation increases from

CF_3-groups to alkyl. On the basis of ν_{CO} values and ^{63}Cu chemical shifts of CuTp′(CO) complexes [9] the following sequence may be suggested, ^{i}Pr, ^{i}Pr ≥ Me, Me ≈ ^{t}Bu, Me > H, H > Ph, Ph > CF_3, CF_3. A final important characteristic of the Tp′ ligands that should be mentioned is their tendency to enforce near octahedral coordination by binding to the metal in a facial, tripodal fashion (the bite angles



Scheme 1. Tp^{Me_2}, hydridotris(3,5-dimethylpyrazolyl)borate; Tp^{Me_2Cl}, hydridotris(4-chloro-3,5-dimethylpyrazolyl)borate; Tp^{Me_3}, hydridotris(3,4,5-trimethylpyrazolyl)borate; pzTp, tetrakis(pyrazolyl)borate; Tp^{CF_3Me}, hydridotris(3-trifluormethyl-5-methylpyrazolyl)borate; $Tp^{(CF_3)_2}$, hydridotris(3,5-ditrifluormethylpyrazolyl)borate; Tp^{Ph} = hydridotris(3-phenylpyrazolyl)borate; Tp^{PhMe}, hydridotris(3-phenyl-5-methylpyrazolyl)borate; Tp^{Th}, hydridotris(3-thienylpyrazolyl)borate; $Tp^{^{i}Pr_2}$, hydridotris(3,5-diisopropylpyrazolyl)borate; Tp^{neo}, hydridotris(3-neopentylpyrazolyl)borate; Tp^{Ms}, hydridotris(3-mesitylpyrazolyl)borate; Tp^{Msi}, hydridobis(3-mesitylpyrazolyl)(5-mesitylpyrazolyl)borate; Tp^{ia}, hydridotris(2H-benz[g]indazolyl)borate; Tp^{iaMe}, hydridotris(5-methyl-2H-benz[g]indazolyl)borate; Tp^{ib}, hydridotris-(2H-benz[g]-4,5-dihydroindazolyl)borate; Tp^{ibMe}, hydridotris(5-methyl-2H-benz[g]-4,5-dihydroindazolyl)borate; Tp^{ic}, hydridotris(1,4-dihydroindeno[1,2-*c*]pyrazolyl)borate; Tp^{Mei}, hydridotris(3-methylindazolyl)borate; Tp^{Menth}, hydridotris(7(*R*)-isopropyl-4(*R*)-methyl-4,5,6,7-tetrahydroindazolyl)borate; $Tp^{MeMenth}$, hydridotris(7(*S*)-tertbutyl-4(*R*)-methyl-4,5,6,7-tetrahydroindazolyl)borate.

are close to 90°). In this geometry, which is particularly favorable for d^6 systems like Rh(III) and Ir(III), the metal is suitably hybridized to form bonds with only three additional ligands, disfavoring coordination numbers higher than six [10–12].

2. Precursor compounds

2.1. Rhodium-and iridium(I) Tp′ compounds

$RhTp(\eta^2\text{-ethene})_2$ was prepared by reacting $[Rh(\mu\text{-Cl})(\eta^2\text{-ethene})_2]_2$ [13] with KTp in DMF in 69% yield [14] (or with THF as the solvent; yield > 84% [58]). $Rh(pzTp)(\eta^2\text{-ethene})_2$ could be obtained analogously [19]. By the same procedure $RhTp^{Me_2}(H_2C{=}CH_2)_2$ is obtained in 80% yield [15,49,110]. For the iridium system the starting material is dimeric $[Ir(\mu\text{-Cl})(coe)_2]_2$ (coe = cyclooctene) [16]. Subsequently $IrTp(H_2C{=}CH_2)_2$ is prepared by treatment with ethylene and KTp in 90% yield [101,102]. The Tp^{Me_2} derivative is prepared analogously in 70% yield (X-ray structure published) [103,104]. It is worth to mention, that the reaction of $[Ir(\mu\text{-Cl})(coe)_2]_2$ with ethylene and $TlTp^{Ph}$ does not give $IrTp^{Ph}(H_2C{=}CH_2)_2$, but $Ir(\kappa^4\text{-N,N′,N″C-Tp}^{Ph})(C_2H_5)(C_2H_4)$, in which one phenyl group of the Tp ligand is matalated [17]. Various diene compounds of Rh(I)Tp′ (olefin, COD; Tp′, Tp, Tp^{Me_2} [18–20]; olefin, norbornadiene, duroquinone; Tp′, Tp, pzTp [20]; olefin, COD, norbornadiene; Tp′, Tp^{CF_3Me}, $Tp^{(CF_3)_2}$ [29,44]; olefin, COD, norbornadiene, Tp′, Tp^{Ph} [21,139]; olefin, COD, norbornadiene; Tp′, Tp^{iPr_2} [22,139]; olefin, COD; Tp′, Tp^{Ms}, Tp^{Msi} [23]), and Ir(I)Tp′ (olefin, COD; Tp′, Tp^{Me_2}; pzTp [24,25]; olefin, butadiene, isoprene, 2,3-dimethylbutadiene, cyclopentadiene, cyclohexadiene; Tp′, Tp, Tp^{Me_2} [105]; olefin, butadiene, isoprene, 2,3-dimethylbutadiene, Tp′, Tp^{Ph}, Tp^{Th} [26]) were prepared. The Rh(I)(COD) compounds of several tris(indazolyl)borate ligands (Tp^{ia}, Tp^{iaMe}, Tp^{ib}, Tp^{ibMe}, Tp^{Mei}) as well as of Tp^{ic}, and Tp^{PhMe}, have been obtained by reacting $[Rh(\mu\text{-Cl})(COD)]_2$ with the corresponding Tp′-salt [27,28]. For iridium a series of COD complexes with the Tp′ ligands Tp, Tp^{Me}, Tp^{iPr}, Tp^{CF_3Me}, Tp^{PhMe}, Tp^{iPr_2}, Tp^{Me_2Cl}, and Tp^{Me_2Br} are known [50].

While the reactions of $[Rh(\mu\text{-Cl})(CO)_2]_2$ with Tp- and pzTp-salts yield a dimeric compound $[RhTp]_2(\mu\text{-CO})_3$ (also available from the reaction of $RhTp(\eta^2\text{-ethene})_2$ with CO) [19,20,61], monomeric $RhTp^{Me_2}(CO)_2$ is obtained at the room temperature reaction of $[Rh(\mu\text{-Cl})(CO)_2]_2$ with KTp^{Me_2} [15,29,34,44]. For Tp^{neo} only $RhTp^{neo}(CO)_2$ is known, which is prepared by reacting $[Rh(\mu\text{-Cl})(CO)_2]_2$ with $TlTp^{neo}$ [30], the same procedure is used to prepare $RhTp^{CF_3Me}(CO)_2$, $RhTp^{(CF_3)_2}(CO)_2$, $RhTp^{PhMe}(CO)_2$, $RhTp^{Me}(CO)_2$, $RhTp^{iPr_2}(CO)_2$, and $RhTp^{iPrBr}(CO)_2$, using the corresponding potassium or sodium salts [27,29,45]. Furthermore the chiral Tp ligands Tp^{Menth} [31] and $Tp^{MeMenth}$ [32] react with $[Rh(\mu\text{-Cl})(CO)_2]_2$ to yield the corresponding Rh complexes. Another not general possibility for accessing $RhTp'(CO)_2$ is available by reacting the corresponding COD-compound with CO. Biscarbonyl compounds with Tp′, Tp^{Ms}, Tp^{Msi}, Tp^{ia},

Tp^{iaMe}, Tp^{ib}, Tp^{ibMe} and Tp^{ic}; were prepared by this method [23,27,28]. In the case of iridium, $IrTp(CO)_2$ and $IrTp^{Me_2}(CO)_2$ were obtained by the reaction of $IrTp'(H_2C{=}CH_2)_2$ with CO [33,101,107].

2.2. Rhodium- and iridium(III) Tp′ compounds

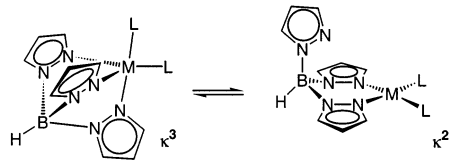
The reaction of equimolar amounts of $NaTp^{Me_2}$ and $RhCl_3$ in refluxing methanol yields two type of complexes, depending on the conditions used [34]. Dilute solutions and a short reflux time (1 h) give $[RhTp^{Me_2}(\mu\text{-}Cl)Cl]_2$ (30% yield), while a more concentrated solution and longer reflux times (3 h 30 min) produces $RhTp^{Me_2}Cl_2(MeOH)$ in 78% yield. The same procedure with NaTp instead of $NaTp^{Me_2}$ gives $[RhTp(\mu\text{-}Cl)Cl]_2$ in 70% yield. $[IrTp^{Me_2}(\mu\text{-}Cl)Cl]_2$ has been reported to form by refluxing an ethanolic solution of H_2IrCl_6 with $NaTp^{Me_2}$ in 62% yield. Selected transformations of these compounds were discussed [34]. $RhTp^{Me_2}(MeOH)Cl_2$ gives with Ph_4AsCl, or Et_4NCl the $[Ph_4As]^+$ or $[Et_4N]^+$ salts of $[RhTp^{Me_2}Cl_3]^-$, with Et_3N and H_2 $[Et_3NH][RhTp^{Me_2}Cl_3]$, this compound reacts with phosphines to give $RhTp^{Me_2}ClH(PR_3)$. $RhTp^{Me_2}Cl_2(MeOH)$ can be transformed with AgOAc or $AgOCOCF_3$ to give $RhTp^{Me_2}(OAc)_2$, or $RhTp^{Me_2}(OCOCF_3)_2(H_2O)$. The dimer $[RhTp(\mu\text{-}Cl)Cl]_2$ is cleaved by L(MeCN or $AsPhMe_2$) to give $RhTp(L)Cl_2$. With $AgOCOCF_3$ the dimer is converted to $RhTp(OCOCF_3)_2$, whilst RhTp(acac)Cl is produced upon addition of Tl(acac). The iridium dimer shows the same chemistry than $[RhTp(\mu\text{-}Cl)Cl]_2$. Furthermore $RhTp^{Me_2}(\eta^3\text{-allyl})_2$ is available from the reaction of $[Rh(\eta^3\text{-allyl})_2(\mu\text{-}Cl)]_2$ with $NaTp^{Me_2}$ [34]. Others [35,36] and we had problems to reproduce the synthesis of the dimers and the alcohol adducts of rhodium and especially iridium, reported in this paper.

