The Tentacular Chemistry of $[Cp^*Ru(OMe)]_2$‡

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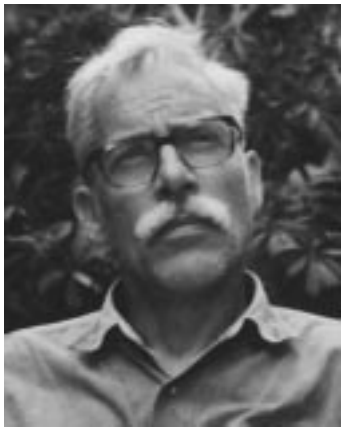
Contents



U. Koelle was born in 1941. He studied Chemistry at the Universities of Tübingen, Hamburg, and Heidelberg in Germany where he obtained his Ph.D. in 1969 on work about hindered internal rotation in conjugated amides. He then joined the group of Sture Forsén at the Chemical Center (Kemicentrum) in Lund, Sweden, as a postdoc to work on restricted intramolecular rotation in hydrogen bonded systems. After a period as a school teacher, he entered the research group of Gerhard E. Herberich in Munich where he became familiar with organometallic chemistry. With Professor Herberich he moved to the University of Technology in Aachen in 1973 and has stayed there as a researcher and lecturer. His interest in organometallic chemistry has been centered around reactive and coordinatively unsaturated transition metal half-sandwich complexes. He has published papers in organometallic electrochemistry, and in his group, preparation and exchange kinetics of organometallic aqua complexes are studied.

1. Introduction

A delineation between coordination chemistry and organometallic chemistry of the transition metals can be drawn, apart from a wide range of conceptual and practical similarities, at the point where the HOMO–LUMO gap of the complex is large enough to impose the 18-electron valence shell to at least the middle part of the transition series. This situation is generally encountered with acceptor ligands and is more stringent in the lower transition series. It is with this type of transition metal complexes that the coordination number is governed by the $9 - N$ ligand rule and any particular complex featuring less than N coordination sites for a $d^{2(9-N)}$ electron configuration can be considered as coordinatively unsaturated. While the concept, applied to square-planar four-coordinated vs pyramidal five-coordinated d^8-4/d^8-5, i.e., 16/18 VE, complexes, would be still ambiguous, it is particularly simple and straightforward for $N = 6$ in d^6-6 complexes. Here a hole in the coordination shell corresponding to a 16 VE complex makes the species a short-lived intermediate, generated by, e.g., photochemical ligand dissociation, dehydrohalogenation, other reductive elimination or reduction of a dihalide, which is subsequently trapped by ligands or substrates present in the reaction mixture. Alternatively coordinative unsaturation may be affected by steric crowding through bulky ligands that prevent completion of the coordination environment. Examples of the first kind are amply provided by photolysis products of coordinatively saturated dialkyl and dihydride complexes or the UV and cryochemistry of transition metal carbonyls.[1] Apart from some Rh(III) complexes examples for the second kind are provided by such classical pentacoordinate complexes as $Ru(Os)(PPh_3)_3X_2$, X = Cl, Br, H.[2] More recent organometallic examples are compounds such as $Cp^*RuCl(P(C_6H_{11})_3)$,[3] $CpRu(PR_3)_2^+$,[4] or $CpFe(dipp)^+$.[5] The Ru(0) species *cis,trans*-$Ru(CO)_2(Pt\text{-}Bu_2Me)_2$,[6] characterized as "isolable, yet highly reactive" shows reactivity, such as addition reactions with very low activation barrier, similar to the examples treated below. Still another approach to coordinative unsaturation are complexes featuring "hemilabile" ligands, mostly chelating ether phosphines, which are formally coordinatively saturated but easily provide a

‡ This article is dedicated to Professor Gerhard E. Herberich on occasion of his 60th anniversary, Nov 24, 1996.

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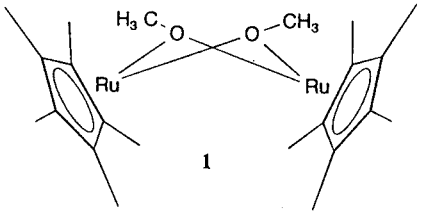
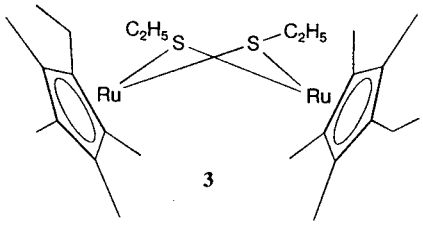
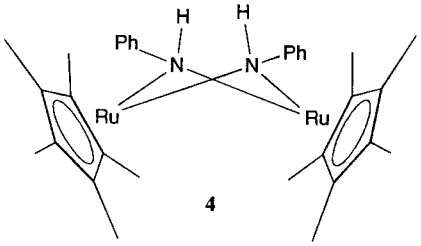
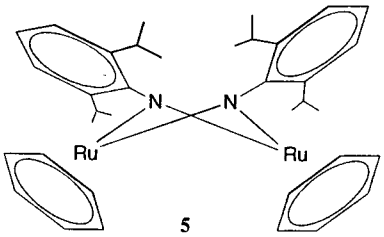
Table 1. Geometrical Parameters of Coordinatively Unsaturated Dimeric Complexes

	Ru - Ru	Ru - X	Ru-X-Ru	X-Ru-X	fold.	Ref.
 1	295.1(5)	205.6(5)	91.9(2)	70.9(2)	123.8	9, 10
 3	307.54(5)	232.3	82.9	75.7	114	11
 4	294.5(4)	211	88.6(3)	74	121.6	13
 5	277.7(3)	196.5				12

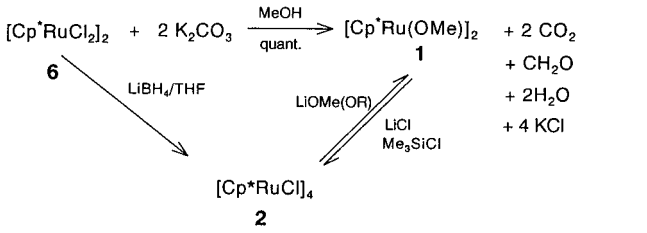
vacant coordination site through dissociation of the weakly bound ether oxygen.[7]

In particular with cationic complexes, the delineation between a solvent-stabilized unsaturated fragment and a true electron-deficient species in many instances is somewhat arbitrary. Whereas in the case of true coordinative unsaturation chemical characterization is limited by the elusive nature of the unsaturated species under ordinary conditions, in the case of bulky ligands, chemical reactivity may often be quenched to a larger or lesser extent by steric congestion.

In the past few years a new class of *coordinatively unsaturated* transition metal complexes, derived from Cp*Ru or (arene)Ru moieties of composition $[(Cp^*,arene)Ru(ER)]_2$ (or Cp*Ru(ER)L) has been explored, where the lack of valence electrons in metal-centered bonding orbitals is compensated in part by internal π-donation to such an extent that complexes exist as isolable and well-characterized compounds. On the other hand, incomplete coordination in these molecules is still manifest by a wide variety of facile reactions such as ligand addition, exchange, insertions, and others. Because most transformations at such molecules, unlike the majority of reactions performed at *coordinatively saturated* metal centers, are not triggered by, e.g., a ligand dissociation, they generally require very little thermal activation and proceed under rather mild conditions.

