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Hydridotris(pyrazolyl)borate ruthenium complexes—properties and applications

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Contents

Abstract

This review deals with ruthenium complexes of the hydrotris(pyrazolyl)borate (Tp) ligand and derivatives thereof. The period covered is from 1993 to 1998 (along with a few earlier references) including more than 40 new references, the majority of which have been published in the last 3 years. Among the co-ligands are hydride, dihydrogen, dinitrogen, CO, phosphines and amines. Particular emphasis is on complexes containing metal–carbon single and

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double bonds. Noteworthy is the synthesis of highly reactive vinylidene complexes and their involvement in stoichiometric C–C coupling reactions with activated alkanes and olefines. Most recent developments include the application of RuTp complexes in catalytic transformations of organic molecules, such as the dimerization and polymerization of acetylenes, and the hydrogenation of ketones.

Keywords: Ruthenium; Hydrotris(pyrazolyl)borate; Coordination chemistry; Catalysis; C–C coupling

1. Introduction

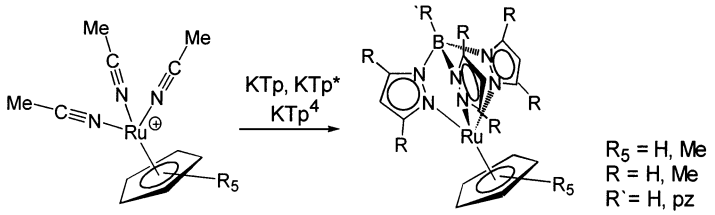
The tris(pyrazolylborate) anion (Tp) as a ligand in transition metal complexes has been introduced by Trofimenko in 1966 [1]. Since then, Tp and its derivatives, such as Tp* (hydrotris(3,5-dimethylpyrazolyl)borate) and Tp^4 (tetrapyrazolylborate), have found increasing applications in coordination chemistry with most of the metals. Work on ruthenium, however, has dramatically accelerated only in the last few years. While in the most recent review [2], covering the time until early 1993, only nine references dealing with RuTp chemistry were cited. The present review covering the period from 1993 to 1998 (along with a few earlier references) includes more than 40 new references, of which the majority have been published in the last 3 years.

Tp is often compared with Cp (cyclopentadienyl) and Cp* (the pentamethyl derivative) due to the same charge and number of electrons donated (6 e donors). Notwithstanding, differences in size and electronic properties are obvious. Thus, the cone angle of Tp close to 180° is well above the 100° and 146° calculated for Cp and Cp*, respectively. The steric bulk of the Tp ligand appears to disfavor higher coordination numbers of the metal center. Note, in addition, the differences in symmetry. Thus, the $[RuTp]^+$ fragment is strongly hybridized biased to bind preferentially three additional ligands for an octahedral six-coordinate structure to be obtained and maintained. Complexes of Cp, in contrast, are capable of forming seven-coordinated species.

2. Coordination chemistry

2.1. Metallocene analogs

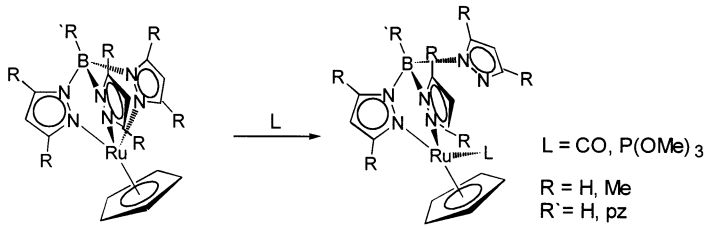
One of the first ruthenium compounds containing the Tp ligand was RuCpTp. This complex was synthesized by Singleton et al. [3,4] by treating RuCp(COD)Cl (COD = 1,5-cycloctadiene) with 1.1 equivalents of NaTp in boiling ethanol. Shortly afterwards, Mann et al. [5] published a more general route to Cp and Cp* compounds of the RuTp fragment by reacting $[RuCp(MeCN)_3]PF_6$ or $[RuCp^*(MeCN)_3]PF_6]$ with KTp, KTp* or KTp^4, in acetonitrile (Scheme 1). The X-ray structure of RuCpTp shows mean Ru–C and Ru–N bond distances of 2.153(3) and 2.128(3) Å, respectively. Electrochemical measurements were carried



Scheme 1.

out with RuCpTp and its derivatives and were compared with ferrocene and ruthenocene. These compounds exhibit a quasi-reversible one-electron oxidation in the range of 0.145–0.463 V vs. Ag/AgCl. Oxidation of RuCpTp* with $AgPF_6$ allowed the isolation of the corresponding Ru(III) species. Furthermore, strongly π-accepting ligands such as CO and $P(OMe)_3$ were found to react with RuCpTp* and $RuCpTp^4$ yielding complexes of the type $RuCp(\kappa^2\text{-Tp})CO$ and $RuCp(\kappa^2\text{-Tp}^4)CO$, featuring κ^2-bonded Tp* and Tp^4 ligands (Scheme 2). It should be mentioned that the synthesis of RuCp*Tp* failed.

Lalor et al. [6] and Ferguson et al. [7,8] reported the synthesis and the X-ray crystal structures of $[RuTp(\eta^6\text{-benzene})]PF_6$ and $[RuTp^4(\eta^6\text{-benzene})]PF_6]$ (mean Ru–C and Ru–N distances in both structures are 2.20(2) and 2.107(15) Å, respectively) by reacting the dimeric species $[RuCl_2(\eta^6\text{-benzene})]_2$ with KTp or KTp^4 in boiling methanol. Whereas Lalor just noted the benzene ligands to be susceptible towards nucleophilic attack, Tocher et al. systematically investigated the reaction of these compounds with nucleophiles Nuc ($Nuc = H^-, D^-, OH^-, CN^-$) [9]. All the conversions are smooth giving neutral η^5-cyclohexadienyl compounds of the formula $RuTp(\eta^5\text{-}C_6H_6Nuc)$. The X-ray structure of $RuTp(\eta^5\text{-}C_6H_6CN)$ confirms that the incoming nucleophile has added in an *exo* fashion. The same group extended this investigation to the related arene ligands *p*-xylene, mesitylene, hexamethylbenzene, *p*-cymene (X-ray structure included), and 1,2,4,5-tetramethylbenzene [10]. Also $[RuTp^*(\eta^6\text{-benzene})]PF_6$ was synthesized [11]. Tocher et al. found that $Ru(\eta^6\text{-arene})(MeCN)Cl_2$ reacts with KTp in CH_2Cl_2 without cleavage of the second Ru–Cl bond to give complexes of the type $Ru(\kappa^2\text{-Tp})(\eta^6\text{arene})Cl$. Crystal structures of some of the complexes are available. Finally, Sheldrick et al. [12] prepared the complex $[RuTp([9]aneS_3)]^+$, a formal analog of $[RuTp(arene)]^+$, by treatment of $[Ru([9]aneS_3)(MeCN)_3]^{2+}$ with KTp.