$RhTp^{Me_2}Cl_2(MeCN)$ was prepared using an acetonitrile solution of $RhCl_3(MeCN)_3$ and reacting it with rigorously purified KTp^{Me_2}, $RhTp^{Me_2}Cl_2(MeCN)$ is subsequently transformed to $RhTp^{Me_2}Cl_2(L)$ ($L = PMe_3$, $C{\equiv}N{-}CH_2CMe_3$) (X-ray structure available) [35]. Very recently, Venanzi et al., presented a comprehensive study covering the synthesis of $RhTp'Cl_2(MeOH)$ ($Tp' = Tp^{Me_2}$, Tp^{Me}, Tp^{Me_3}, Tp^{Me_2Cl}), starting from $RhCl_3$ in MeOH (Tp^{CF_3Me} gave $RhTp^{CF_3Me}Cl_2(pz^{CF_3Me}H)$) and their conversions to the anionic compounds $[PPh_4][RhTp'Cl_3]$ with PPh_4Cl. It was demonstrated, that the clean formation of $RhTp'Cl_2(L)$ (L = MeOH MeCN) is dependent on the Tp′ ligand, the counterion of the Tp′-ligand, the Rh-source and the solvent used [36].

3. Coordination chemistry

3.1. Question of the coordination mode

Complexes of the type $M(I)Tp'L_2$ (M = Rh, Ir) often show a somewhat more complex coordination behavior, like their Cp analogs, with both κ^2 and κ^3 binding modes being accessible, depending upon the nature of the Tp′-ligand, the metal and the coligands L. While κ^3 coordination yields an 18-electron trigonal-bipyramidal structure, κ^2 binding results in a 16-electron square-planar species.



Scheme 2.

Though solid-state coordination information is provided by X-ray crystallography, the assignment of the binding modes of the Tp′-ligand in solution is complicated by the dynamic nature of bonding of the Tp′ (Scheme 2). In both ^{1}H- and ^{13}C-NMR spectra, static square-planar and trigonal-bipyramidal structures would provide a 2:1 pattern of the pyrazolyl resonances. However, many $MTp'L_2$ complexes display only a single set of pyrazolyl resonances even at low temperatures. This equilibration is consistent with rapid exchange of coordinated and uncoordinated pyrazolyl rings, whereby no information of a κ^2- or κ^3-binding mode is provided.

In case of carbonyl compounds the CO stretching can be used as an indicator of the coordination mode, thus pentacoordinated $MTp'(CO)_2$ show both stretching vibrations (symmetrical and asymmetrical) at lower energy compared with their four-coordinated isomers [44].

In the case of M-olefin complexes, the ^{13}C-NMR shift data of the olefinic carbons has been reported to be of use for ascertaining the coordination mode of the Tp′ ligand. It has been shown, that κ^3-Tp′ olefin compounds give rise to the olefinic carbon signal at higher field than their κ^2-Tp′ olefin analogs, although the trend is not very pronounced [21,29,43,44].

Very powerful, when accessible are the ^{15}N-NMR-shift data for the Tp′-ligands. In the free pyrazolylborates, the nitrogen chemical shifts of N^2, which are mainly determined by low-lying n–π* electronic transitions have values, which are ca. 50–70 ppm higher than those of N^1 (for assignment of N^1 and N^2 cf. Scheme 1). This difference decreases on coordination so that a large change from −75 ppm to ca. −138 ppm occurs upon coordination of a pyrazolyl ring. Thus, the average value for this parameter, in case of fast exchange between two coordinated and one free ligand arm in the κ^2-form of the complex is expected to be close to ca. −117 ppm. More negative values of the observed chemical shifts indicate increasing proportions of the κ^3-form of the complex [29,43,44]. It should be noted, that Venanzi et al. reported, that the very convenient way to obtain nitrogen shifts using ^{15}N–^{1}H-correlations, which rely on suitable heteronuclear long-range coupling constants just works with pyrazolylborates which have no substituents in the ring 3-position [44].

Furthermore ^{103}Rh-NMR spectroscopy can be useful in determining the denticity of the Tp′-ligand. In four-coordinate RhTp′-compounds the ^{103}Rh chemical shift can be found at ca. 1350 ppm, whereas for penta-coordinated complexes it is

significantly shifted to high-field (ca. 1130 ppm) [29,44]. It is worth mentioning, that ^{103}Rh-NMR data are available in cases where the ^{103}Rh chemical shift is correlated with different ligand properties [37–40].

^{11}B-NMR spectroscopy seems very useful in this respect and ^{11}B-NMR shifts of the Tp′-B have been shown to correlate with the denticity of the Tp′-ligand. For a series of Tp^{Me_2} complexes it has been demonstrated, that the κ^3-form gives ^{11}B-NMR shifts at lower field (about 2–3 ppm) than the κ^2-form [41]. Additionally, the ^{11}B longitudinal relaxation time may provide useful data in this context [44].

Recently, Akita, Moro-oka and coworkers have found a useful criterion for the denticity of Tp′ ligands, which so far has proved very reliable [22]. This is based on the value of the B–H stretching frequency, that for complexes of the type $RhTp^{^{i}Pr_2}$(diene) appears around 2540 cm^{-1} when the ligand acts as tridentate and about 2480 cm^{-1} for κ^2-coordination. However, the limiting ν(B–H) values for the different binding modes appear to change with the nature of the pyrazolyl ring substituents, wave-numbers of ca. 2520 and 2480 cm^{-1} being for example typical of κ^3-Tp^{Me_2} [22] and κ^3-Tp [42], respectively. It is likely that the electron-donating or -accepting properties of the coligands, and the presence of a positive or negative charge on the metal, may also shift significantly the above ν(B–H) values, but the dearth of information presently prevents a more precise statement to be made.

In the following table (Table 1), we summarize structurally elucidated compounds of the type $MTp'L_2$ and their spectroscopic data when accessible. Note that the solid state structure does not necessarily correspond to the solution structure, and also note that it has been shown that changes in the solvent may alter the population of the κ^2- and κ^3-electronic states [29] and that these effects may originate different or additional species in the solid state. Thus, not only subtle electronic and steric effects, but also solubility factors and crystal packing forces may determine whether these complexes form four- or five-coordinate species in solution or even in the solid state. An expressive example is the coexistence of the κ^2- and κ^3-isomers of $RhTp^{^{i}Pr_2}$(nbd) in their crystal cell [22].

From our point of view, it seems likely that for the majority of the Rh(I)- and Ir(I)-$MTp'L_2$ compounds, the κ^3-Tp′ trigonal bipyramid and the κ^2-Tp′ square-planar structures, are either in a detectable equilibrium or are accessible, one from the other, under ordinary reaction conditions. Likely exceptions to this are for instance those κ^2-Tp′ compounds for which the κ^3 form presents severe steric interactions.

It has become evident in the past few years that both the κ^3- and the κ^2-coordination can be achieved by means of a B–H–M interaction, i.e. κ^3-H,N,N′ and κ^2-H,N, respectively. In addition, for the bidentate κ^2-N,N′ binding, the third pyrazolyl ring may be axial or equatorial, as shown in Scheme 3.

While the κ^3-H,N,N′ coordination mode finds so far no precedent in Group 9 metal-Tp′ compounds, complexes of this type are known in ruthenium chemistry [52,53]. A somewhat related weak interaction of a hydrogen with rhodium (Rh–H = 2.42(4) Å) has been observed and structurally confirmed with Rh((cyclooctane-1,5-diyl)bis(pyrazol-1-yl)borate)(COD) [54].

The different isomers expected for the κ^2-coordinated $MTp'L_2$ molecules are well documented in literature e.g. $RhTp^{Ph}$(COD) exists as an equilibrium mixture of the

Table 1

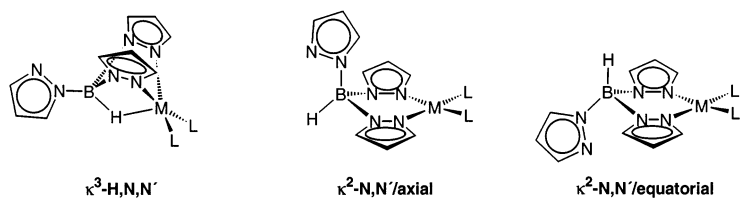
Entry	Compound	NMR-pattern	ν(B–H)	^{11}B-NMR	Denticity	M-N1 (Å)	M-N2 (Å)	M-N3 (Å)	References
1	Rh(pzTp)(nbd)	1	–	–	κ^2	2.065(3)	2.069(3)	–	[20]
2	$RhTp^{Me}_{Me}$(nbd)	1	–	–	κ^3	2.145(2)	2.229(3)	2.242(2)	[43]
3	$RhTp^{Me}$(nbd)	1	–	–	κ^3	2.147(7)	2.247(9)	2.25(1)	[44]
4	$RhTp^{Ph}$(nbd)	1	–	–	κ^2	2.094(6)	2.094(6)	–	[21]
5	$RhTp^{iPr_2}$(nbd)	1	2472	–	κ^2	2.119(4)	2.134(4)	3.392(4)	[22]
6	$RhTp^{iPr_2}$(nbd)	1	2539	–	κ^3	2.146(4)	2.260(4)	2.273(4)	[22]
7	Rh(pzTp)(dq)	1+ Free pz	–	–	κ^3	2.085(3)	2.130(4)	2.184(3)	[20]
8	Rh(pzTp)(COD)	1	–	–	κ^2	2.099(2)	2.099(2)	–	[20]
9	$RhTp^{Ph}$(COD)	2:1 And 1	–	–	κ^2	2.091(3)	2.096(3)	–	[21]
10	$RhTp^{iPr_2}$(COD)	1	2475	–	κ^2	2.099(3)	2.133(3)	3.719(3)	[22]
11	$RhTp^{Mei}$(COD)	1	–	–	κ^2	2.105(6)	2.120(6)	–	[28]
12	$RhTp^{iPr_2}$(coe)(MeCN)	2:1	2544	–	κ^3	2.109(5)	2.215(6)	2.258(6)	[45]
13	$RhTp^{iPr_2}$(dppm)	1	2488	–	κ^2	2.106(3)	2.140(2)	3.081(3)	[45]
14	$RhTp^{iPr_2}$(dppe)	1	2486	–	κ^2	2.095(6)	2.099(5)	3.419(7)	[45]
15	$RhTp^{iPr_2}$(dppp)	2:1	2488	–	κ^2	2.086(4)	2.120(4)	3.381(5)	[45]
16	$RhTp(PPh_3)(EtO_2CC{\equiv}CCO_2Et)$	2:1	2460	–	κ^3	2.125(4)	2.166(4)	2.180(4)	[66]
17	$RhTp^{CF_3Me}(CO)_2$	1	2571	−9.0	κ^2	2.114(5)	2.116(4)	2.636(5)	[29]
18	$RhTp^{ib}(CO)_2$	2:1	2456	–	κ^2	2.091(3)	2.093(4)	2.779(4)	[26]
19	$RhTp^{Menth}(CO)_2$	1	2476	–	κ^2	2.082(2)	2.105(2)	–	[32]