Table 1 lists four representative complexes which have been prepared since 1989. They share in common two Cp or arene Ru moieties linked by heteroatoms in the form of an upfolded rhombus. In each molecule the Ru centers conform to a 16 valence electron count. Note that apart from the Cp/arene ring, the metal is devoid of acceptor ligands. This latter feature ascertains an exeptionally broad reaction chemistry for the compounds although only the

Scheme 1. Synthesis of 1 and 2



(1)

chemistry of complexes **1** and **3** has been investigated in some detail.

Our entry into the field started with the fortuitous discovery of the title complex **1** by Scheme 1.[8] The intense cherry red, air-sensitive, pentane-soluble reaction product (formed in an experiment that was intended to produce an organometallic carbonate or oxide [Cp*RuO]$_n$) immediately pointed toward unexpected and then unconventional structural features. These were first established through spectroscopy[8] and shortly after by single-crystal X-ray diffraction presented by the group of Don Tilley,[9] who had prepared the compound from the halide [Cp*RuCl]$_4$ **2** with NaOMe, and by ourselves.[10]

The same type of folded dimer was subsequently disclosed in the thio analogues **3**, which are most easily prepared by thiol exchange from **1** according to Scheme 6[11] and in two more recent imido, **5**,[12] and amido, **4**,[13] complexes shown in Table 1.

In Table 1 characteristic figures of the geometrical arrangement in these molecules are collected. All compounds are folded dimers with a Ru−Ru separation in **1**, **3**, and **4** around 300 pm. By virtue of the high reactivity of the compounds (as far as their chemistry has been explored) this distance is considered as nonbonding. Metal−metal separation in **5** corresponds to a Ru−Ru (single) bond, but in view of the similar chemical appearance (deep-colored and air-sensitive) bonding is expected to be similar to the other cases.

The electronic situation in these molecules may be viewed from two different points and has been explored on different quantum chemical levels. Let us first concentrate on the coordinative unsaturated character. Evidently this is not provoked by steric congestion but must be electronically stabilized and is linked to the presence of two oxygen atoms as π-donors. In Figure 1 the EH MO scheme of CpRu(CO)$_2^+$ is contrasted with that of CpRu(OMe)$_2^-$ in the same two-legged piano stool arrangement. As one can see, the small HOMO−LUMO difference in CpRu(CO)$_2^+$ becomes much larger when the acceptor ligands CO are replaced by donor ligands which push up the empty Ru(yz/py) combinations 24 and 26 Å respectively (the *z* axis is taken as the Ru midpoint Cp vector). The HOMO−LUMO distance in CpRu(OMe)$_2^-$ is still small compared to e.g. valence-saturated CpRu(CO)$_3^+$ which is reflected in a band at 490 nm in the visible spectrum of **1a**, giving the compound the characteristic cherry red color.

The next question is the folding of the Ru−E−Ru−E four-membered ring. In Figure 2 is given a Walsh diagram, again at the extended Huckel level,

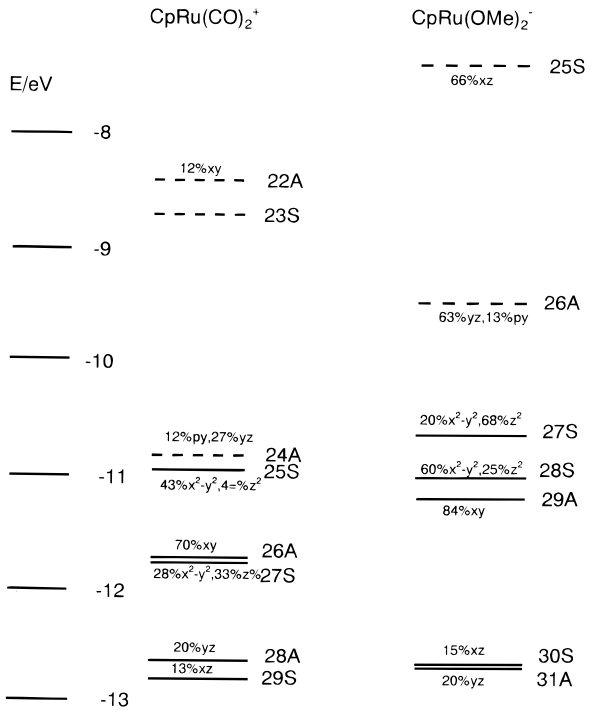


Figure 1. Comparison of the frontier MOs of π-acceptor vs π-donor coordinatively unsaturated CpML$_2$.

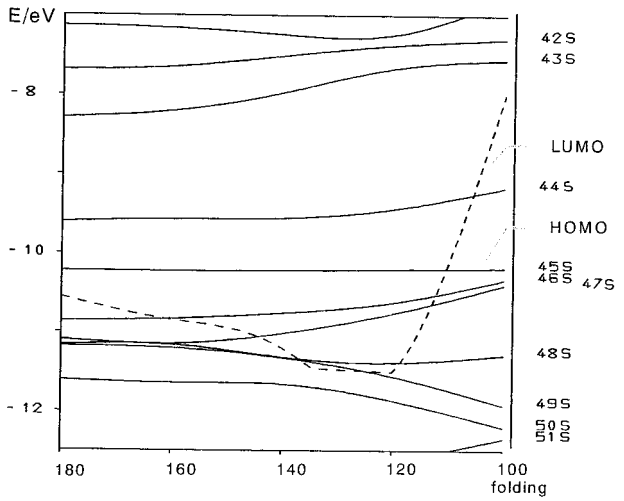


Figure 2. Walsh diagram showing total electronic energy (- - -) and orbitals of [CpRuOMe]$_2$ as a function of folding angle defined in Table 1.

showing frontier orbitals of principally metal character at different folding angles. Fortuitously the energy minimum is at a folding angle of about 125° close to the experimental value (Table 1). The experimental geometry is thus a compromise between stabilized and destabilized levels at a certain folding angle. Symmetry reduction in the folded dimer causes orbital mixing mainly of *yz* with x^2-y^2 and of x^2-y^2 with z^2. MO 45 is Ru−Ru bonding and is little affected by bending. MOs 46 and 47 are out of phase x^2-y^2 and *xy* combinations respectively which become less bonding on folding. This effect is counterbalanced by the bonding combinations 48, 49, and 50 which are stabilized on folding. The qualitative MO analysis shows that there is considerable metal−metal interaction in a bonding as well as an antibonding way. The overall stabilization due to orbital

mixing by lowering the symmetry has been considered a second-order Jahn−Teller effect.[12]

A second remarkable structural feature of the folded dimers is a relatively short Ru−E distance, in particular when E = O, S. The same observation has been made more recently for mononuclear 16 VE analogues $Cp^*RuPR_3(OR')$ which can be prepared and are stable with bulky phosphines such as PCy_3 or $PPh(i\text{-}Pr)_2$.[14] A careful analysis of the bonding situation in these molecules including halide derivatives $Cp^*RuPR_3(X)$ by ab initio SCF methods[15] revealed π-back-bonding from filled E lone pairs into an empty Ru d orbital of proper symmetry as the main factor for stabilizing the formal 16 electron count. Consequently in **4**, where bridging N atoms are devoid of a lone pair, this effect can no longer be operative and Ru−N distance is significantly longer than in **5**, featuring a nitrogen lone pair. E-π−Ru-*d* back-donation requires the Ru−O−E angle to deviate from 180° as was found also experimentally for $Cp^*Ru(PCy_3)(OCH_2CF_3)$ (123°) and $Cp^*Ru(PCy_3)(OSiPh_3)$ (153.5°).[14b] As will become evident from observations detailed below, puckering of the four-membered ring is quenched to a larger or lesser extent by addition of σ-donor/π-acceptor ligands to the metal.