Scheme 2.

The complexes $RuTp_2$, $RuTpTp^4$ and $RuTp^4_2$ could be prepared from $Ru(MeCN)_4Cl_2$ and the corresponding TlTp compounds in CH_2Cl_2 [13,14]. $RuTp_2$ and $RuTp^4_2$ showed reversible dichlorine uptake

$$[RuTp_2]_{(solid)} + 0.5Cl_{2\,(gas)} \leftrightarrow [RuTp_2]Cl_{(solid)} \quad (1)$$

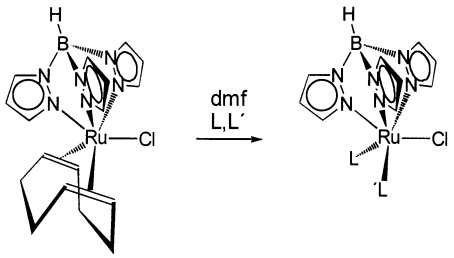
and release cycles in the solid state, with their one-electron [Ru(III)]/[Ru(II)] redox couples (Eq. (1)). The formation of a ground state charge-transfer species was also observed for these complexes with some halocarbon solvents [15].

2.2. Precursor compounds

Onishi et al. [14] developed the synthesis of $RuTp(NCPh)_2Cl$ and $RuTp^4(NCPh)_2Cl$ and reported on their substitution chemistry resulting in $RuTp^4(4\text{-Me-py})_2Cl$, $RuTp^4(NCPh)(2,4\text{-dimethylpyridine})Cl$, $RuTp^4(PEt_3)_2Cl$, $RuTp^4(PPh_3)(NCPh)Cl$, $RuTp^4(MeCN)_2Cl$, $[RuTp^4(MeCN)_3]^+$ and $[RuTp^4(CO)_3]^+$ in low to moderate yields.

According to Jalón et al. [16] $RuTp(tht)_2Cl$ (tht = tetrahydrothiophene) can be synthesized by reacting $Ru(tht)_4Cl_2$ with KTp. As a by-product (17%), the complex $Ru(\kappa^2\text{-Tp})(tht)_2$ was formed. In the presence of excess KTp, $RuTp(tht)_2Cl$ is converted to $RuTp_2$. In the same article, two synthetic routes to obtain RuTp(-COD)Cl have been described. The COD polymer $[Ru(COD)Cl_2]_n$ reacts with KTp to give directly RuTp(COD)Cl, while the Ru(bpzm)(COD)(H)Cl (bpzm = bis(pyrazolyl)methane) reacts with KTp to yield initially RuTp(COD)H, which then transforms into RuTp(COD)Cl on treatment with chlorinated solvents. RuTp(COD)Cl was originally prepared by Singleton et al. [17] several years ago by the reaction $Ru(COD)(NH_2NMe_2)_3H]PF_6$ with KTp via the hydrido complex RuTp(COD)H. It has been found that RuTp(COD)Cl is a valuable precursor for a series of RuTp complexes. It should be mentioned, however, that the COD is substitutionally inert in this complex, in contrast to the analogous complexes RuCp(COD)Cl and RuCp*(COD)Cl [18], requiring vigorous conditions to be applied. Thus, in boiling DMF, RuTp(COD)Cl converts with L or L_2 (mono- and bidentate *N* and *P* donor ligands) to $RuTp(L_2)X$ and $RuTp(L)_2X$ [19]. This is a convenient and general synthetic route provided the ligands L and L_2 are stable under this condition. The substitution products so obtained are listed in Table 1. If one equivalent of a tertiary phosphine PR_3 is employed, the second vacant coordination sphere is occupied by a DMF molecule forming compounds of the general formula $RuTp(PR_3)(DMF)Cl$. The DMF molecule is easily replaced by other monodentate ligands yielding $RuTp(PPh_3)(L)Cl$ (L = PPh_3, pyridine, CH_3CN) [24]. The chloride ligand in RuTp(COD)Cl is also readily replaceable in the presence of KX (X = Br^-, I^-, CN^-) to give the corresponding RuTp(COD)X complexes [25]. Chloride abstraction by means of $AgCF_3SO_3$, $TlCF_3SO_3$ or $NaBPh_4$ in a coordinating solvent, leads to the formation of cationic $[RuTp(COD)(solvent)]^+$ (solvent = DMSO, pyridine, CH_3CN, H_2O) complexes. In the non-coordinating solvent CH_2Cl_2, the aquo complex $[RuTp(COD)(H_2O)]^+$ has been formed in 96% yield with the water molecule stemming from the residual water in the CH_2Cl_2 solution,

Table 1
Some RuTp complexes obtained by the reaction of RuTp(COD)Cl with L in boiling DMF



Ligand (L or L_2)	Complex	Reference	Yield (%)
dppm[a]	RuTp(dppm)Cl	[19]	84
tmeda[b]	RuTp(tmeda)Cl	[19]	85
pyridine	$RuTp(py)_2Cl$	[19]	95
dmso	$RuTp(dmso)_2Cl$	[21]	81
3-Mepy	$RuTp(3\text{-}Mepy)_2Cl$	[19]	87
pn[c]	RuTp(pn)Cl	[19]	92
pnEt[d]	RuTp(pnEt)Cl	[22]	89
pnPr[e]	RuTp(pnPr)(dmf)Cl	[22]	61
PPh_3	$RuTp(PPh_3)_2Cl$	[25]	94
PPh_3	$RuTp(PPh_3)(dmf)Cl$	[23]	89
Pbu_3^n	$RuTp(Pbu_3^n)_2Cl$	[24]	44
$P(OPh)_3$	$RuTp(P(OPh)_3)_2Cl$	[25]	85
$AsPh_3$	$RuTp(AsPh_3)_2Cl$	[25]	82
po[f]	RuTp(po)Cl	[25]	78
PCy_3	$RuTp(Pcy_3)(dmf)Cl$	[26]	ni[g]
Acpy[h]	RuTp(Acpy)Cl	[27]	97
4-MeAcpy[i]	RuTp(4-MeAcpy)Cl	[27]	90
N-Et-4-MeAcpy[j]	RuTp(*N*-Et-4-MeAcpy)Cl	[27]	89
Phschiff[k]	RuTp(Phschiff)Cl	[28]	59
$Ph–CH{=}NCH_2CH_2Nme_2$[l]	$RuTp(Ph–CH{=}NCH_2CH_2NMe_2)Cl$	[25]	86
Spy[m]	$[RuTp(\kappa^2(N,S),\mu^2(S)\text{-}Spy)]_2$	[28]	59
acac[n]	$[RuTp(acac)Cl]^-$	[28]	ni[g]