Table 1 (*Continued*)

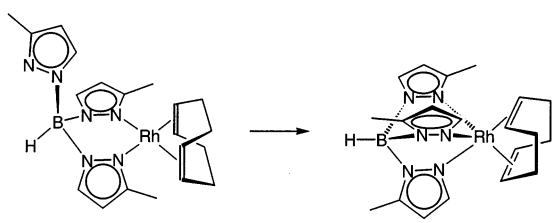
Entry	Compound	NMR-pattern	ν(B–H)	^{11}B-NMR	Denticity	M-N1 (Å)	M-N2 (Å)	M-N3 (Å)	References
20	$RhTp^{Me_2Cl}(CO)(PPh_2Me)$	–	2477	–	κ^2	2.092(2)	2.092(2)	3.800(2)	[46]
21	$RhTp^{Me_2}(CO)(PMe_3)$	1 (2:1 183 K)	2471	−6.4	κ^2	2.101(3)	2.113(3)	3.632(3)	[47]
22	$RhTp^{Me_2}(CO)(PPh_3)$	1	–	–	κ^2	2.108(4)	2.119(5)	3.537(5)	[48]
23	$RhTp^{Me_2}(C{\equiv}N\text{-}tBu)_2$	1	2464	−7.0	κ^2	2.069(9)	2.092(8)	–	[41]
24	$RhTp^{Me_2}(C_2H_4)(C{\equiv}N\text{-}2,6\text{-}xylyl)$	2:1	2520	−9.3	κ^3	2.178(7)	2.1987(8)	2.195(7)	[90]
25	$RhTp^{Me_2}(C{\equiv}N\text{-}2,6\text{-}xylyl)_2$	1	2465	−6.6	κ^2	2.079(3)	2.089(3)	–	[87]
26	$RhTp^{Me_2}(C{\equiv}N\text{-}2,6\text{-}neopentyl)_2$	1	2463	−5.9	κ^2	2.072(8)	2.085(7)	–	[87]
27	$RhTp^{Me_2}(\eta^2\text{-}O_2)(PEt_3)$	2:1	2520	−8.9	κ^3	2.084(4)	2.092(4)	2.143(5)	[49]
28	$RhTp^{Me_2}(C_2H_4)(PEt_3)$	2:1	2520	–	κ^3	2.206(6)	2.219(6)	2.227(6)	[49]
29	IrTp(COD)	1	2479		κ^3	2.086(9)	2.218(9)	2.242(9)	[50]
30	$IrTp^{Me_2Cl}(COD)$	1	2486		κ^2	2.082(5)	2.100(6)	3.478(7)	[50]
31	$IrTp^{Th}$(2,3-dimethylbutadiene)	2 × 2:1	2406	−2.7	κ^2	2.055(7)	2.079(8)		[26]
32	$IrTp^{Me_2}C_2H_4)_2$	1	2521	−8.9	κ^3	2.15(1)	2.17(1)	2.17(1)	[104]
33	$IrTp^{Me_2}(C_2H_4)(PPh_2Me)$	2:1	–	–	κ^3	2.16(1)	2.17(1)	2.18(1)	[107]
34	$RhTp^{Me_2}(\eta^2\text{-}O_2)(PMe_3)_2$	2:1	2477	−6.5	κ^2	2.100(7)	2.118(7)	-	[58]
35	$RhTp^{Me_2Cl}(CO)(PMe_2Ph)_2$	2:1	2350	–	κ^2(N,H)	2.105(3)	2.35(3) (Rh–H)	-	[46]
36	$RhTp^{Me_2}P(C_7H_7)_3$	-	1822	−1.9	κ^2(N,H)	2.139(6)	1.8(1) (Rh–H)	-	[59]
37	$RhTp^{Me_2}(PMe_3)_3$	2:1	2390	−2.0	κ^1	2.116(2)			[51]

two isomeric square-planar complexes, with the third, uncoordinated pyrazolyl ring occupying either an equatorial or an axial position [21]. The same accounts for $IrTp^{Ph}$(2,3-dimethylbutadiene) and $IrTp^{Th}$(2,3-dimethylbutadiene) [26]. Venanzi has found that the axial isomer is the major one and that substitution in the pyrazolyl 5-position strongly disfavors the dangling pyrazolyl ring from being equatorial due to steric repulsion between the 5-substituents of the coordinated and the uncoordinated rings. This conformation change is in general slower than the κ^2(axial) to κ^3 conversion of the Tp′-ligand [51,50]. Substitution on the 5-position also plays a crucial role in preventing 1,2-borotopic rearrangements of the pyrazolyl rings. For instance, during the attempted preparation of $IrTp^{Me}$(COD) compounds, $Ir(HB(pz^{3Me})_2(pz^{5Me}))$(COD) and $Ir(HB(pz^{3Me})(pz^{5Me})_2)$(COD) have been isolated. Furthermore, $IrTp^{Me}$(COD) rearranges upon heating at 70°C for 45 min to give solely $Ir(HB(pz^{3Me})(pz^{5Me})_2)$(COD) (Scheme 4). No evidence for rearrangements in $IrTp^{Me_2}$(COD) has been found [50].

The above mentioned rearrangements may be connected with sometimes observed decomposition of the Tp′ ligand upon reaction with $[IrCl(COD)]_2$ or analogous starting materials. In some cases, significant amounts of a violet byproduct $[Ir_2(\mu\text{-}N,N'\text{-}(pz')_2)(COD)_2]$ [55–57] have to be separated. Decomposition of already-formed $IrTp'(olefin)_2$ to these dimers has also been observed. Decomposition rates vary strongly with the substitution pattern of the pyrazolyl rings, solvent used, and moisture content [50,58]. It seems probable, that the decomposition proceeds by direct interaction of water with the B and N atoms of an uncoordinated ring in a Tp-type ligand. The decomposition is more often reported for iridium compounds, an observation that may be connected with the slower rates of substitution in iridium(I) compounds, as compared with their rhodium-analogs.



Scheme 3.



Scheme 4.

An interesting observation is the change in coordination observed when Rh(κ^2-N,N′-Tp^{Me_2})(CO)(PPh_3) undergoes one-electron oxidation with a ferrocenium salt. The cationic Rh(II) compound [Rh(κ^3-N,N′,N″-Tp^{Me_2})(CO″)(PPh_3)][PF_6] is readily formed [48], in a reaction that illustrates the tendency of Tp′ to be tris-coordinated.

By addition of phosphines to complexes of the type RhTp′(L_2) unusual Tp′ coordination changes can be induced. The reaction of $RhTp^{Me_2}$(η^2-O_2)(PMe_3) with PMe_3 gives Rh(κ^2-N,N′-Tp^{Me_2})(η^2-O_2)(PMe_3)$_2$ [58], whereas from $RhTp^{Me_2}$(η^2-ethene)(PMe_3) and an excess of PMe_3, Rh(κ^1-N-Tp^{Me_2})(PMe_3)$_3$ has been isolated [51]. Two examples for a κ^2-H,N coordination mode of a Tp′-ligand include, (a) $RhTp^{Me_2Cl}$(CO)(PPh_2Me)$_2$, obtained by the reaction of $RhTp^{Me_2Cl}$(CO)(PPh_2Me) with PPh_2Me (exhibiting a weak Rh–H interaction, Rh–H = 2.35(3) Å) [46]; and (b) $RhTp^{Me_2}P(C_7H_7)_3$ ($P(C_7H_7)_3$ = tris(1-cyclohepta-2,4,6-trienyl)phosphine) featuring a strong Rh–H interaction (^1J(RhH) = 19.6 Hz, ^1J(BH) = 71.6 Hz, ν_{B-H-Rh} = 1822 cm^{-1}, Rh–H = 1.8 (1) Å) [59]. In this context it has to be noted, that in Rh(III) and Ir(III)-compounds the κ^3 binding mode of the Tp′-ligand, associated with the octahedral coordination geometry of the metal, is by far the commonest. Nevertheless the dihydride complexes RhTp′H_2(PMe_3) (Tp′ = Tp, Tp^{Me_2}), react in a stepwise manner with PMe_3 to give first Rh(κ^2-N,N′-Tp′)(H)$_2$(PMe_3)$_2$, and then, under more forcing conditions [Rh(H)$_2$(PMe_3)$_4$][Tp′]. These compounds constitute the first structurally characterized example (X-ray structure for the Tp derivative published) of a Tp′ acting as a naked counterion in transition metal chemistry [51]. The analogous transformation of the corresponding iridium derivative has also been reported [138]. It is worth to comment that Tp′ anions have a strong tendency to coordinate to metals and that even in salts like NaTp · H_2O, coordination of two of the Tp N-donor atoms is observed [60].

3.2. General coordination chemistry

$RhCl_3$ reacts with KTp in the presence of NH_4PF_6 to give the rhodacene analog [Rh(Tp)$_2$]PF_6 [61]. Related compounds with carborane coligands were prepared and X-ray structure determinations of RhTp(*closo*-3,1,2-$C_2B_9H_{11}$) and RhTp(*closo*-2,1,7-$C_2B_9H_{11}$) were performed [62]. Furthermore, $RhTp^{Me2}$(1-NH_2Bu^t-1-$CB_{10}H_{12}$) exhibiting a *closo*-1-carba-2-rhodadodecaborane structure was synthesized and characterized [63]. Another sandwich-like complex [RhTp(1,4,7-trithiacyclononane)][CF_3SO_3]$_2$ was obtained by the reaction of [RhCl(1,4,7-trithiacyclononane)($MeCN$)$_2$][CF_3SO_3]$_2$ with NaTp and characterized by means of X-ray crystallography [64]. RhTp(η^5-(1-phenylborole) was synthesized during the study of triple-decker complexes of the type Rh_2(1-phenylborole)$_3$ [65].