2. Preparation and General Properties of $[Cp^*Ru(OR)]_2$ (1)

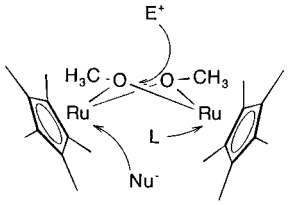
Complexes **1** are accessible by reactions depicted in Scheme 1 either through the chloro complex **2** or by direct reaction of the common precursor $[Cp^*RuCl_2]_2$[16] with K_2CO_3 in MeOH (or other alcohol).[8,9] For the preparation of the methoxo derivative **1a**, the horizontal reaction in Scheme 1 is the method of choice[8,17] giving quantitative conversion with no side products in a few hours at ambient temperature. It will be preferred in all cases where no special bridging groups are intended. The product can be obtained quite pure after filtration from KCl and excess K_2CO_3 and evaporation of the solvent.

The route via the tetrameric chloride **2** is the more general one and is preferred for higher alcohols $C_nH_{2n+1}OH$ (derivatives up to $n = 4$ were prepared), since yields in the direct conversion drop sharply with increasing n.[8] Even an O-*t*-Bu derivative was obtained in this way which is, however, not stable at ambient temperature but tends to eliminate di-*tert*-butyl ether.

Complexes **1** are air-sensitive but thermally stable (vide infra). Alcoholic solutions seem to be indefinitely stable, the solid is preferably stored at low temperature for longer periods. Cyclovoltammetry of **1** in methanol gave a single chemically reversible oxidation/reduction wave with peak potentials $E_p^{ox} = 0.02$ and $E_p^{red} = -0.10$ ($E_{1/2}$ −0.04) V vs SCE, assigned to a Ru^{II}/Ru^{III} transition. Cp*Ru(III) alkoxo complexes have, however, never been isolated.

Transformations of **1** can be classified according to three different reaction modes, outlined in Scheme 2, which are: (i) addition of two- and four-electron ligands with or without cleavage of the dimer; (ii) attack of electrophiles on the bridge atoms; (iii) substitution of the bridging group by nucleophiles.

Scheme 2. Reaction Patterns of 1



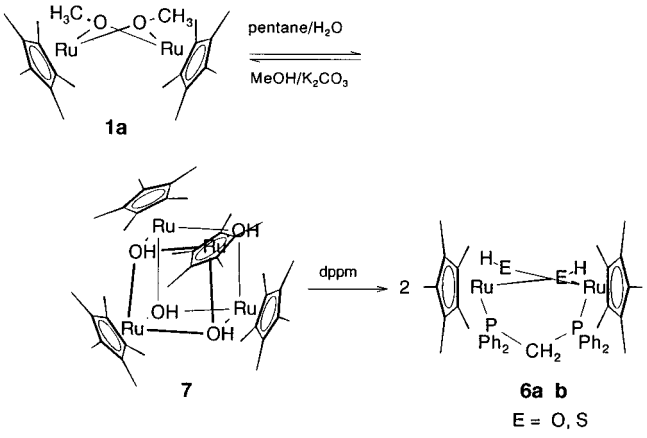
Each type of reaction has led, in high yield and generally under very mild conditions, to products which in turn form the basis of an extended chemistry as will be shown below. Reaction i gives easy access to virtually any desired complex of the general composition Cp^*RuL_2X. Reaction ii will lead to bridge exchange or generation of the 12-electron fragment Cp^*Ru^+, whereas iii apart from bridge exchange has led to a variety of novel reactions. Examples for each reaction mode will be presented in the following.

3. Nucleophilic Exchange, Dimer vs Tetramer

In the ^1H NMR spectrum bridging alkoxo groups are characterized by OCH_n protons at low field (δ 4.8 for **1a**, OMe). They are readily exchanged by alcohol. Thus, if **1a** in C_6D_6 is treated with excess CD_3OD, the OCH_3 group is rapidly exchanged for CD_3. Compound **1a** treated with $PhCH_2OH$ (1:1.1) in the same solvent shows signals for the mixed complex with OMe and OCH_2Ph bridge as well as the doubly OCH_2Ph-bridged species. Exchange is thus slow on the NMR but fast on a preparative time scale. Equilibria between different alcohols place the more acidic one in the bridge: the OMe/OEt equilibrium at equal alcohol concentration contains about 30% bridging OEt,[9] whereas, with CF_3CH_2OH, the bridging position is occupied entirely by the latter.

Bridge exchange reactions have been effected also in addition products, e.g., in particular **6** (with dppm) (Scheme 3). Hydrolysis of $[Cp^*Ru(OMe)]_2$(dppm) has

Scheme 3. Hydrolysis of 1



given the hydroxy derivative $[Cp^*Ru(OH)]_2$ (dppm) (**6a**) and likewise with H_2S has been obtained a bridged hydrosulfide $[Cp^*Ru(SH)]_2$(dppm) (**6b**). Those exchange reactions in coordinatively saturated derivatives $[Cp^*Ru(OR)L]_2$ are orders of magnitude slower than in the unsaturated parent compounds.

Hydrolysis of **1a**, dissolved in pentane, with a small amount of water leads to a hydroxo complex $[Cp^*Ru(OH)]_4$ (**7**) which, by X-ray structure analysis of the Cp^ ($Cp^\wedge = \eta^5$-C_5Me_4Et) analogue[18] was identified as a tetramer like the chloro complex **2**. In the cyclic voltammogram **7** is oxidized in four successive quasi reversible one-electron steps from the $Ru^{II}/Ru^{II}/Ru^{II}/Ru^{II}$ to the $Ru^{III}/Ru^{III}/Ru^{III}/Ru^{III}$ state. At the same time the hydroxy tetramer was obtained in the group of Suzuki by hydrolysis of $[Cp^*Ru(H)(OOCCF_3)]_2$ with KOH in toluene.[19] Analogous sulfur complexes $[Cp^*RuS]_4$ have been isolated in different oxidation states.[20]

Complex **7** was found to be a rather inert compound, being air stable and resistant to electrophilic as well as nucleophilic attack. Thus, O*H* protons, resonating in the NMR at δ −0.14, withstand treatment with *n*-BuLi, and likewise did the reaction with Me_3SiCl fail. In $MeOH/K_2CO_3$ **7** slowly reverts back to **1a**, in a silmilarly slow reaction it is cleaved by dppm to **6a**.