[a] Bisdiphenylphosphinomethan.
[b] Tetramethylaminoethylendiamin.
[c] *N*,*N*-dimethyl-2-diphenylphosphinoethanamine.
[d] *N*,*N*-diethyl-2-diphenylphosphinoethanamine.
[e] *N*,*N*-diisopropyl-2-diphenylphosphinoethanamine.
[f] Methyl-2-diphenylphosphinoethylether.
[g] Not isolated.
[h] *N*-acetyl-2-aminopyridine.
[i] *N*-acetyl-4-methylaminopyridine.
[j] *N*-acetyl-*N*-ethyl-4-methylaminopyridine.
[k] *N*,*N*′-bis-(phenylmethylene)-1,2-ethane-diamine.
[l] *N*-dimethyl-*N*′-phenylmethyleneethanediamine.
[m] 2-Thiopyridine.
[n] Acetylacetonate.

despite rigorous drying. Also, a tetranuclear Ru(IV) aquo species has been reported [20]. From RuTp(COD)Cl, also the neutral complexes RuTp(η^4-diene)Cl (diene = butadiene, isoprene, 2,4-hexadiene) can be obtained [29], where the diene ligand is coordinated in *s-trans* fashion as proven by X-ray crystallography. In the synthesis, RuTp(COD)Cl is heated in xylene in the presence of air. The dark-green paramagnetic (i.e. trivalent) complex, tentatively formulated as $[RuTp(Cl)]_x$ thus obtained is redissolved in MeOH. Upon addition of Zn in the presence of the diene, RuTp(η^4-diene)Cl is formed.

2.3. Amine and phosphine complexes

RuTp complexes containing aliphatic amines as co-ligands are rare. Above all, RuTp(tmeda)Cl should be mentioned [28]. Chloride abstraction with $NaBPh_4$ or $NaPF_6$ in the presence of L (L = acetone, DMF, CH_3CN, HC≡CPh, HC≡CSiMe$_3$) led to the formation of the cationic complexes $[RuTp(tmeda)(L)]^+$ (L = acetone, DMF, MeCN, =C=CHPh, =C=CHSiMe$_3$) [30]. X-ray crystal structures of $[RuTp(tmeda)(L)]^+$ with L = acetone, DMF and =C=CHPh are available. Concerning the molecular structure, extended Hückel molecular orbital calculations point to a practically regular square pyramid (C_{4c}) held together by mainly σ bonds without any significant participation of the d_π atomic orbitals (AOs) (d_{xy}, d_{xz}, d_{yz}) of the ruthenium for the $[RuTp(tmeda)]^+$ fragment. This fragment has a high affinity to coordinate a sixth ligand because of the highly localized and directed d_{z^2} AO.

Similarly, the coordination chemistry of RuTp(pn)Cl has been studied [31]. Complexes $[RuTp(pn)(L)]^+$ (L = H_2O, acetone, CH_3CN, N_2, CO, =C=CHPh) were prepared and structurally characterized. Attempts to prepare a coordinatively unsaturated compound were unsuccessful. If halide abstraction is performed under a N_2 atmosphere, $[RuTp(pn)(N_2)]^+$ is obtained with the dinitrogen ligand coordinated in an end-on fashion. This is the first RuTp complex of N_2.

The most prominent RuTp complex with tertiary phosphines is $RuTp(PPh_3)_2Cl$ prepared by Hill et al. [32] from $Ru(PPh_3)_3Cl_2$ and KTp in 90% yield. The X-ray structure of this compound is reported. The reactivity of $RuTp(PPh_3)_2Cl$ towards $[Me_4N]^+[B_3H_8]^-$ was investigated giving $RuTp(B_3H_8)(PPh_3)$ [33]. $RuTp(PPh_3)_2Cl$ is a valuable precursor for complexes of the types $RuTp(PPh_3)(L)Cl$ and $[RuTp(PPh_3)(L)(L')]^+$, as shown by Jia et al. [34,51] and our group [23,35]. The synthesis of the following complexes is described: $RuTp(PPh_3)(L)Cl$ (L = pyridine, =C=CHPh, CO, PMe_3) [23,35], $RuTp(PPh_3)(L)X$ (L = CH_3CN, X = Cl; L = CH_3CN, X = H) [34,51]. Furthermore, $RuTp(PPh_3)_2Cl$ was treated with $NaBH_4$ to yield $RuTp(PPh_3)_2H$. Upon protonation conversion to the cationic dihydrogen complex $[RuTp(PPh_3)_2(H_2)]^+$ takes place. The dihydrogen ligand is labile and is readily displaced by L = CH_3CN, H_2O and N_2. This process is reversible when $[RuTp(PPh_3)_2(L)]^+$ is pressurized with H_2 [34]. Similar reactions were studied by Jia using $[RuTp(dppe)(H_2)]^+$, $[RuTp(PPh_3)(CO)(H_2)]^+$, and $[RuTp(PPh_3)(MeCN)(H_2)]^+$ and comparisons with other co-ligands such as Cp and 1,4,7-triazacyclononane were undertaken [36].