Wilkinson's complex RhCl(PPh_3)$_3$ when reacted with KTp gives RhTp(PPh_3)$_2$ in 66% yield [66]. The coordination chemistry of this compound was communicated briefly. One of the two PPh_3 ligands in RhTp(PPh_3)$_2$ is labile, and can be exchanged with different ligands to give compounds of the type RhTp(PPh_3)(L) (L=O_2, ethene, CS_2, $SCNMe_2$, MeOOC–C≡C–COOMe) [66]. The reaction of IrTp(PPh_3)$_2$ to give Ir(κ^3(N,N,C^5_{pyr})Tp(PPh_3)$_2$H in an equilibrium cf. [109] has not been reported for RhTp(PPh_3)$_2$.

Entry to σ- and π-allyl chemistry of Rh(III)Tp^{Me_2} can be achieved by reacting $RhTp^{Me_2}$(η²-coe)(MeCN) or $RhTp^{Me_2}$(η²-ethene)(MeCN) (but not $RhTp^{Me_2}$(COD)) with allyl bromide. The reaction is shown to proceed trough $RhTp^{Me_2}$(σ-allyl)Br(MeCN) and finally ends up in $RhTp^{Me_2}$(η³-allyl)Br. This compound can be converted to $RhTp^{Me_2}$(η³-allyl)Me and $RhTp^{Me_2}$(η³-allyl)H upon reaction with MeMgBr or Li[$BHEt_3$], respectively [67]. In turn, $RhTp^{iPr_2}$(η²-coe)(MeCN) reacts with chelating diphosphines (P–P = dppm, dppe, dppp) to give $RhTp^{iPr_2}$(P–P) which reacts with I_2, H_2SiEt_2, or H_3SiPh to give the corresponding oxidative addition products [45]. $RhTp^{iPr_2}$(dppe) reacts with O_2 to give depending on the conditions used, η²-peroxo or hydroperoxo complexes. The structural characterization of these compounds has been reported [68].

Rh(III)Tp′ sources ($[RhTpCl_2]_2$, $RhTp^{Me_2}Cl_2$(MeOH), and $RhTpCl_2$(MeCN)) were reacted with a basic solution (KOH) of aminoacids $H_2NCHRCOOH$ (R=H, Me, $CHMe_2$, Ph, CH_2Ph). The corresponding neutral amino carboxylate complexes RhTp′(κ²(N,O)-$H_2NCHRCOO$)Cl were isolated and the diasteromeric excess of the reactions determined by ^{1}H-NMR spectroscopy. An X-ray structure determination of RhTp′(κ²(N,O)-$H_2NCHMeCOO$)Cl is available. Furthermore glycine amide and di- and triglycine esters were employed as ligands [69].

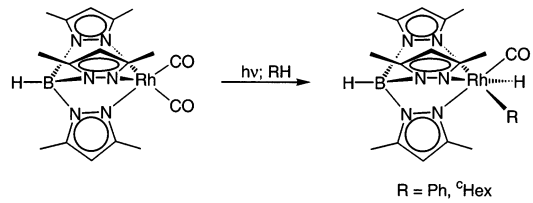
A sole X-ray structure determination (without preparation method mentioned) of RhTpIMe(PPh_3) has been performed [70].

4. Carbonyl compounds in C–H activation reactions

4.1. Photochemical reactivity-C–H activation

Graham et al. reported the first and very efficient C–H bond activation with a Group 9-Tp′-compound [71], namely $RhTp^{Me_2}(CO)_2$. Its irradiation in the presence of benzene or cyclohexane yielded the Rh(III) compounds $RhTp^{Me_2}$(phenyl)H(CO) and $RhTp^{Me_2}$(cyclohexyl)H(CO), respectively. Solutions of $RhTp^{Me_2}$(phenyl)H(CO) in benzene-d_6 undergo exchange forming $RhTp^{Me_2}$(d_5-phenyl)D(CO) with $t_{\frac{1}{2}} = 1.5$ h at 60°C. Highly unstable $RhTp^{Me_2}$(cyclohexyl)H(CO) was trapped with CCl_4 and characterized as $RhTp^{Me_2}$(cyclohexyl)Cl(CO). When a solution of $RhTp^{Me_2}$-(cyclohexyl)H(CO) is purged with CH_4, the corresponding complex $RhTp^{Me_2}$-(methyl)H(CO) forms.

The elucidation of the mechanism of this reaction was the subject of several papers. Rest et al. undertook low temperature IR and electronic spectroscopy studies and found that photolysis of $RhTp^{Me_2}(CO)_2$ in argon or methane matrices, at 12 K, produces CO loss and ligand dechelation products. In a nitrogen matrix $RhTp^{Me_2}(CO)(N_2)$ is formed, but for a C–H activation process also thermal inducement is necessary ($RhTp^{Me_2}$(CO) does not react with nujol at 12 or 77 K, while at 298 K nujol activation was found) [72]. Solution photochemistry of $RhTp^{Me_2}(CO)_2$, including a determination of the absolute quantum efficiencies for intermolecular C–H bond activation at several excitation wavelengths, has been undertaken. In the near-UV, activation reactions of alkanes proceed exceptionally



Scheme 5.

cleanly at room temperature. Quantum yields for the reaction of the biscarbonyl-compound with *n*-pentane are found to be at 313 nm, $\phi_{CH} = 0.34$; at 366 nm, $\phi_{CH} = 0.32$, and in the visible region at 405 nm, $\phi_{CH} = 0.15$. Furthermore it has been shown, that $RhTp^{Me_2}(CO)_2$ exists as an equilibrium mixture of $Rh(\kappa^3\text{-}Tp^{Me_2})(CO)_2$ and $Rh(\kappa^2\text{-}Tp^{Me_2})(CO)_2$. Estimates of $K_{eq} \approx 0.01$ and $\Delta G^0 \approx 3.0$ kcal mol^{-1} (at 298 K) have been obtained for this equilibrium in CH_2Cl_2 [73]. Furthermore, longer-wavelength irradiation (458 nm) was found to facilitate this $\kappa^3-\kappa^2$ conversion [74,75].

In 1997, time-resolved ultra fast infrared studies of the activation process allowed insight into the structures of the intermediates involved in this reaction and moreover of the energy barriers for each reaction step. Upon UV irradiation, $RhTp^{Me_2}(CO)_2$ loses one CO in less than 100 fs, and the resulting 16 electron compound is quickly solvated by RH to form $Rh(\kappa^3\text{-}Tp^{Me_2})(CO)(RH)$ and cools down vibrationally (20 ps). All subsequent processes that take place at the Rh center are found to be thermal. Subsequently, the compound traverses a 4.2 kcal mol^{-1} barrier ($k = 1/200$ ps) and forms $Rh(\kappa^2\text{-}Tp^{Me_2})(CO)(RH)$, which is now prone to the C–H activation process occurring with a barrier of 8.3 kcal mol^{-1} (a time constant of 230 ns). Finally rechelation to form $Rh(\kappa^3\text{-}Tp^{Me_2})(R)(H)(CO)$ takes place with a velocity of $\ll 200$ ns [76,77]. Recently, density functional calculations on these systems have been carried out. They suggest two different alkane adduct compounds $Rh(\kappa^3\text{-}Tp^{Me_2})(CO)(RH)$, one with a weakly and one with a more strongly bound alkane moiety [78].

Alkane activation reactions with other Tp′ ligands are rare in the literature, but there are some transformations with $RhTp'(CO)_2$ ($Tp' = Tp^{Ph}$, Tp^{iPr_2}, Tp^{CF_3Me}) mentioned in a review that deals with sterically hindered Tp ligands [79] and a thesis [80]. The only example in primary literature is a diastereoselective intramolecular C–H bond activation of an optically active Tp^{Menth} ligand upon irradiation of the corresponding $RhTp^{Menth}(CO)_2$-complex (cf. Schemes 1 and 5). In this case, one of the isopropyl groups is metalated by the rhodium center [32].

4.2. Coordination chemistry

Thermal reactions of $RhTp^{Me_2}(CO)_2$ include the activation of benzene at 140°C to give $RhTp^{Me_2}(Ph)H(CO)$ and decomposition products. The complexes $RhTp^{Me_2}(CO)(olefin)$ (olefin = ethene, propene or cyclooctene) were prepared by

reacting $[Rh(\mu^2\text{-}Cl)(CO)(olefin)]_2$ (olefin = ethene, cyclooctene) [81] with KTp^{Me_2}, or in the case of propene by irradiation of $RhTp^{Me_2}(CO)_2$ in the presence of the olefin. All three compounds reacted in benzene give $RhTp^{Me_2}(Ph)H(CO)$ at lower temperatures (70–100°C) [82]. If $RhTp^{Me_2}(CO)(C_2H_4)$ is irradiated in benzene as the solvent, the two compounds $RhTp^{Me_2}(Ph)H(CO)$ and $RhTp^{Me_2}(Ph)(C_2H_5)(CO)$ (X-ray structure published) can be isolated in approximately equal yield. If a hexane solution of $RhTp^{Me_2}(Ph)(C_2H_5)(CO)$ is pressurized with CO at 950 psi and heated for 2 weeks, complete conversion to the propionyl-compound $RhTp^{Me_2}(CO–CH_2CH_3)(Ph)(CO)$ and an unknown carbonylation product is observed. Treating $RhTp^{Me_2}(CO–CH_2CH_3)(Ph)(CO)$ with $ZnBr_2$, propiophenone is liberated, while the fate of the metal is unknown [83].