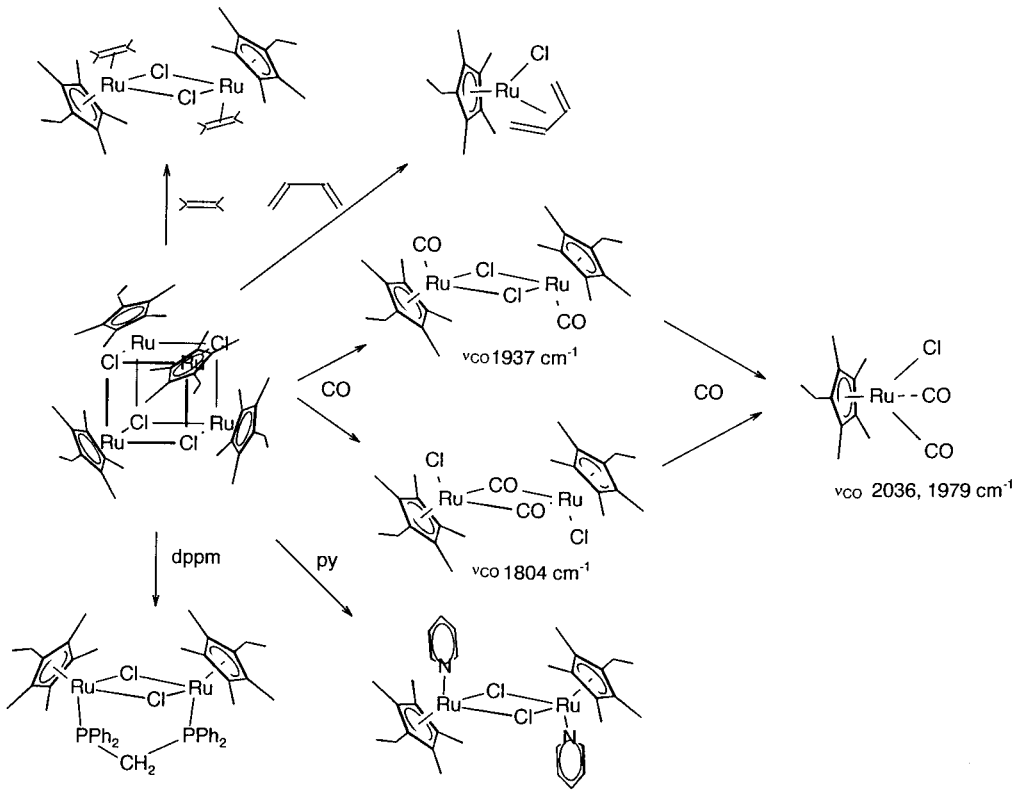
Model calculations on an OMe tetramer revealed serious steric interference of the OMe groups with methyl Cp*. We thus believe that the hydroxo complex, apart from S and Cl analogues with longer Ru−X bonds, is the only one that meets steric requirements for a tetramer. Geometrical distortion of the tetramer from a regular cube is such that again the dihedral angle between Ru−O−Ru planes has decreased and the Ru−O distance increased (to 2.15 Å mean), although somewhat less dramatic than in acceptor ligand addition products (vide infra). Contrasting the inertness of **7** with the high reactivity of **1** reveals that this latter is entirely due to the coordinatively unsaturated character of the compound and is lost completely on coordinative saturation through tetramer formation. The tetrameric chloride **3** (see below) in contrast is cleaved by all kinds of ligands with great ease. Obviously oxygen as a σ/π-donor forms much more solid bonds to Ru than does for instance chlorine (cf. also complexes featuring a $(NH_3)_nRu-O-Ru(NH_3)_n$ link like in "Ru-red").

4. Addition and Cleavage Reactions of $[Cp^*RuCl]_4$ (2)

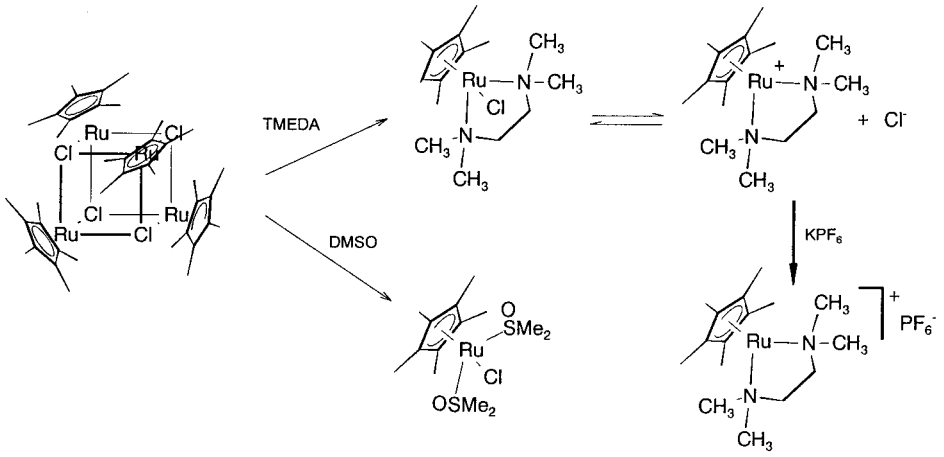
Electrophilic attack at bridging oxygen atoms of **1** is seen with Lewis and Brønsted acids. HX and, more specifically, Me_3SiX cleave **1** with formation of the respective halides $[Cp^*RuX]_n$.[21] Even LiCl in ether solution will shift the equilibrium **1** ⇌ **2** to the right, possibly driven by the low solubility of LiOMe in diethyl ether. The chloro complex has been structurally characterized and is a distorted cube shaped tetramer $[Cp^*RuCl]_4$ with Ru−Cl 2.524 Å (mean).[22] The bromo and iodo congeners can be prepared by treating **1** with e.g. NH_4X in acetone but are less stable and less well characterized than **2**. Compound **2**, similar to **1**, due to its broad reactivity spectrum and ease of cleavage, has found widespread application as a synthon in Cp*Ru chemistry and the preparation using **1** and Me_3SiCl was found in our hands as being particularly simple and straightforward.

The spectrum of ligands that can be added to **2**, giving either monomeric or dimeric complexes, is considerably more extended in comparison to the number of ligands that gave isolable adducts with **1**. Thus, excess ethylene or pyridine as well as CO in stoichiometric amounts cleave the tetramer to coordinatively saturated dimers (Scheme 4).[23] Alkynes

Scheme 4. Cleavage of 2 by Addition of σ-Donor Ligands



Scheme 5. Addition Products of 2 with Acceptor Ligands



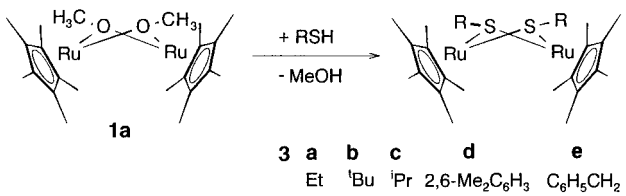
cleave the tetramer, giving unsymmetrically bridged dimeric complexes.[24] Dienes have given monomeric complexes Cp*Ru(diene)Cl;[22] with bipy Cp*Ru(bipy)-Cl[8] is obtained; and recently, with bisphosphinine, an analogous complex Cp*Ru(2,2-bis(4,5-dimethylphosphinine))Cl was isolated.[25] Remarkably **2** is also cleaved by pure σ-donor ligands such as TMEDA, sulfoxides (Scheme 5), or amino acids (vide infra).[26] In Cp*Ru(TMEDA)Cl Ru−N (2.262(4), 2.295(3) Å) as well as Ru−Cl (2.512(1) Å) distances are rather long compared to Ru(II) coordination complexes featuring these ligands. In contrast to analogous phosphine complexes Cp*Ru(CH_2PR_2)$_2$Cl, obtained by cleavage of **2** with phosphines, which show a static piano stool arrangement of the P and Cl ligands on the NMR time scale, N−Me groups in the ^{1}H and ^{13}C NMR spectra of Cp*Ru(TMEDA)Cl were found to be equivalent down to low temperature. This fact was interpreted as a rapid ionization equilibrium by Cl^- dissociation. Recently the coordinatively unsaturated 16 VE cation [Cp*Ru(TMEDA)]$^+$ was obtained through Cl^- abstraction and has been structurally characterized,[27] showing a TMEDA ligand arranged perpendicular to the Cp* plane.