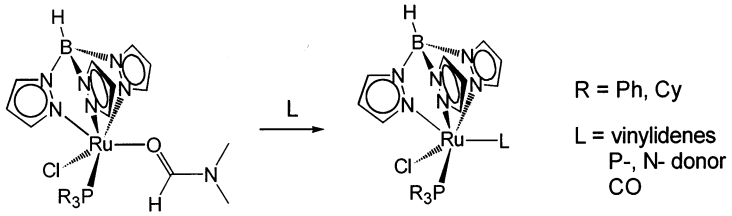
Tenorio et al. [37] reacted $RuTp(PPh_3)_2Cl$ with dippe (dippe = 1,2-bis(diisopropylphosphino)ethane) and isolated RuTp(dippe)Cl in 55% yield. Upon chloride abstraction in the presence of L (L = CO, $CNBu^t$, acetone, THF, N_2) the corresponding cationic $[RuTp(dippe)L]^+$ complexes are formed. The paramagnetic compound $[RuTp(dippe)(OMe)]^+$ has been obtained by treating $[RuTp(dippe)(H_2)]^+$ with methanol. A similar reaction was reported by us. Reacting RuTp(COD)Cl with PCy_3 in boiling DMF yields $RuTp(PCy_3)(DMF)Cl$, which readily reacts with $HOCH_2R$ (R = H, CH_3) to give the paramagnetic complex $RuTp(PCy_3)(OCH_2R)Cl$ ($\mu_{eff} = 1.83\mu_B$ at 295 K) in moderate to good yield [26]. $RuTp(PCy_3)(OCH_3)Cl$ has been characterized by X-ray crystallography. Both complexes react with $L = CH_3CN$, pyridine, CO, $P(OMe)_3$ and PMe_3 to afford the (diamagnetic) Ru(II) compounds $RuTp(PCy_3)(L)Cl$ according to Eq. (2).

$$2RuTp(PCy_3)(OCH_2CH_3)Cl + 2L \rightarrow 2RuTp(PCy_3)(L)Cl + H_3C\text{–}CHO + EtOH \quad (2)$$

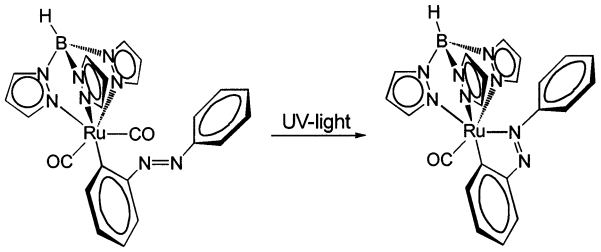
With terminal alkynes HC≡CR (R = Ph, COOEt, Bu^n, $SiMe_3$) neutral vinylidene complexes $RuTp(PCy_3)(=C=CHR)Cl$ are formed. $RuTp(PPh_3)(DMF)Cl$ (X-ray structure determined) reacts readily with terminal acetylenes to afford the neutral vinylidene complexes $RuTp(PPh_3)(=C=CHR)Cl$ (R = Ph, $SiMe_3$, Bu^t, Bu^n, COOEt) due to the lability of the DMF ligand (Scheme 3) [23]. For comparison, with $RuTp(PPh_3)_2Cl$, a vinylidene complex is formed only with HC≡CPh [35].

2.4. Carbonyl and nitrosyl complexes

$Ru_3(CO)_{12}$ reacts with KTp and halogens to give moderate yields of the compounds $RuTp(CO)_2X$ ($X = Cl^-$, Br^-, I^-), whereas with $[Ru(CO)_3Cl_2]_2$ and TlTp, $RuTp(CO)_2Cl$ is obtained directly [38]. Similarly, $[Ru(\kappa^2(C,N)\text{-azb})(CO)_2Cl]_2$ (azp = diphenyldiazene) reacts with KTp to give $RuTp(CO)_2(\kappa^1(C)\text{-azb})$, which loses one CO ligand upon irradiation with UV light producing $RuTp(\kappa^2(C,N)\text{-azb})(CO)$ (Scheme 4) [39]. The reaction of the polymer *catena*-$[Ru(O_2CMe)(CO_2)]_n$ with either KTp or KTp^4 yields the neutral dimers $[RuTp(CO)_2]_2$ and $[RuTp^4(CO)_2]_2$, respectively. The X-ray structure of this dinuclear complex shows that the two Tp ligands, coordinate as NN′N″ tridentate ligands in a *cis* staggered configuration around the dimetal core. The Ru–Ru distance of 2.882(1) Å corresponds to a metal–metal single bond [40]. Sørlie and Tilset [41] investigated the



Scheme 3.

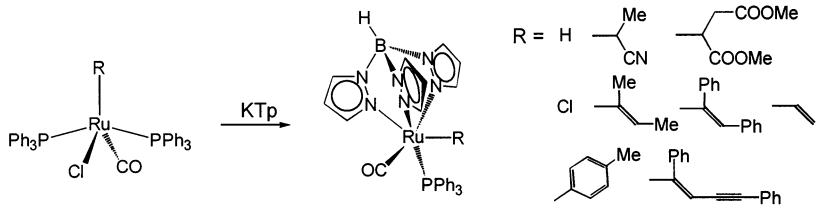


Scheme 4.

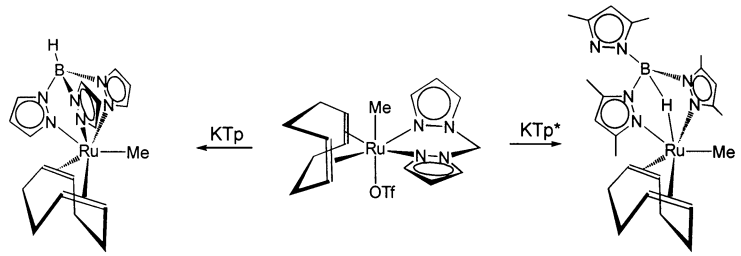
oxidation of $[RuTp(CO)_2]_2$ leading to cleavage of the Ru–Ru bond and the formation of the solvent complexes $[RuTp(CO_2)L]^+$ ($L = CH_3CN$, H_2O, THF, acetone). For this process an associative mechanism is implicated by the large and negative enthropies of activation. The dimer is oxidized at $E° = 0.15$ V vs. Cp_2Fe/Cp_2Fe^+ in CH_3CN as the solvent. Angelici et al. [42] reported the reaction of $[RuTp(CO)_2]_2$ with CF_3SO_3H yielding the dimeric complex $[(RuTp(CO)_2)_2(\mu\text{-}H)]^+$.