Further reactivity of carbonyl compounds has been reported as follows, $RhTp(CO)_2$ reacts with I_2 releasing one equivalent of CO to yield $RhTpI_2(CO)$, and forms an adduct with $HgCl_2$ namely $RhTp(CO)_2 \cdot HgCl_2$ (a related adduct is also formed with $RhTp(\eta^2\text{-}C_2H_4)_2$) [19]. The corresponding Tp^{Me_2} bis(carbonyl)-derivative shows the same reactivity with I_2 to form $RhTp^{Me_2}(I)_2(CO)$ [34]. Protonation of $RhTp^{Me_2}(CO)_2$ with $HBF4 \cdot OEt_2$ yields the pyrazolyl-protonated $[Rh(\kappa^2\text{-}Tp^{Me_2}(pz^{Me_2}H)(CO)_2][BF_4]$ (X-ray crystal structure presented). The reaction is reversed by addition of NEt_3. On the contrary, protonation in the same fashion of $IrTp^{Me_2}(CO)_2$ provided $[IrTp^{Me_2}H(CO)_2][BF_4]$, which could not be deprotonated with NEt_3, only the strong non-nucleophilic base DBU removes the proton to regenerate the biscarbonyl compound. This differing behavior was attributed to the greater basicity of iridium as compared with rhodium. Moreover, in case of $[IrTp^{Me_2}H(CO)_2][BF_4]$ nucleophilic bases like NaOMe or ^{n}BuLi attack one of the CO molecules to form the acyl derivatives $IrTp^{Me_2}H(COR)(CO)$ (R = OMe, ^{n}Bu) [33]. A related behavior has been found for $IrTp(CO)_2$, which upon protonation ($HBF_4 \cdot OEt_2$) gives $[IrTpH(CO)_2][BF_4]$. In protic solvents (H_2O, MeOH, or EtOH) $IrTp(CO)_2$ is converted to IrTpH(COOR)(CO) (R = H, Me, Et), which can be transformed into $[IrTpH(CO)_2][BF_4]$ by adding $HBF_4 \cdot OEt_2$ [84]. One CO ligand of $IrTp(CO)_2$ is also prone to nucleophilic attack by primary amines [85] (e.g. propylamine or hexylamine).

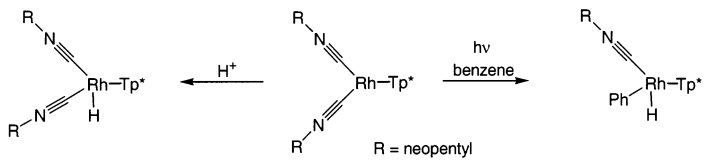
5. Isonitrile compounds

In 1989, Jones et al. mentioned, during a study of isonitrile insertion into activated C–H bonds, the synthesis and photochemistry of $RhTp^{Me_2}(CNR)_2$ (R = neopentyl). The bis(isocyanide)complex is prepared by the reaction of $[RhCl(\eta^2\text{-}ethene)_2]_2$ with $NaTp^{Me_2}$ followed by addition of neopentyl isonitrile. Irradiation in benzene results in oxidative addition of a benzene molecule to give $RhTp^{Me_2}(Ph)H(CNR)$ (Scheme 6) [86]. Further elaboration of this class of compounds includes the preparation of different isonitrile derivatives $RhTp^{Me_2}(CNR)_2$ (R = 2,6-xylyl, Me), the protonation chemistry of the neopentyl derivative (which yields upon protonation with $HBF_4 \cdot Et_2O$ the hydride compound $[RhTp^{Me_2}H(CN\text{-}neopentyl)_2][BF_4]$ (Scheme 6)) and the crystal structure determinations of

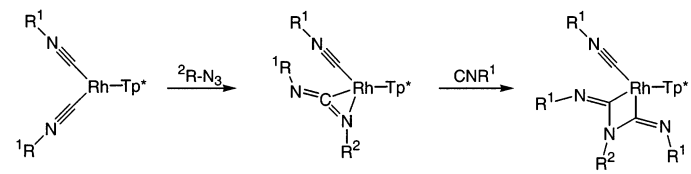
$RhTp^{Me_2}(CNR)_2$ (R = 2,6-xylyl, neopentyl) and $[RhTp^{Me_2}H(CN\text{-}neopentyl)_2][BF_4]$ [87]. Recent work from these laboratories has allowed the characterization of $[RhTp]_2(\mu\text{-}CNCy)_3$ (X-ray structure) and $RhTp^{Me_2}(C_2H_4)(CNR)$ (R = Cy, Bu^t) [49].

1,3-Dipolar cycloaddition of phenyl azide to $RhTp^{Me_2}(CNR)_2$ (R = 2,6-xylyl, neopentyl) produces the κ^2(N,C)-carbodiimide complexes $RhTp^{Me_2}(\eta^2$-Ph–N=C=NR)(CNR). The solid state structure of $RhTp^{Me_2}(\eta^2$-2,4-xylyl–N=C=N-2-tolyl)(CN-tolyl) has been obtained by X-ray diffraction. $RhTp^{Me_2}(\eta^2$-Ph–N=C=NR)(CNR) reacts with additional C≡NR to give a 3-azarhodacyclobutane derivative (Scheme 7). Photolysis of the carbodiimide compounds in benzene produces $RhTp^{Me_2}$(Ph)H(CNR) (the corresponding Cp* derivative is unreactive under these conditions). This conversion can also be effected thermally, although the rate is slow at 100°C. In the solid state, irradiation of $RhTp^{Me_2}(\kappa^2$-Ph–N=C=NMe_3)($CNC(Me_3)_3$) yields an intramolecular activation product ($RhTp^{Me2}H(\kappa^1(C^{ortho})$-Ph–N=C=$NCMe_3$))(CNR)). [88].

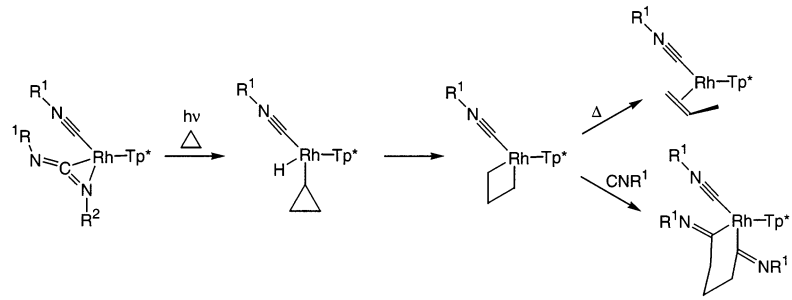
Irradiation of $RhTp^{Me_2}(\eta^2$-Ph–N=C=NR)(CNR) (R = neopentyl) in benzene, toluene, mesitylene, cyclopentane, cyclohexane, propane or pentane solvent leads to both the clean elimination of the carbodiimide ligand and the formation of the corresponding C–H oxidative addition products. Also methane can be activated by exchange of the cyclohexyl derivative. The resulting compounds $RhTp^{Me_2}H(R)(CNR)$ were trapped with CCl_4 and characterized as $RhTp^{Me_2}Cl(R)(CNR)$. Mechanistic insights in the reductive elimination of $RhTp^{Me_2}H(R)(CNR)$-complexes allows the estimation of the relative Rh–R bond strengths (selected bond strengths decrease in the following order Rh–Ph ≫ Rh-mesityl > M-cyclopentyl > Rh–methyl), competitive studies show that both benzylic and aromatic C–H bonds react under conditions of kinetic control but that the aromatic activation products are thermodynamically preferred. Activation of primary alkane C–H bonds is preferred over secondary activation, with the surprising result, that benzylic C–H activation in mesitylene is favored over that of primary C–H bonds in pentane [89].



Scheme 6.



Scheme 7.



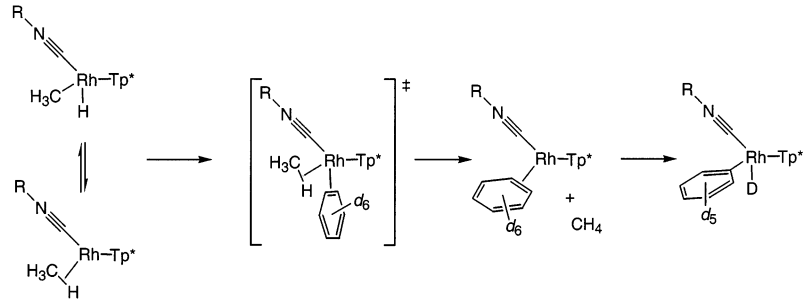
Scheme 8.

Generation of the 16-electron fragment $RhTp^{Me_2}(CNR)$ in the presence of cyclobutane and cyclopropane results also in C–H activation. However, only the latter rearranges in benzene solvent to the rhodacyclobutane compound (X-ray structure given). Thermolysis of this produces an η^2-propylene complex, while the presence of C≡N-neopentyl leads to insertion of isocyanide into the two Rh–C bonds of the rhodacycle (Scheme 8) [90].

The complexes $RhTp^{Me_2}Cl(R)$(CN-neopentyl) (R = Me, Me-d_3, *n*-propyl, isopropyl, cyclopropyl, vinyl) may also be obtained by the reaction of $RhTp^{Me_2}Cl_2$(CN-neopentyl) with the corresponding Grignard reagent. A two-step procedure for the halide exchange of compounds $RhTp^{Me_2}X(R)$(CN-neopentyl) (X = Br, I) by reacting with AgOTf and subsequently with $[Bu^n_4][Cl]$ was presented as well as the crystal structures of $RhTp^{Me_2}Cl(R)$(CN-neopentyl) (R = isopropyl, cyclopropyl) [35]. The residual halide can be exchanged against hydride by treatment with $ZrCp_2H_2$ [90] or deuteride by $ZrCp_2D_2$ [91]. Furthermore, $RhTp^{Me_2}$(CN-neopentyl)$_2$ reacts at room temperature with CH_2Cl_2 to give $RhTp^{Me_2}Cl(CH_2Cl)$(CN-neopentyl) (X-ray structure presented) [41].

The reductive elimination of benzene from $RhTp^{Me_2}(Ph)H(CNR)$ in the presence of added neopentyl isocyanide has been shown to proceed by an associative mechanism. A kinetic isotope-labeling study has provided evidence that the reductive elimination of benzene is reversible. The mechanism proposed includes initial reductive elimination of benzene to give a η^2-benzene intermediate in which the rhodium atom can rapidly migrate around the π-system of the coordinated benzene as shown by thermolysis of isotopically labeled $RhTp^{Me_2}(H)(D_5\text{-Ph})(CNR)$. Associative displacement of the benzene with isocyanide occurs in a second step [91].

Very recently, the reductive elimination of methane from $RhTp^{Me_2}H(Me)$(CN-neopentyl) has been studied [92]. Two sets of experiments have been described that provide indirect evidence for the involvement of alkane σ-complexes in the oxidative addition/reductive elimination reactions. First, the methyl deuteride complex $RhTp^{Me_2}D(Me)$(CN-neopentyl) is observed to rearrange to $RhTp^{Me_2}H(CH_2D)$(CN-neopentyl) prior to loss of CH_3D. Similarly, $RhTp^{Me_2}H(CD_3)$(CN-neopentyl) rearranges to $RhTp^{Me_2}D(CHD_2)$(CN-neopentyl) prior to loss of CHD_3. Second, the rate of elimination of methane from these complexes in benzene/hexafluorobenzene



Scheme 9.

solvent mixtures is found to be dependent upon the concentration of benzene, indicating an associative component to the reductive elimination of methane. Both of these processes, and their rates, are accommodated by the reversible formation of alkane σ-complexes prior to dissociation of alkane (Scheme 9).