This type of complexes, due to the ease of replacement of the coligands, has recently been found most useful in enantioselective π-complexation (see section 12).

*5. Formation and Reaction of Sulfur Analogues [Cp*Ru(SR)]$_2$ (3)*

A most easily proceeding nucleophilic exchange reaction of **1** of paramount importance was found in the exchange with thiols RSH to give sulfur analogues **3**. The equilibrium **1** ⇌ **3** (Scheme 6) lies

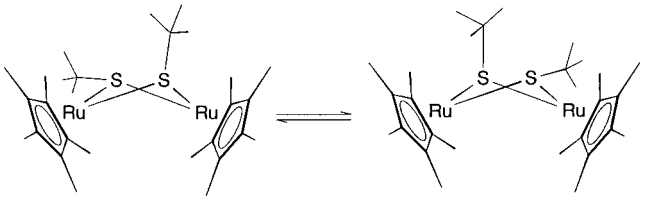
Scheme 6. Formation of 3



entirely to the right such that thiol dimers can be recrystallyzed from e.g. methanol without destruction. X-ray structure determination of [Cp^Ru(SEt)]$_2$ [11] has revealed the same basic geometry of a folded dimer as found for **1** (see Table 1). The molecular geometry of a 2,6-dimethylphenyl derivative[28] **3d** differs in one respect: the folding angle along the S−S′ vector is wider (139° as compared to 114°) and the Ru−Ru distance is 3.50 Å, 0.5 Å longer than in **3a**. Concomitantly has Ru−S been found as 2.350(4) Å, indicating absence of S→Ru π-bonding. Thus **3d** has a geometry intermediate between that of a 16 VE dimer and an addition product [Cp*Ru(SR)L]$_2$ which may be due to steric interference of Cp* with the bridging group. Note that the complex containing a closely related phenol, prepared on the same route from **2** and 2,6-*t*-$Bu_2C_6H_3OLi$, gave the π-oxacyclohexadienyl sandwich exclusively (see also section 10).[9] The intense blue color of complexes **3** can be assigned to an S→Ru CT transition and is characteristic for the unsaturated complex as well. The same blue color was also found for the mononuclear 16-electron analogue (C_6H_6)Ru(SR)$_2$.[29]

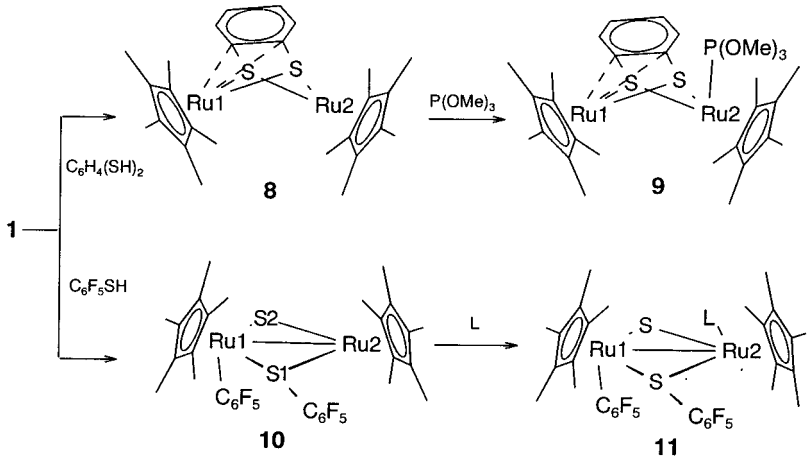
In [Cp*Ru(S-*t*-Bu)]$_2$ (**3b**) a splitting of the *t*-Bu signal in the ^{1}H NMR into two singlets at low temperature is interpreted as the interchange of *syn* and *anti* *t*-Bu groups by inversion of the Ru−S−Ru−S ring, Scheme 7, assigning an anti configuration

Scheme 7. Inversion of [Cp*Ru(μ-S-*t*-Bu)]$_2$



to the compound:[28] From VT NMR spectra a free energy of activation $\Delta G^{\ddagger}_{283}$ = 55 kJ/mol was calculated. Similarly was the NMR spectrum of the *i*-Pr derivative found to be temperature dependent although separate signals for syn and anti *i*-Pr groups could not be resolved at low temperature. A sharp spectrum with equivalent Cp* and 2,6-Me_2 groups in **3d** over the whole NMR temperature range has been taken as evidence for rapid interchange of two syn configurations with R groups in equatorial or axial positions, respectively. However, in view of the solid-state structure of **3d** showing the bis-equatorial syn

Scheme 8. Modifications of [Cp*RuSR]$_2$



conformation (like **3a**) it seems more likely that this will also be the one prevalent in solution and no net inversion takes place. (In case a symmetrical syn conformation undergoes ring inversion, sulfur inversion is required as well to leave chemical shifts unchanged. Inversion at sulfur, however, is generally a high-energy process.) The anti configuration seems to be adopted only in the case of two bulky *t*-Bu groups in the bridge which otherwise would sterically interfere with Cp* methyl hydrogens. (The 500-MHz LT ^{1}H NMR spectrum of [Cp*Ru(μ-O-*t*-Bu)]$_2$, however, recently prepared from **2** and LiO-*t*-Bu,[30] did not give any indication of an inversion process.)

The bonding situation is again modified in a dithiocatechol derivative **8** (Scheme 8), readily prepared from **1** and *o*-(SH)$_2$C$_6$H$_4$, where the sulfur atoms are rigidly linked as ortho substituents at an arene ring. Obviously π-back-donation from sulfur lone pairs greatly has suffered from the altered stereoelectronic arrangement such that one of the Ru centers now binds to the central double bond of the arene ring (Ru1−C 2.245 Å (mean)) rendering the molecular halves inequivalent with respect to the S−S mirror plane (Ru1−S 2.44 (mean), Ru2−S 2.275 (mean) Å). One Ru (Ru2) stays coordinatively unsaturated and is prone to add two electron ligands such as P(OMe)$_3$, in **9**, or CO.[31]

A further structural variation was encountered when reacting a perfluorinated thiol C$_6$F$_5$SH (Scheme 8).[32] In that case exchange is accompanied by oxidative addition of one C$_6$F$_5$S moiety across a Ru center to give **10**. X-ray structural characterization revealed a short Ru2−S2 bond (Ru2−S2 2.199(1), Ru2−S1 2.285(1), Ru1−S1 2.305, Ru1−S2 2.337 Å), indicating some double-bond character between low-coordinated Ru2 and the bridging S. Similar to **8**, **10** has one coordinatively saturated and one unsaturated Ru center where ligands add to the latter to **11**.