A promising route to RuTp complexes containing hydrido, alkyl, vinyl and CO co-ligands is the reaction of complexes of the general type $Ru(PPh_3)_2(CO)RCl$ (R = H, alkyl, vinyl, Cl) with KTp. The first example of this conversion is the preparation of $RuTp(PPh_3)(CO)(CH(Me)CN)$ by reacting $[Ru(PPh_3)_2(CO)Cl(CH(Me)CN)]_2$ with KTp [43]. Similarly, $Ru(PPh_3)_2(CO)(\kappa^2(C,O)CH–C(COOMe)CH_2COOOMe)Cl$ reacts with NaTp to yield $RuTp(PPh_3)(CO)(CH–C(COOMe)CH_2COOOMe)$ [44]. Hill et al. extended this reaction to other derivatives with R = vinyl, 1,2-dimetyhlvinyl, 1,2-diphenylvinyl, 1-phenyl-2-phenylethinylvinyl (X-ray structure determined), and 4-metyhlphenyl substituents [45,46]. The reaction sequence starts from $Ru(PPh_3)_3(CO)(H)Cl$, which is first reacted with an alkyne and subsequently treated in situ with KTp (Scheme 5). Simpson et al. [47] prepared similar complexes of the type $[RuTp(PPh_3)(CO)(L)]^+$ ($L = CO$, Bu^tCN, $P(OMe)_3$, PMe_3) by reacting $RuTp(PPh_3)(CO)Cl$ with $NaPF_6$ in the presence of L. $RuTp(PPh_3)(CO)Cl$ results from the conversion of $RuTp(PPh_3)(CO)H$ with chlorinated solvents. The X-ray structure of $[RuTp(PMe_3)(PPh_3)(CO)]PF_6$ is available.

$Ru(PPr^i_3)_2(CO)(H)Cl$ is reported to react with NaTp to give $Ru(\kappa^2\text{-}Tp)(PPr^i_3)_2(CO)H$, which upon heating liberates one PPr^i_3 ligand to afford $RuTp(PPr^i_3)(CO)H$ [48]. The latter can easily be protonated with HBF_4 giving



Scheme 5.



Scheme 6.

$[RuTp(PPr^i_3)(CO)(H_2)]^+$. The dihydrogen ligand in turn can easily be displaced by acetone. From the reaction of $Ru(PPh_3)_3(CO)(H)Cl$ with KTp at r.t. in CH_2Cl_2, $Ru(\kappa^2\text{-}Tp)(PPh_3)_2(CO)H$ could be isolated and crystallographically characterized [49]. Likewise, Hill et al. isolated the related thiocarbonyl complexes. At elevated temperatures, the corresponding $RuTp(PPh_3)(CX)H$ (X = O,S) complexes are formed. The complexes *cis*, *trans*-$Ru(CO)_2(PMe_3)_2(Me)I$ and $Ru(CO)_3(PMe_3)(Me)I$ reacted with KTp (or NaTp) to give the acetyl complexes $Ru(\kappa^2\text{-}Tp)(PMe_3)_2(CO)COMe$ and $RuTp(PMe_3)(CO)COMe$, respectively [50]. $Ru(\kappa^2\text{-}Tp)(PMe_3)_2(CO)COMe$ could not be converted to $RuTp(PMe_3)(CO)COMe$.

Very recently, Jia et al. [51] reported on a new approach for obtaining complexes of the type $Ru(PPh_3)_3(CO)(R)Cl$ by reacting $RuTp(PPh_3)(MeCN)Cl$ with $NaBH_4$ and primary alcohols RCH_2OH (R = H, Et, Pr^n, Ph, 4-MePh, 4-ClPh). The decarbonylation of the alcohols was studied extensively and a mechanistic rationale involving metal η^2-aldehyde and η^2-dihydrogen intermediates has been proposed.

Onishi described the preparation of $RuTp(NO)Cl_2$ and $RuTp^*(NO)Cl_2$ from $Ru(NO)Cl_3$ [52]. Both substances were found to be Ru(II) species.

2.5. Ruthenium–carbon single bonds

As already mentioned in the previous section, RuTp complexes containing Ru–C single bonds are readily available and stable, even in the presence of β-H atoms, provided there is one phosphine and one CO ligand present. Otherwise, it is more difficult to introduce an alkyl ligand into the RuTp fragment. As shown by Jalòn et al. [53], the conversion of $Ru(bpzm)(COD)Cl_2$ (bpzm = bis(pyrazolyl)methane) with MeMgCl yields Ru(bpzm)(COD)(Me)Cl, which on treatment with $AgCF_3SO_3$ affords the complex $Ru(bpzm)(COD)(Me)(CF_3SO_3)$. The latter complex reacts with KTp to give RuTp(COD)Me, while with KTp* the compound $Ru(\kappa^3(N,N,H)\text{-}Tp^*)(COD)Me$ is obtained featuring an unusual three-center B(μ-H)Ru bond as proven by X-ray crystallography (Scheme 6).

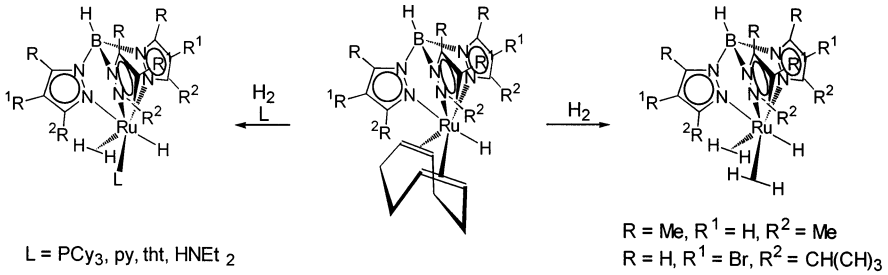
According to Ozawa et al. [54], direct alkylation of RuTp(COD)Cl with Me_3Al or Et_3Al results in the formation of RuTp(COD)Me and RuTp(COD)Et, respectively, both in high yields. Other alkylating reagents such as Et_2Mg, EtMgBr and EtLi turned out to be less efficient.