Finally, to lead over to the next chapter, the energetics of intermolecular vinyl and allyl carbon–hydrogen bond activation by the unsaturated fragment $RhTp^{Me_2}$(CN-neopentyl) are summarized. Complexes of the type $RhTp^{Me_2}H(R)$(CN-neopentyl) (R = ethenyl, 2-propenyl, 2-methyl-2-propenyl, 3-dimethyl-1-butenyl) (X-ray structure of $RhTp^{Me_2}Cl$(3-dimethyl-1-butenyl)(CN-neopentyl) presented) are prepared by either oxidative addition of the parent olefin or reaction of $RhTp^{Me_2}Cl(R)$(CN-neopentyl) with $ZrCp_2H_2$. Their behavior in reductive elimination reactions has been studied and relative Rh–C bond strength for rhodiumallyl- and vinyl-hydride complexes has been deduced from kinetic experiments. The results show that the trend for relative Rh–C bond strengths parallels that of hydrocarbon C–H bond strengths, i.e. Rh–Ph > Rh–vinyl > Rh–methyl > Rh–benzyl > Rh–allyl, but that differences in M–C bond strengths typically exceed the differences in C–H bond strengths. $RhTp^{Me_2}H$(alkenyl)(CN-neopentyl) compounds rearrange to the η^2-olefin complexes (ethenyl, $t_{\frac{1}{2}} = 8$ h; 22°C; 2-propenyl, $t_{\frac{1}{2}} = 3$ days; 22°C; benzene), while relatively stable $RhTp^{Me_2}H$(3-dimethyl-1-butenyl)(CN-neopentyl) under the same reaction conditions yields $RhTp^{Me_2}H$(Ph)(CN-neopentyl) ($t_{\frac{1}{2}} = 113$ days; 22°C), presumably due to the increased steric constrain of the substrate [93].

6. Olefin compounds

6.1. Vinylic C–H activation of Rh(I)- and Ir(I)-coordinated olefins

The transformation of transition metal ethylene complexes into their hydride-vinyl isomers is typically thermodynamically uphill for mononuclear systems [94–98]. Up to now, the only exception to this rule are Ir(I) olefin complexes with coligands of the tris(pyrazolyl)borate family (but not the related rhodium compounds). At

variance with the analogous IrCp*(III) system [98], IrTp′ hydride-vinyl derivatives are found to be the products of the thermal or photochemical activation of the Ir(I) olefin species IrTp′(η^2-C_2H_4)L. This unusual behavior may be traced to the properties of the Tp′ ligand [10–12], firstly, its hard nature (as compared with the Cp′) and its favorable binding interaction with the harder Ir(III) center; and secondly its well-known propensity to impose octahedral-coordination at the metal center which is highly favorable for d^6 Ir(III). Ab initio quantum mechanical calculations on models for Graham's compounds (cf. next paragraph and Scheme 10) show the thermodynamic preference for Rh(κ^2-Tp′)(η^2-C_2H_4)$_2$ with exothermicities from -20 to -28 kcal mol^{-1} and a barrier of about 12 kcal mol^{-1}, whereas for iridium, Ir(κ^3-Tp)(η^2-C_2H_4)$_2$ is favored with exothermicities from -2 to -10 kcal mol^{-1}. With an increase of the steric effect of the pyrazolyl groups (TpMe^2 complex) the oxidative addition product becomes exothermic by -6.3 to -0.8 kcal mol^{-1} [99]. These observations are a reflection of the preference of late second-row transition metals to have d^{n+1} ground states with high-lying $d^n s^1$ excited states, while late third-row transition metals have either $d^n s^1$ ground states or $d^n s^1$ low-lying excited states. Thus, the third-row transition metal undergoes oxidation-addition more easily than its second-row transition metal congener.

Scheme 10.

First reports on activation of olefins by Tp′Ir and Tp′Rh compounds were made in the year 1989 by Graham [100], Crabtree [101] and Oro [102]. Graham et al. observed the thermal conversion of IrTp$^{(CF_3)_2}$(CO)(η^2-C_2H_4) to IrTp$^{(CF_3)_2}$(C_2H_3)H(CO) (Scheme 10), while RhTp^{Me_2}(C_2H_3)H(CO) rapidly ($t_{\frac{1}{2}} = 3.2$ min, 25°C) converts to RhTp^{Me_2}(CO)(η^2-C_2H_4) (cf. Section 5, last paragraph, rearrangement of RhTp^{Me_2}(C_2H_3)H(C≡NR)) is much slower). Crabtree et al. reported the synthesis of IrTp(C_2H_4)$_2$, and its conversion to IrTp(C_2H_3)H(C_2H_4) upon irradiation. Contradictory reports have led to some confusion regarding the room-temperature reaction of [Ir(μ-Cl)$_2$(coe)$_2$]$_2$ with MTp (M = Na, K) in the absence of added olefin. Two different formulations, namely IrTp(η^3-cyclooctenyl)H (Crabtree) and IrTp(σ^1-1-cyclooctenyl)H(η^2-cyclooctene) (Oro), has been, respectively, advanced for the resulting product, but only the latter proposal has been authenticated by X-ray methods. Furthermore Oro et al. carried out the protonation of IrTp(σ^1-1-cyclooctenyl)H(η^2-cyclooctene) with HBF_4 isolating [IrTpH(η^2-cyclooctene)$_2$]BF_4. In 1992, Carmona et al. [103] reported the synthesis of IrTp^{Me_2}(C_2H_4)$_2$ and the subsequent formation of IrTp^{Me_2}(η^3-crotyl)H upon heating (Scheme 11, right path). The reaction was shown to proceed via IrTp^{Me_2}(C_2H_3)H(C_2H_4), which can be isolated or independently prepared by irradiation of IrTp^{Me_2}(C_2H_4)$_2$.

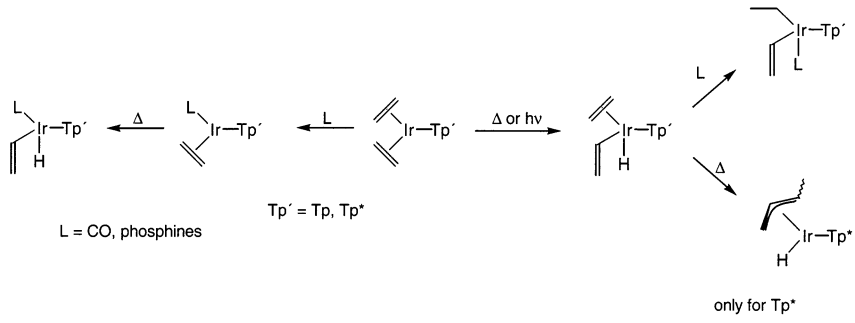
A comprehensive investigation of this new olefin dimerization pathway was undertaken [104], including different olefins (ethene, propene, butene, 2-butene,

cyclooctene), mechanistic and other studies (X-ray structure determinations of two allyl complexes were performed). This was complemented with the investigation of the photochemical activation of IrTp- and $IrTp^{Me_2}(\eta^4$-diene) compounds (diene = butadiene, 2-methylbutadiene, 2,3-dimethylbutadiene, cyclopentadiene, and cyclohexadiene) to give $IrTp'(\eta^3$-allyl)H derivatives as the C–H activation product [105].

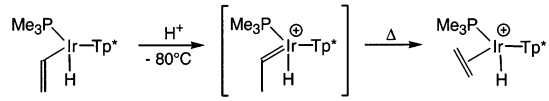
The reactivity of $MTp'(C_2H_4)_2$ with hard and soft donor ligands has been reported. Soft donors such as phosphines simply replace ethene and give compounds of the type $IrTp^{Me_2}(\eta^2\text{-}C_2H_4)(PR_3)$ ($PR_3 = PMe_3$, $PPhMe_2$, PEt_3), which exhibit a five-coordinate, distorted trigonal bipyramidal geometry in solution and in solid state (X-ray structure of $IrTp^{Me_2}(C_2H_4)(PPhMe_2)$ presented for the analogous Tp compounds see [106]). Dmpe ($dmpe = Me_2PCH_2CH_2PMe_2$) reacts with two equivalents of $IrTp^{Me_2}(C_2H_4)_2$ to give the binuclear species $[IrTp^{Me_2}(C_2H_4)]_2$(dmpe), in which the diphosphine ligand bridges the two equivalent metallic centers [107]. With CO as the nucleophile the related $IrTp^{Me_2}(C_2H_4)(CO)$ (the same reactivity was observed for $IrTp(C_2H_4)_2$ and NMR studies concerning the orientation of the ethene ligand as well as protonation reactions of $IrTp(C_2H_4)_2$ and $IrTp(C_2H_4)(CO)$ were undertaken [108]) is initially formed to finally produce $IrTp^{Me_2}(CO)(COOH)H$ [107]. Harder N-donors like MeCN or pyridine react differently and give Ir(III) ethyl-vinyl adducts (Scheme 11, top-right) [122].

The analogous Tp-compound, $IrTp(PPh_3)(C_2H_4)$ gives equilibrium mixtures with the pyrazolyl cyclometalated $Ir(\kappa^3(N,N,C^5_{pz})Tp)H(PPh_3)_2$, when reacted with PPh_3 [109]. The latter reaction is thought to proceed via an $IrTp(PPh_3)_2$ intermediate, which is eventually converted to $Ir(\kappa^3(N,N,C^5_{pz})Tp)H(PPh_3)_2$. This report shows, once again, the strong tendency of the IrTp system to activate sp^2 C–H bonds, even in the absence of olefins.

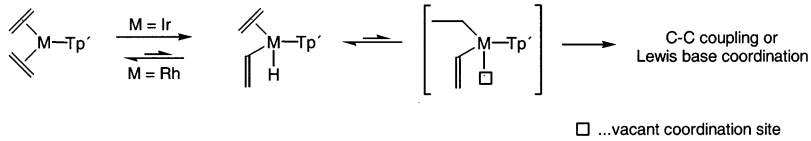
Complexes $IrTp^{Me_2}(C_2H_4)(PR_3)$ rearrange upon heating to $IrTp^{Me_2}(C_2H_3)H(PR_3)$ (X-ray structure for $IrTp^{Me_2}(C_2H_3)H(PPhMe_2)$ available) (Scheme 11, left path), with the conversion of the $PPhMe_2$ compound being about one order of magnitude slower compared with $IrTp^{Me_2}(C_2H_4)(PMe_3)$. The same thermal activation of $IrTp(C_2H_4)(PR_3)$ gives no clean product [107]. The protonation reaction of $IrTp^{Me_2}(C_2H_3)H(PMe_3)$ with $[H(OEt_2)_2][BAr_4]$ (Ar = 3,5 bis(trifluoromethyl)benzene) has been studied and shown to proceed via a cationic hydride



Scheme 11.