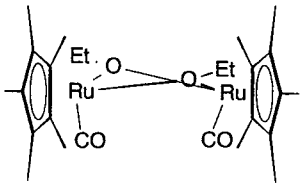
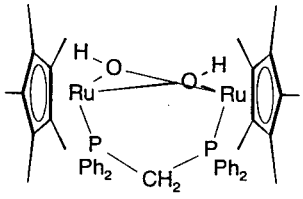
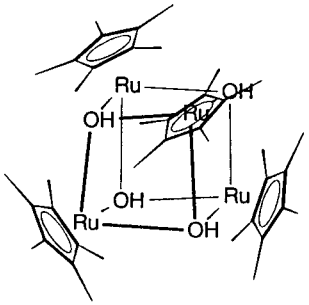
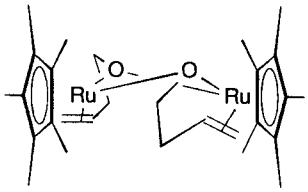
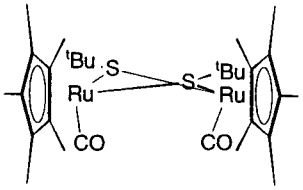
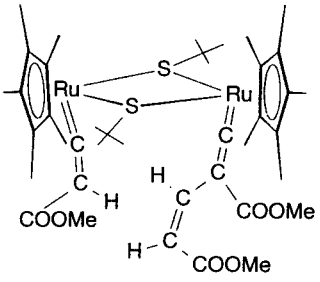
6. Ligand Addition and Cleavage of 1 and 3

The propensity for ligand addition in **1** is restricted to mostly acceptor ligands with phosphines as the most important group. Thus, with dppm is obtained [Cp*Ru(OMe)]$_2$(μ-dppm) (cf. **6a**),[33] whereas dppe has given a mixture of the dinuclear complex analogous to **6a** and mononuclear Cp*Ru(OMe)(dppe).[8] Bulky phosphines cleave **1** to give a monomeric coordinatively unsaturated alkoxo complex such as Cp*Ru(OMe)PCy$_3$, whereas, with somewhat less demanding PPhCy$_2$, a hydride Cp*RuH(PPhCy$_2$), obviously formed by β-elimination, was obtained.[34]

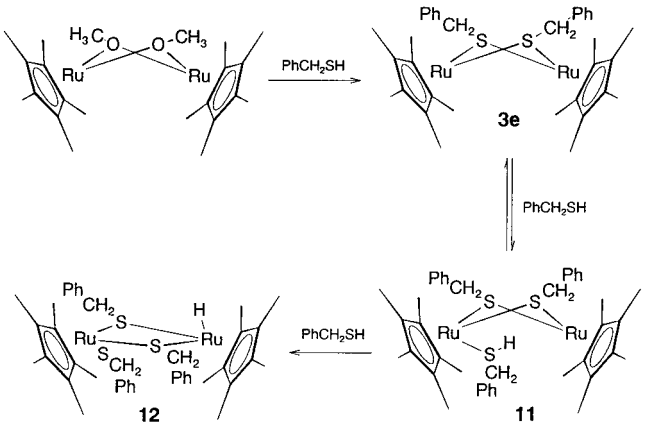
Olefins such as ethylene can bee seen to complex, forming at low temperature what we believe to be a monoadduct which reversibly dissociates at ambient temperature into constituents (see section 9) the same as has been observed with mononuclear Cp*Ru(PPhPr$_2$)(OCH$_2$CF$_3$).[35] Addition of alkynes is obvious from a color change but no stable addition products could be isolated. CO has been shown to give *cis*-bis adducts, which in the case of [Cp*Ru(OEt)CO]$_2$ has been structurally characterized[9] and shows a largely flattened Ru−O−Ru−O rhombus with elongated Ru−O bonds (Table 2). From reaction of [Cp*Ru(OMe)]$_2$ with stoichiometric CO in benzene was isolated [Cp*Ru(OMe)CO]$_2$ (Cp* δ = 1.43, OMe δ = 3.70) in 80% yield.[36] Further treatment of this adduct with excess CO gives a product assigned the structure Cp*Ru(CO)$_2$(OMe) (Cp* δ = 1.624, OMe δ = 3.574) which finally converts to [Cp*Ru(CO)$_2$]$_2$ (Cp* δ = 1.71, all values in C$_6$D$_6$). The bis-*cis* adducts of **1** contrasts to CO and ethylene adducts of **2** which in the latter case have been shown to adopt the trans configuration[23] (except, of course, [Cp*RuCl]$_2$(dppm)). The difference may be of kinetic origin since in the case of **2** the products of stoichiometry [Cp*RuClL]$_2$ are formed through cleavage of the tetramer, whereas in **1** ligands can directly add to the open coordination sites. A bis-*cis* configuration is then preformed by the geometry of the unsaturated precursor molecule.

In contrast, sulfur analogues **3** are much more prone to add σ-donor as well as π-acceptor ligands.[32] In the presence of excess thiol the blue color of the unsaturated dimer changes into green, indicating the coordination of one additional molecule of thiol. Reaction of e.g. PhCH$_2$SH with **1** monitored by NMR showed successively formation of bis-benzylthiolato complex **3e**, the addition product of **3e** with one molecule of benzylsulfide (**11**), characterized by an AB pattern for benzylic protons (δ 4.0, 4.5) in the

Table 2. Geometrical Parameters of Coordinatively Saturated Addition Products (reference values for coordinatively unsaturated complexes see Table 1)

	Ru------Ru	Ru-E	dihedr. ∢ between Ru-E-Ru planes	Ref.
	3.39	2.12	197.5	9
	3.45	2.159	180	30
	3.43	2.12-2.22	161	18, 19
	3.54	2.13-2.166	171	63
	3.751	2.42	175	31
	3.767	2.38-2.43		39

Scheme 9. Equilibria Involving Benzyl Sulfide



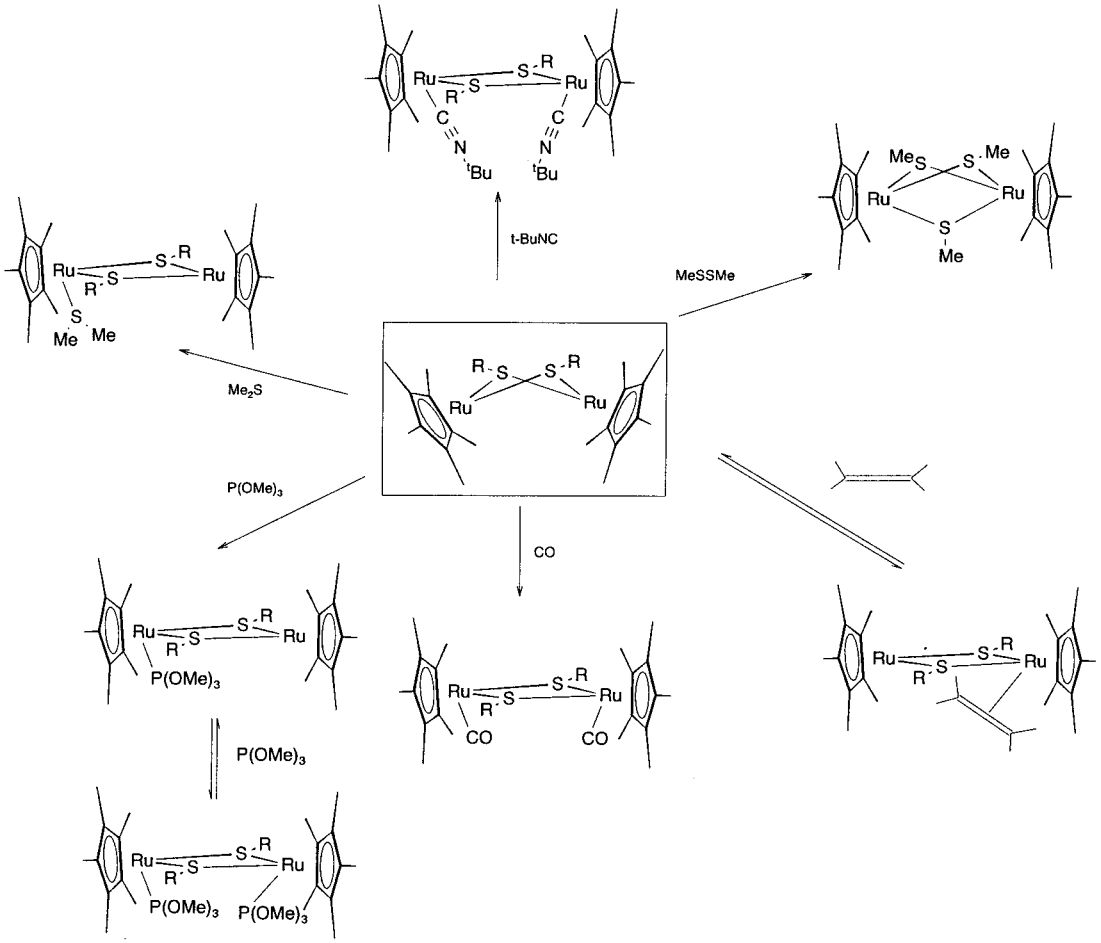
bridging ligands, and finally the hydride from oxidative addition of benzyl sulfide (**12**), Scheme 9.