2.6. Hydride complexes

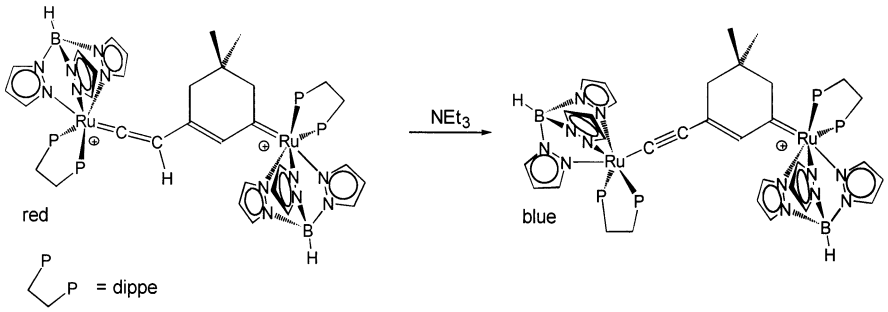
Chaudret et al. [55,56] prepared the complexes RuTp(COD)H, RuTp*(COD)H, and RuTp$^{\#}$(COD)H by reacting Ru(bpzm)(COD)(H)Cl with KTp, KTp* and KTp$^{\#}$ (hydridotris(3-isopropyl-4-bromopyrazolyl)borate), respectively. RuTp-(COD)H can also be synthesized by heating RuTp(COD)Cl in methanol in the presence of base. Hydrogenation of RuTp*(COD)H and RuTp$^{\#}$(COD)H under H_2 (3 bar) yielded RuTp*$(H_2)_2$H and RuTp$^{\#}(H_2)_2$H. With RuTp(COD)H no reaction took place. From RuTp*$(H_2)_2$H and RuTp$^{\#}(H_2)_2$H and D_2, the corresponding isotopomers RuTp*$^{(\#)}H_{5-x}D_x$ ($x = 1$–4) were obtained. The nature of the hydride ligands has been established by T_1 measurements and the J_{HD} coupling is interesting in that the presence of two η^2-bound dihydrogen ligands and one hydride ligand is indicated. Hydrogenation of RuTp*(COD)H and RuTp$^{\#}$(COD)H in the presence of one equivalent of L (L = PCy_3, tht, pyridine, $HNEt_2$) leads to the formation of the hydrido dihydrogen complexes RuTp*(L)(H_2)H and RuTp$^{\#}$(L)(H_2)H (Scheme 7). In the presence of a large excess of L (L = pyridine, tht, CO) over the ruthenium complex, the compound RuTp*$(L)_2$H was obtained. RuTp*$(H_2)_2$H did not react with MeI or CF_3COOH but with $HBF_4{\cdot}Et_2O$ and CF_3SO_3H to afford, in the presence of CH_3CN, the complex [RuTp*$(CH_3CN)]^+$. Chaudret et al. [57] also reported the syntheses of RuTp$(PCy_3)(H_2)$H and RuTp*$(PCy_3)(H_2)$H by treating Ru$(PCy_3)_2(H_2)$HI with KTp or KTp* under a H_2 atmosphere in 40 and 4% yield, respectively.

The decarbonylation reaction mentioned above could proceed via a RuTp$(PPh_3)(H_2)$H intermediate as proposed by Jia et al. [51]. These authors independently prepared this compound by reacting RuTp$(PPh_3)(CH_3CN)$H with H_2 (40 atm).

Very recently Akita and Moro-oka et al. [58] reported a series of ruthenium hydridotris(3,5-diisopropylpyrazolyl)borate complexes (Tp$^{i\mathrm{Pr}}$). The precursor Ru(Tp$^{i\mathrm{Pr}}$)H_5 is protonated by CF_3SO_3H resulting in a cationic diaquo aduct, which is shown to be a precursor for Ru(Tp$^{i\mathrm{Pr}}$) chemistry.



Scheme 7.



Scheme 8.

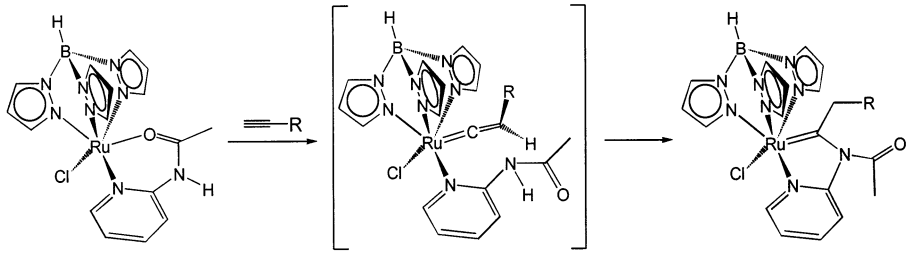
2.7. Ruthenium–carbon double bonds

Cationic vinylidene complexes $[RuTp(L_2)(=C=CHR)]^+$ can be obtained from $[RuTp(L_2)(L)]^+$, where L is a labile ligand such as acetone or DMF. Chelate ligands L_2 used are tmeda [30], pn [31] and Phschiff [28]. The complexes are not air-sensitive but are readily deprotonated giving neutral alkynyl complexes. A similar behavior was observed for $[RuTp(dippe)(=C=CHR)]^+$ (R = COOMe, Ph, H), which was prepared by converting RuTp(dippe)Cl with the HC≡CR in the presence of $NaBPh_4$ [59]. $[RuTp(dippe)(=C=CHR)]^+$ reacts with $KOBu^t$ to give RuTp(dippe)(–C≡CR), while with CH_3OH, cationic carben complexes of the type $[RuTp(dippe)(=C–C(OMe)HR)]^+$ are obtained. With propargylic alcohols, in general, allenylidenes are formed. Only in the case of $HC≡C–C(OH)Me_2$, an intermolecular dimerization of the allenylidene ligands takes place to yield a vinylidene–carbene complex. In the presence of base, this dimeric complex transforms into the corresponding alkynyl–carbene ruthenium complex (Scheme 8).