Scheme 12.



Scheme 13.

ethylidene complex $[IrTp^{Me_2}(H)(=CHMe)(PMe_3)]^+$ resulting from protonation at the alkenyl β-carbon to give finally $[IrTp^{Me_2}H(C_2H_4)(PMe_3)]^+$ (Scheme 12) [110].

In its reaction with soft donor ligands, $RhTp^{Me_2}(C_2H_4)_2$ also undergoes in the initial step substitution of one ethene resulting in compounds $RhTp^{Me_2}(C_2H_4)(L)$ (L = CO, PMe_3, ^{t}BuNC). With harder donor ligands (L′ = MeCN, pyridine) the reaction proceeds to the Rh(III) complexes $RhTp^{Me_2}(C_2H_3)(C_2H_5)(L')$, which upon heating can finally be converted to $RhTp^{Me_2}(C_2H_4)(L')$. Furthermore, $RhTp^{Me_2}(C_2H_3)(C_2H_5)$(MeCN) reacts in benzene to give $RhTp^{Me_2}(Ph)(C_2H_5)$-(MeCN) [49,111,112]. Similar reactions with the dihydrobis(3,5-dimethylpyrazolyl)-borate (Bp^{Me_2}) complex $RhBp^{Me_2}(C_2H_4)_2$ were also investigated [113]. It thus appears that MTp′(olefin)$_2$ compounds are able to transform into their M(III) hydride-vinylisomers (e.g. MTp′$(CH{=}CH_2)H(C_2H_4)$) as shown in Scheme 13. For Ir, the latter are thermodynamically favored and may be trapped by a donor (e.g. MeCN, cyclic ethers, vide infra) or undergo C–C coupling to finally give their hydride-allyl isomers [104]. As for the rhodium analogs, they may also be trapped by Lewis bases ($RhTp^{Me_2}(CH{=}CH_2)(C_2H_5)$(MeCN) [110]) but under thermodynamic control they convert back into Rh(I) adducts.

6.2. Vinyl hydride complexes in C–H activation reactions

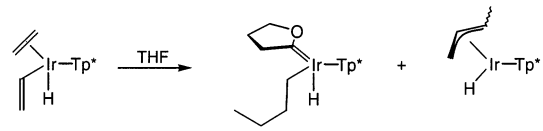
The thermal activation of benzene, thiophene, acetonitrile and cyclic ethers with $IrTp^{Me_2}(C_2H_3)H(C_2H_4)$ proceeds via the unsaturated key intermediate of Scheme 13 (which may be stabilized by an agostic ethyl interaction). THF and other cyclic ethers undergo with $IrTp^{Me_2}(C_2H_3)H(C_2H_4)$ a double C–H activation to yield $IrTp^{Me_2}(C_4H_9)$(1-oxocyclopent-2-ylidene)H. Inefficient trapping by the cyclic ether of the active $IrTp^{Me_2}(C_2H_3)(C_2H_5)$ intermediate is responsible for a side reaction that gives $IrTp^{Me_2}(\eta^3\text{-}C_4H_7)H$ (Scheme 14) [114].

A detailed mechanistic study concerning this reaction, an X-ray structure determination on $IrTp^{Me_2}(C_4H_9)$(1-oxocyclopent-2-ylidene)H, as well as the mechanistic elaboration of the related benzene activation process was published in 1998 [115]. The latter reaction was briefly communicated before [116]. $IrTp^{Me_2}(C_2H_3)H(C_2H_4)$

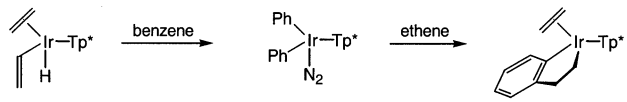
reacts in benzene at 60°C to give a mixture of $IrTp^{Me_2}(Ph)_2(\kappa^1\text{-}N_2)$ and $[(IrTp^{Me_2}(Ph)_2]_2(\mu^2\text{-}N_2)$ (X-ray structure published). Nitrogen from the inert-gas used replaces the ethene from $IrTp^{Me_2}(Ph)_2(\eta^2\text{-}C_2H_4)$. If additional ethene is present the insertion product $IrTp^{Me_2}(\kappa^2(C^{et},C^{Ph2})\text{-ethylbenzene})(C_2H_4)$ is formed instead of $IrTp^{Me_2}(Ph)_2(\kappa^1\text{-}N_2)$ (Scheme 15). In $IrTp^{Me_2}(Ph)_2(\kappa^1\text{-}N_2)$ the dinitrogen ligand can be replaced by PMe_3, CO, ^{t}BuNC, and, upon hydrogenation, $IrTp^{Me_2}H_4$ forms. Heating $IrTp^{Me_2}(Ph)_2(\kappa^1\text{-}N_2)$ in THF produces cleanly $IrTp^{Me_2}$(Ph)(1-oxocyclopent-2-ylidene)H.

Heating $IrTp^{Me_2}(C_2H_4)_2$ in neat thiophene results in $IrTp^{Me_2}$(2-thienyl)$_2(\kappa^1$(S)-thiophene), in which the sulfur-bonded thiophene can be replaced by PMe_3 or CO. Hydrogenation forms $IrTp^{Me_2}(\kappa^1$(S)-thiophene)H_2. When $IrTp^{Me_2}(\kappa^1$(S)-thiophene)H_2 is heated in C_6H_{12} in the absence of H_2 it is converted to a mixture of hydride products in which the hydride-thienyl bridged binuclear species $[(\mu^2\text{-H}, \mu^2(S,C^1)\text{-thienyl})(IrTp^{Me_2}H)_2]$ (40% yield; X-ray structure available) is the major component (Scheme 16) [117]. The full paper on this topic includes the reaction with substituted thiophenes (2-methylthiophene and 3-methylthiophene), the reaction of $IrTp^{Me_2}$(2,3-dimethylbutadiene) with these thiophenes, and a detailed mechanistic discussion of the activation and hydrogenation reactions [118].

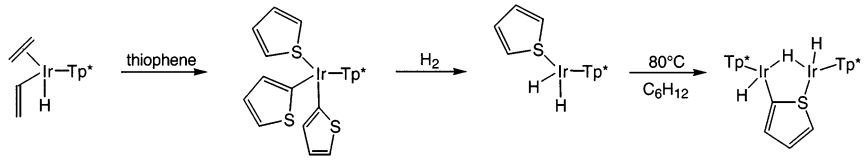
The rhodium analog, $RhTp^{Me_2}(C_2H_4)(PMe_3)$, experiences both C–H and C–S activation in different amounts depending upon the reaction conditions. Thermally, the heterorhodacycle derived from C–S rupture $RhTp^{Me_2}(\kappa^2(S,C^4)\text{-thiobutadienolate})(PMe_3)$ is the minor product and $RhTp^{Me_2}$(2-thienyl)H(PMe_3) the favored compound, but the distribution is reversed under photochemical conditions (Scheme 17) [112,119]. This result contrasts with that of the $RhCp^*PMe_3$-system,



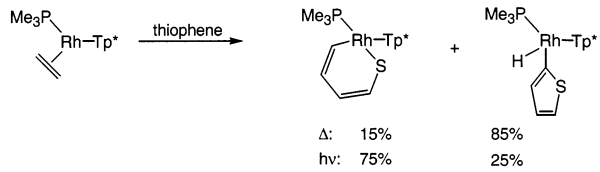
Scheme 14.



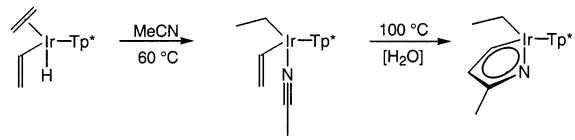
Scheme 15.



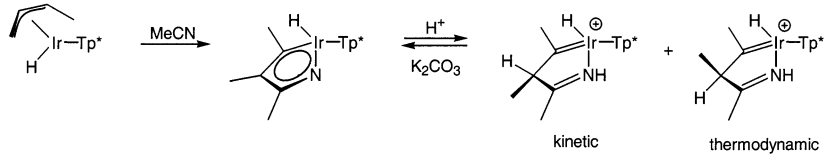
Scheme 16.



Scheme 17.



Scheme 18.



Scheme 19.

where the C–S oxidative addition products are preferred under thermal conditions [120,121]. Once obtained, the ratio of the products can be modified to some extent, by irradiation or heating, respectively.

If acetonitrile is reacted (60°C) with either $IrTp^{Me_2}(C_2H_4)_2$ or $IrTp^{Me_2}(C_2H_3)H(C_2H_4)$, the Ir(III) compound $IrTp^{Me_2}(C_2H_3)(C_2H_5)(MeCN)$ is initially formed. At higher temperatures and in the presence of catalytic amounts of water intramolecular coupling of the ethenyl and the acetonitrile ligands occurs to give a delocalized, five membered iridapyrrole ring (Scheme 18). The reaction was extended to other olefinic substrates [122].