Other ligands that have been reacted with **3** are shown in Scheme 10.[32] Monoadducts, such as formed with R_2S, $P(OMe)_3$ in stoichiometric amount, and with ethylene, are deduced from the inequivalency of Cp* signals as well as splitting of CH_2 protons when present in a bridging group. According to NMR, intramolecular exchange of L between Ru centers in the monoadducts, if any, is slow.

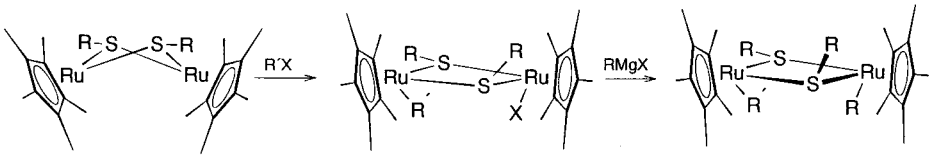
With stronger acceptor ligands bis adducts are formed. The bis CO adduct of $[Cp^*Ru(SEt)]_2$ has been structurally characterized and was shown to have cis configuration with a nearly planar Ru−S−Ru−S rhombus, analogous to the CO adduct of **1** (Table 2). The bis-isonitrile adduct was formulated analogously with a cis configuration. With $P(OMe)_3$, both a mono- and a bisadduct can be generated according to stoichiometry. The propensity for ligand addition in derivatives **3** can be predicted in view of the more open structure found for **3a** in comparison to **1**.[11]

Apart from adduct formation with two-electron ligands, complexes **3** readily undergo oxidative addition with RX or XH including hydrogen (cf. also the reaction with BzSH above). Ru(III) dimers $Cp^*RuR'(\mu\text{-}SR)_2RuXCp^*$ can then be alkylated to symmetrical dimeric $[CpRu(III)R'(\mu\text{-}SR)]_2$ (Scheme 11).[37] Similar complexes are available from $[Cp^*RuCl_2]_2$ and sulfides.[38]

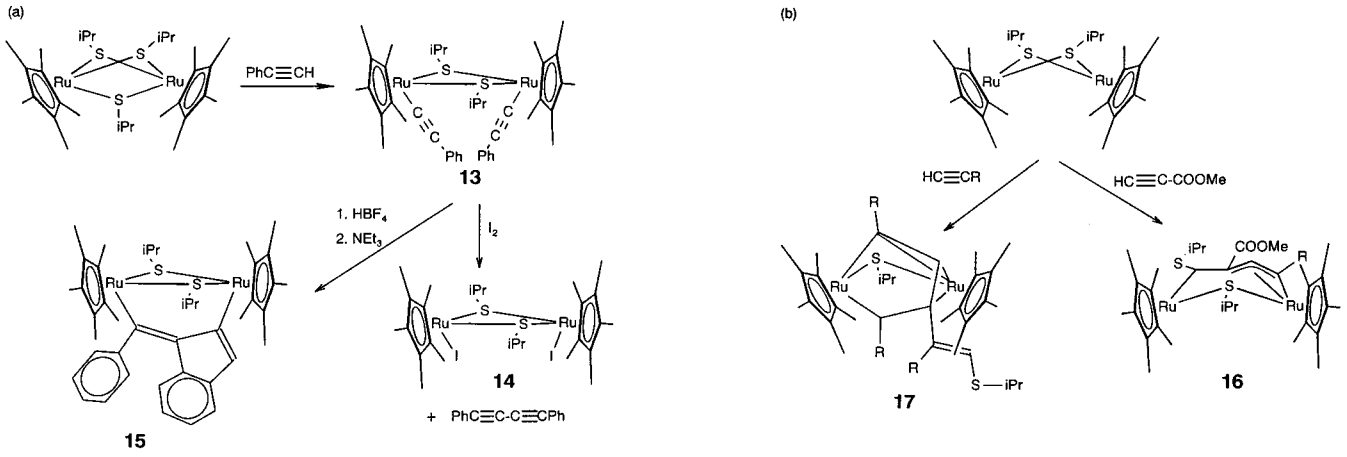
Scheme 10. Adducts of 3



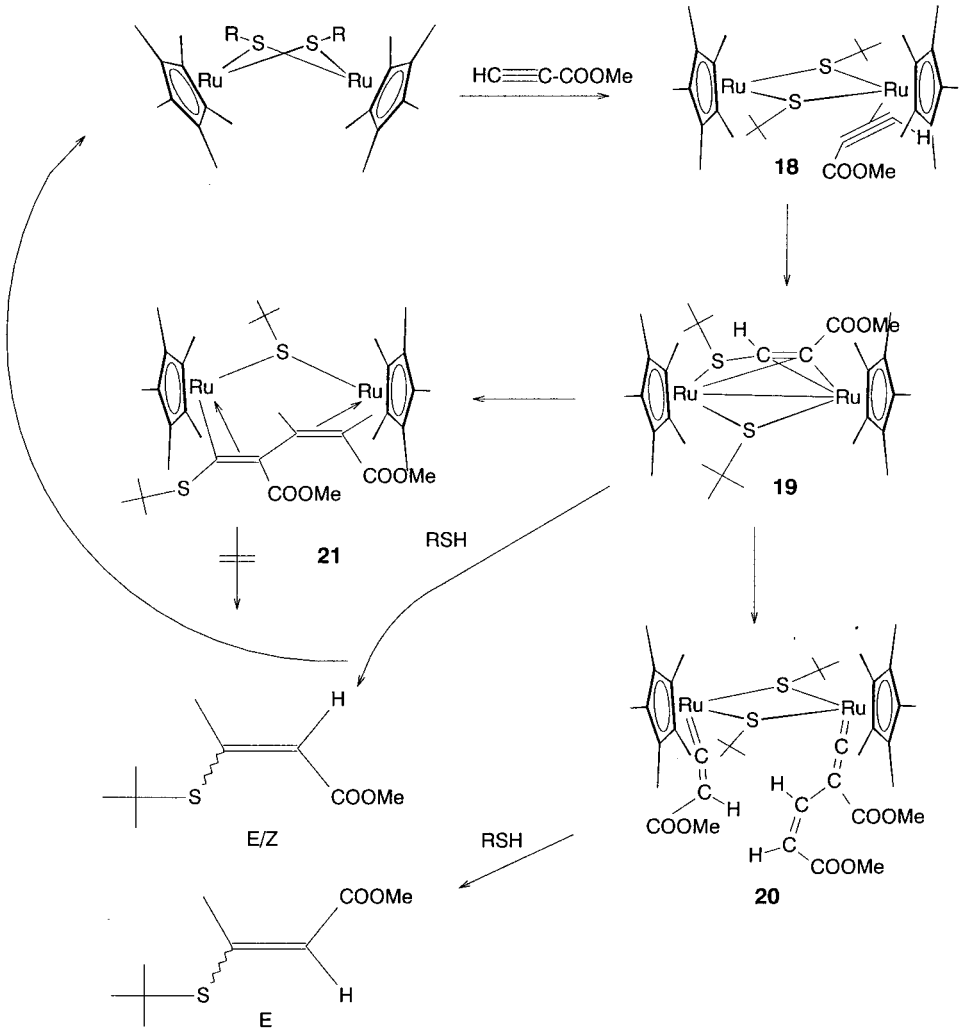
Scheme 11. Oxidative Addition and Alkylation of 3