In sharp contrast to the stability of cationic vinylidene complexes towards air, neutral vinylidene complexes of the type $RuTp(PR_3)(=C=CHR^2)Cl$ convert readily into the corresponding carbonyl compounds $RuTp(PR_3)(CO)Cl$ and the aldehyde R^2CHO in solution. This process was intensively studied by Bianchini et al. using a similar precursor [60]. In addition, neutral vinylidene complexes are substitutionally labile. Thus, the vinylidene moiety is easily replaced by L (L = py, PMe_3, CO). In fact, even metathesis with other terminal alkynes (added in excess) is feasible (Eq. (3)) [23].

$$RuTp(PR_3)(=C=CHR^2)Cl + HC≡C–R^3 \leftrightarrow RuTp(PR_3)(=C=CHR^3)Cl + HC≡C–R^2 \quad (3)$$

RuTp complexes containing hemilabile ligands were found to facilitate the formation of vinylidene complexes. An example is $RuTp(\kappa^2(P,O)\text{-po})Cl$, which reacts with HC≡CPh to give $RuTp(\kappa^1(P)\text{-po})(=C=CHPhR)Cl$ [25]. In cases where the hemilabile ligand is (even weakly) nucleophilic, attack at the α-carbon of the vinylidene moiety occurs. Thus, RuTp(Acpy)Cl reacted with HC≡CR (R = Ph, Bu^n, CH_2Ph, c-hexenyl, COOMe) to yield neutral amidocarbene complexes as shown in Scheme 9 [27].

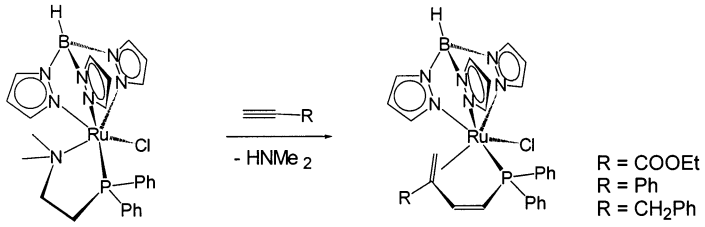


Scheme 9.

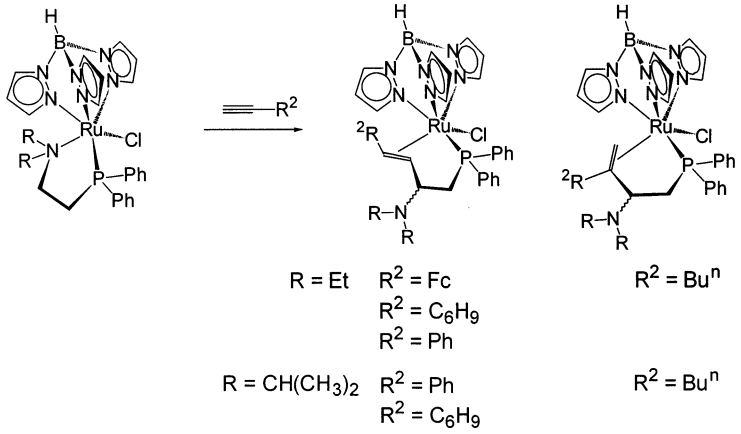
The same reactivity pattern is found with allyl alcohols as ligands. $RuTp(HOCH_2–CH=CH_2)Cl$, formed in situ by the reaction of $RuTp(py)_2Cl$ with allyl alcohol, reacts with terminal alkynes to afford allyloxycarbenes of the type $RuTp(=C(CH_2R)=CH_2CH=CH_2)Cl$ [25].

Neutral vinylidene complexes are key intermediates in alkyne insertion reactions into aliphatic C–H bonds. Complexes $RuTp(\kappa^2(P,N)–PPh_2CH_2CH_2NR_2)Cl$ (R = Me, Et) and $RuTp(\kappa^1(P)–PPh_2CH_2CH_2NPr^i_2)(DMF)Cl$ react with terminal alkynes $HC\equiv CR^2$ (R^2 = Ph, CH_2Ph, COOEt) to yield coupling products of the alkyne and the pn ligand. Depending on the substituents of the amino group, two different types of ligand, namely butadienyldiphenylphosphine (Scheme 10) [61] and 4-diphenylphosphino-1-buten-3-amine are formed (Scheme 11) [22]. These are coordinated via the phosphorus atom and the terminal double bond. A mechanistic rationale for this transformation is as follows. As the first step, cleavage of the Ru–N bond and formation of a vinylidene complex $RuTp(\kappa^1(P)–PPh_2CH_2CH_2NR_2)(=C=CHR^2)Cl$ is suggested. This species is readily deprotonated by the pendant NR_2 group affording the 16-e alkynyl complex $[RuTp(\kappa^1(P)–PPh_2CH_2CH_2NHR_2)(–C\equiv CR^2)]Cl$. Concomitant γ-C–H activation and insertion of the alkynyl ligand gives the final products in a highly diastereoselective fashion. Unsaturated alkynyl complexes, generated in situ from neutral vinylidene complexes on treatment with strong bases, such as BuLi, could be trapped as the CO complex $RuTp(PPh_3)(CO)(–C\equiv CPh)Cl$ [24,35].

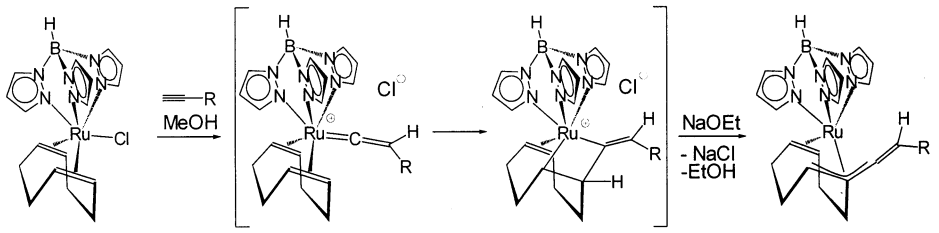
Furthermore, selective couplings of olefines and terminal acetylenes were reported [62] to take place in the coordination sphere of the RuTp fragment via the successive intermediacy of vinylidene and ruthenacyclobutane complexes. Subse-



Scheme 10.

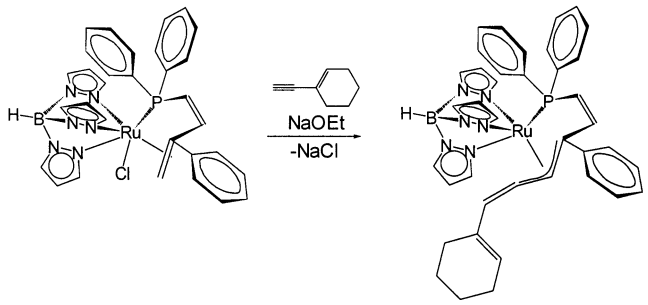


Scheme 11.