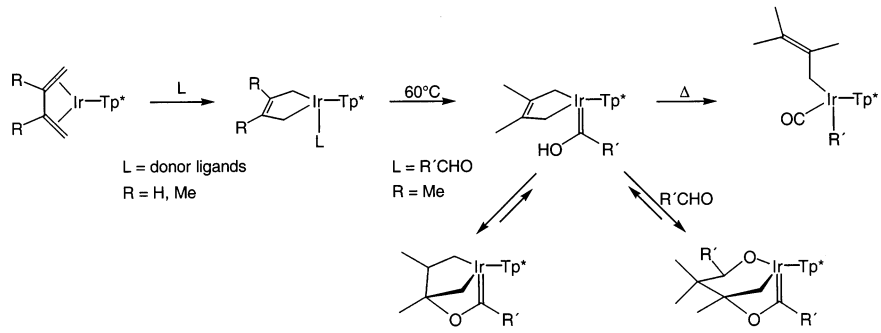
Hydride-η^3-allyl derivatives like $IrTp^{Me_2}$(syn-η^3-butenyl)H also transform by heating in MeCN to give related structures, albeit with a hydride, instead of the ethyl group, attached to iridium. The iridapyrrole ring of these compound exhibits significant alkenyl character at the hydrocarbyl terminus and may therefore be protonated at the β carbon. In this way, treatment of the iridapyrrole derivative of Scheme 19 with $[H(OEt_2)_2][BAr_4]$ allows the isolation of the two possible diastereomeres of the cationic hydride-alkylidene Ir(III) complex (the kinetic product was characterized by X-ray crystallography). As expected in view of the parallel orientation of the Ir–H bond with respect to the pπ orbital of the carbene carbon, hydride migration is extremely facile. However, in the absence of a donor solvent (e.g. MeCN) it is unproductive and the hydride-alkylidene is the only detectable structure. Clearly, β-H elimination is hindered due to the absence of H

atoms sufficiently close to the vacant coordination site created by the migration [123].

Very recently, the reactivity of $IrTp^{Me_2}(\eta^4$-2,3-dimethylbutadiene) with aldehydes (benzaldehyde, 4-methoxybenzaldehyde, 4-dimethylaminobenzaldehyde, crotonaldehyde, acetaldehyde) was examined. The reaction gives first the aldehyde adduct $IrTp^{Me_2}(\sigma(1,4)$-2,3-dimethylbut-2-endiyl)$(\kappa^1$(O)-RCHO), which then undergoes an unusual transformation to the corresponding hydroxycarbene derivative $IrTp^{Me_2}(\sigma(1,4)$-2,3-dimethylbut-2-endiyl)(=C(OH)R). When R = aryl groups, the latter type of product reacts further with ArCHO to yield cyclic alkoxycarbene structures which finally render the decarbonylation products $IrTp^{Me_2}$(R)(σ-2,3-dimethylbut-2-enyl)(CO) (Scheme 20) [124].

The first step, namely the formation of an Ir(III) adduct, appears to be general when $IrTp^{Me_2}(\eta^4$-diene) (η^4-diene = 2,3-dimethylbutadiene, 2-methylbutadiene, butadiene) react with different donor ligands L (L = CO, PMe_3, MeCN, pyridine, tetrahydrothiophene (THT), ethene). A series of competition and exchange experiments, carried out both under kinetic and thermodynamic control has allowed to establish the order of reactivity of the Lewis bases and that of stability of the Lewis base adducts [125]. The X-ray structure of $IrTp^{Me_2}(\sigma(1,4)$-2-butendiyl)(PMe_3) has been determined.

Very recently, Bergman et al. published a communication dealing with C–H activation reactions of $IrTp^{Me_2}$(Me)(PMe_3)(κ^1-N_2) (note added in proof) [126].



Scheme 20.

7. Hydride compounds

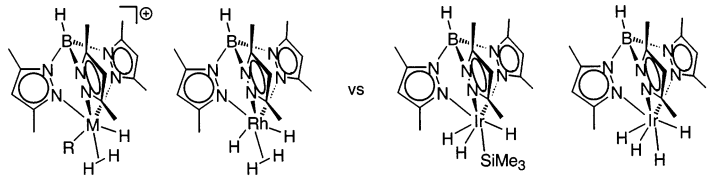
The iridium compound $IrTp^{Me_2}$(COD) reacts with H_2 under high-pressure conditions. Thus exposure of $IrTp^{Me_2}$(COD) to 500 atm of H_2 for 75 h produces $IrTp^{Me_2}H_2$(coe), whereas under somewhat milder conditions (200 atm H_2 for 28 h) $IrTp^{Me_2}H_2(\eta^2$-COD) is obtained. An X-ray diffraction study of the former complex shows that the C=C fragment roughly bisects the angle defined by the H–Ir–H moiety, an observation that has been extensively discussed and rationalized on the

basis of extended Hückel calculations [127]. Photolysis of $IrTp^{Me_2}H_2$(coe) in benzene and in the presence of $P(OMe)_3$ gives $IrTp^{Me_2}(Ph)H(P(OMe)_3)$. However, using Et_2O as the solvent the dihydride $IrTp^{Me_2}H_2(P(OMe)_3)$ is obtained, although if 'butyl acrylate is employed instead of $P(OMe)_3$, $IrTp^{Me_2}H_2(H_2C{=}CHCOOBu^t)$ readily forms. The above reactions proceed in all cases through the five-coordinate $IrTp^{Me_2}H_2$ as the primary photoproduct, as shown by several deuteration studies [128].

Dihydrides of the general formula $MTp'H_2(L)$ ($Tp' = Tp^{Me_2}$; M = Ir; $L = PMe_3$, PMe_2Ph, dmpe, CO; Tp' = Tp; M = Ir; $L = PMe_2Ph$) [107], (Tp' = Tp; M = Ir, Rh; $L = PPh_3$, PCy_3) [105], (Tp' = Tp or Tp^{Me2}; M = Rh; $L = PMe_3$, PEt_3, PMe_2Ph) [49] have been prepared by hydrogenation of $MTp'L(\eta^2$-ethene) under mild conditions in good yields. Kinetic studies carried out by Heinekey and co-workers [106] on the iridium system showed that the H_2 addition reaction proceeds by rapid reversible dissociation of a pyrazolyl arm, through a square-planar $Ir(\kappa^2$-Tp)$L(\eta^2$-ethene) intermediate.

Polyhydrides complexes of the general formula ML_mH_n ($n \geq 3$), can be formulated in some instances as $ML_m(H_2)H_{n-2}$ [129]. Compounds with the latter formulation show short T_1 (spin-lattice relaxation time) values and exhibit significant J_{HD} couplings in the ^{1}H-NMR spectrum upon partial deuteration. In this context, a $M(H_2)H$ formulation has been proposed for the complex $[IrTp(PMe_3)(H_2)H]BF_4$ on the basis of T_1 measurements of 21 ms at 182 K, and of unusual temperature dependent isotopic perturbation of resonance (IPR) and isotopic perturbation of coupling (IPC) effects. These phenomena were explained in terms of the preference of deuterium to occupy the terminal hydride site over a dihydrogen ligand site in this complex [130]. Note that the analogous Cp- or Cp*-compounds have to be formulated as trihydride complexes [131]. A comprehensive discussion of these observations and a general method to synthesize the cationic complexes $[MTp'(PR_3)(H_2)H]X$ (M = Ir, Rh; R = Me, Ph; $X = BF_4^-$, BArF$^-$) by protonation of $MTp'(PR_3)H_2$ can be found in a subsequent publication [132] (Scheme 21).

Treatment of $[PPh_4][RhTp^{Me_2}Cl_3]$ with $NaBH_4$ in MeOH results in virtually complete conversion to $RhTp^{Me_2}(H_2)H_2$, reported [133] as the first non-classical polyhydride compound stabilized by N-donor ligands. Its characteristic relaxation time T_1 has a minimum value of 42 ms at 166 K, thus supporting the $Rh(H_2)$ formulation. NMR studies on the deuterium-labeled complex indicate that the $Rh(HD)H_2$ structure is thermodynamically more stable then $Rh(H_2)(H)(D)$. Since the molecule is highly fluxional the measured J(H, D) of 4.7 Hz is an average that results from the dynamic exchange of H and D between the H_2 molecule and the two hydride ligands [134]. The barrier for the rotation of the H–H ligand (0.56(2) kcal mol^{-1}) and the H–H separation of 0.94 Å, both determined by means of inelastic neutron scattering spectroscopy, indicate weak π-back donation from Rh to H_2 and/or a significant interaction between the H_2 and the *cis*-H ligands [135]. A theoretical study by means of DFT methods justifies the structures $TpRh(H_2)H_2$ and $CpRhH_4$ adopted by the respective compounds and attribute the difference in behavior between Tp and Cp to the stronger electron-donor character of the latter when compared with the former, and to the tendency of Tp to impose a near octahedral coordination [136].



Scheme 21.

Interestingly, the analogous iridium compound $IrTp^{Me_2}H_4$, obtained from $IrTp^{Me_2}(C_2H_4)_2$ and H_2 (2 atm, 90°C, 3 days) has a classical, highly fluxional, tetrahydride structure and displays a very unusual IPR effect explained on the basis of the existence of two kinds of Ir–H bonds (a C_{3v} ground-state structure is proposed in which a unique hydride caps the face defined by the other hydrides in a distorted octahedral structure). A T_1 (min) of ca. 400 ms clearly stands in favor of the Ir(V) polyhydride structure. This compound not only shows a remarkable variation of δ_H upon deuteration but moreover exhibits an estimated coupling of 4.7 Hz between the two hydride sites [137]. The related compound $IrTp^{Me_2}H_3(SiEt_3)$ shows no IPR effect upon deuteration and exhibits a similar C_{3v} geometry in which the $SiEt_3$ group acts as the capping ligand of the hydrides face in the distorted octahedral geometry of the $Ir(V)Tp^{Me_2}(H)_3$ entity. This assumption was supported by X-ray studies [138].

8. Catalysis

The published applications of Group 9 Tp′ compounds in catalysis involve the complexes RhTp′(COD) ($Tp' = Tp^{Me_2}$, $Tp^{(CF_3)_2}$, Tp^{iPr_2}) as catalysts for the stereoregular polymerization of *para*-substituted phenylacetylenes (*p*-R-C_6H_4–C≡CH; R = H, Me, Cl, CN, COOMe, COMe, NO_2) with $M_n > 10^4$ and $M_w/M_n \approx 2$. Reaction conditions employed were 1:100 catalyst to substrate ratio, in CH_2Cl_2 as the solvent at 40°C. $RhTp^{iPr_2}(COD)$ was found to be the superior catalyst, presumably due to the highest tendency to form the κ^2-isomer. *Ortho*-substituted phenylacetylenes and non-aromatic terminal alkynes do not react under the reaction conditions mentioned [139].

Another catalysis was realized using amongst others RhTp(COD) for the regioselective homogeneous hydrogenation of quinoline [140].

Preliminary studies carried out in this laboratory show that $RhTp^{Me_2}(C_2H_4)(PEt_3)$ catalyzes the dimerization of terminal alkynes [141].

$IrTp(C_2H_4)_2$ has been proven to be ineffective as a catalyst for hydrosilylation of alkynes [142]. On the contrary, $RhTp^{Me_2}(C_2H_4)_2$ is active for the catalytic hydrosylilation of ethylene [141].

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