Scheme 12.

quent deprotonation of one of the β-hydrogen atoms of the latter with NaOEt yields η^3-butadienyl complexes, while in the presence of Cl^-, rearrangement takes place to give neutral η^2-butadiene complexes via a β-hydrogen elimination/reductive elimination sequence (Scheme 12). Starting materials were both RuTp(COD)Cl and RuTp(η^3-(P,C,C)-$Ph_2PCH{=}CH(Ph){=}CH_2$)Cl (Scheme 13), which were reacted with HC≡CR (R = Ph, c-hex, ferrocenyl, CH_2Ph, Bu^n).



Scheme 13.

Table 2
Catalytic reduction[a] of ketones by RuTp and RuTp* complexes

Catalyst	Substrate	T (°C)	P (bar)	t (h)	Conversion (%)
RuTp*$(H_2)_2$H	Cyclohexanone	80	3	2	93
RuTp*(COD)H	Cyclohexanone	80	3	2	92
RuTp*(COD)H	Acetone	80	3	2	63
RuTp*(COD)H	Acetone	80	32	2	6
RuTp(COD)H	Cyclohexanone	80	3	2	0
RuTp(COD)H	Cyclohexanone	120	4	15	98

[a] Conditions: [catalyst] = 1mmol; [substrate] = 100 mmol; solvent: n-heptane (10 ml).

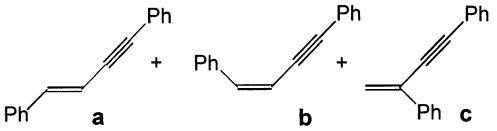
3. Catalytic reactions

3.1. Hydrogenation

Onishi et al. [13] performed the hydrogenation of methylacrylate and 3-phenylpropene with RuTp$(PhCN)_2$Cl and RuTp$^4(PhCN)_2$Cl (substrate to catalyst ratio is 200:1 (mol:mol)) in MeOH in the presence of NEt_3 under a H_2 pressure of 50 kg cm^{-2} at 50°C. Under this condition, methylacrylate was quantitatively converted to methylpropionate (turnover number per catalysis is 200) with both catalyst precursors. In the case of 3-phenylpropene, 100% conversion was observed with RuTp$^4(PhCN)_2$Cl, but only 57% with RuTp$(PhCN)_2$Cl. In either case, E- and Z-1-phenylpropenes were formed as by-products via an olefin double bond migration.

Complexes RuTp*$(H_2)_2$H, RuTp*(COD)H and RuTp(COD)H were catalytically active in the reduction of unactivated ketones to alcohols either by dihydrogen or by hydrogen transfer from alcohols in basic media, as shown by Chaudret et al.

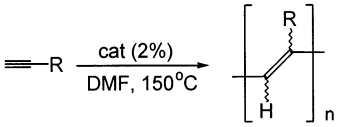
Table 3
Conversion and product distribution of the catalytic dimerization of HC≡CPh with some RuTp pre-catalysts.



Catalyst (2 mol.%)	Conversion (%)[a]	a (%)	b (%)	c (%)
RuTp$(PPh_3)_2$Cl	98[a]	91	6	–
RuTp(PPh_3)(=C=CHPh)Cl	98[a]	91	5	–
RuTp$(PPh_3)_2$H	99	92	8	–
RuTp(PPh_3)(CO)Cl	–	–	–	–

[a] Small amounts of a polymeric by-product.

Table 4
Catalytic polymerization of some terminal acetylenes.



HC≡CR	Time (h)	Yield (%)	M_n [a]	PDI[b]	n[c]
Ph	0.5	98	7056	1.48	69
Ph	20	99	3972	1.39	39
Bu^n	20	77	1109	1.31	15
COOEt	5	60	1062	1.30	10

[a] M_n, the number average molecular weight.
[b] PDI, the polymerization distribution index.
[c] n, the number average degree of polymerization.

[63]. Some results are summarized in Table 2. Both $RuTp^*(H_2)_2H$ and RuTp*(COD)H exhibit similar activities in the reduction of cyclohexanone suggesting that, under the reaction conditions applied, RuTp*(COD)H is rapidly hydrogenated. High pressures of H_2 inhibit the catalytic reaction, whereas the presence of olefins has a promoting effect. Also briefly discussed in the article is transfer hydrogenation of ketones and olefins.

Jia et al. [34] reported on catalytic hydrogenation of olefins with $[RuTp(PPh_3)_2(MeCN)]^+$ and $[RuTp(PPh_3)(MeCN)_2]^+$ as catalyst precursors. Conversions could be increased in the presence of H_2O or NH_3. The authors demonstrated that dihydrogen complexes are involved in the catalytic cycle.

3.2. Coupling reactions

$RuTp(COD)Cl$, $RuTp(py)_2Cl$ and RuTp(tmeda)Cl are found to catalyse the coupling of HC≡CPh with benzoic acid. *E*- and *Z*-vinylesters were formed in a ratio varying from 1:1 to 2:1. Similar effects has $RuTp(py)_2Cl$ on the coupling of HC≡CPh with allyl alcohol leading to the corresponding *Z*-vinylether and 1-phenyl-3-butenal in a 1:1 ratio. The latter is formed via a Claisen rearrangement of the *E*-vinylether [19].

$RuTp(PPh_3)_2Cl$ and especially $RuTp(PPh_3)_2H$ are effective catalysts for the dimerization of terminal alkynes to give enynes (Table 3). These reactions were run in boiling toluene for 20 h.

With RuTp(COD)Cl as the catalyst precursor, oligo- and polymerization products were obtained (Table 4).

Very recently Ozawa et al. [64] showed, that the neutral Ruthenium vinylidene complex $RuTp(PPh_3)(=C=CHPh)Cl$ is active in the ring-opening metathesis poly-

merisation (ROMP) of norbornene. The efficiency of the catalyst is enhanced by adding Lewis acids such as BF_3 Et_2O to the system.

4. Conclusions

RuTp chemistry has been exhibiting a steady growth especially in the last few years. Particular emphasis is on RuTp complexes featuring hydrido and dihydrogen ligands as well as metal–carbon single and double bonds. For the latter, the involvement of carbene and vinylidene complexes as reactive intermediates in stoichiometric as well as catalytic transformations of organic molecules is deemed to become increasingly important. To date, interestingly, neither carbyne complexes nor coordinatively unsaturated complexes of the RuTp fragment have been reported. In using sterically more demanding Tp derivatives, such species should become accessible.

Acknowledgements

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