Scheme 12. Reactions of 3 and Alkynes



Scheme 13. Intermediates in the Catalyzed Formation of Vinyl Thioethers



An extended chemistry using **3c** and alkynes has been developed, mostly by the group of Hidai.[39] A large number of complexes were isolated and structurally characterized which all contain the dimeric $[Cp^*Ru]_2$ moiety coordinated to a chain of two or three alkyne units which is formed in the reaction. An experiment showing multicenter C−C coupling of two acetylides on protonation is shown in Scheme 12a.[39b] Coupling of the two adjacent acetylides in **13**, which involves head to tail connection, occurs on protonation with HBF_4. The initial coupling product is subsequently deprotonated to **15**. A straightforward head to head C−C coupling to give the bisalkyne **14** was effected with iodine. By using a polar alkyne such as HC≡C−COOMe stepwise alkyne coupling could be followed in detail (Scheme 12b). The first step is the insertion of the alkyne into a Ru−S bond (see also **19** in Scheme 13) followed by insertion of a second alkyne (the same or a different one) into the newly formed Ru−C bond to give **16**. Less polar

alkynes such as TolC≡CH or Me_3SiC≡CH preferentially give complexes of type **17** with a carbon ligand formed from the alkyne molecules.[39d]

Adduct formation with polar alkynes to give **18** has been recognized as the first step in the addition of thiols to alkynes to produce *E*/*Z*-vinyl thioethers catalyzed by **3** (Scheme 13).[40] The next step in the catalytic cycle has been shown to be insertion of alkyne into a Ru−S bond of **3**. With **19**, a complex was stucturally characterized that is still active as a catalyst. A second catalytically active species was found in the bis-vinylidene complex **20** which is formed during the reaction. Both complexes react with excess thiol to generate a vinyl thioether and, in the case of **19**, to regenerate **3**. Turnover numbers of about 900 could be demonstrated with the catalyst still being active. Double insertion product **21** in contrast, acted as a stop complex of the catalytic cycle but was formed only if insufficient thiol with respect to alkyne was present in the reaction mixture. The reactions of Scheme 13 constitute one of the relatively rare cases where active catalysts species, i.e., complexes that constitute real intermediates in the catalytic cycle, could be isolated and completely characterized.

Another reaction where **3** acted as a catalyst was found in the disproportionation of hydrazines by **3c**.[41] Whereas the decomposition of $PhNHNH_2$ into $PhNH_2$ and NH_3 was slightly more than stoichiometric with reference to complex concentration, the disproportionation of N_2H_4 into NH_3 and N_2 occurred catalytically with high turnover numbers.

7. Reaction with $P(OMe)_3$ and $HPO(OR)_2$, Ru-Based Tripodal Oxygen Ligands

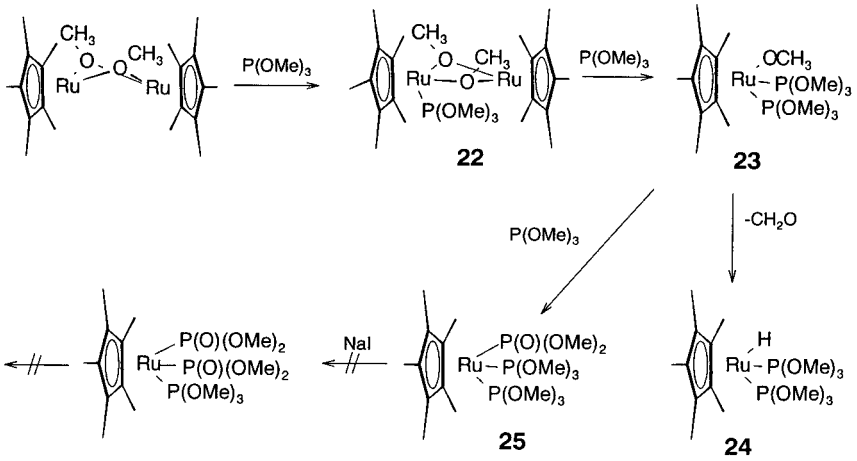
Compared to phosphine addition a more complicated reaction course was encountered when **1a** was reacted with phosphites, in particular $P(OMe)_3$ (Scheme 14).[42] In this case a monoadduct **22**, and a monomeric bisadduct **23** were observed in sequence on addition of increasing amounts of $P(OMe)_3$ to **1a**. The dimeric bisadduct seems not to be present in detectable quantities. On the other hand **23** did eliminate CH_2O to give the hydride **24**—a reaction not uncommon with platinum metal alkoxides in general,[43] but which has been observed in the RuOMe system only in one instance[34]—or undergo an Arbuzov rearrangement to the bisphosphite (phosphonate) derivative **25**. A second such rearrangement to produce the phosphite-bis-(phosphinate) anion and further a tris-phosphinate dianion could not be effected but the target molecule could be successfully synthesized along a different route.

Thus, **1** smoothly reacts with phosphinic acid esters $HPO(OR)_2$ (R = Me, Et) under cleavage and substitution to give $Cp^*Ru(PO(OR)_2)_3H_2$, **26** (Scheme 15).[44] This compound is the diprotonated Ru analogue to the very versatile oxygen tripod ligands $[Cp^*M(PO(OR)_2)_3]^-$, M = Co, Rh, Ir,[45] but is a dianion in its deprotonated form. Stability of **26** in polar solvents is less than that of the Co triad congeners due to rather facile nucleophilic substitution of OR groups at phosphorus (which can be utilized to exchange OR substituents), but when complexed to a high oxidation state central metal, air, and moisture insensitive coordination complexes are formed. Apart from lower valent metal ions (Co^{II}, Cr^{III}, and Fe^{III}), in particular central metals in high oxidation states (viz. Si^{IV},Ti^{IV}, and Nb^{IV}) are stabilized in a perfect octahedral environment through complexation by **26**. A variant is the analogous compound **27** prepared from $HOPPh_2$ which is thermally more stable and has given mono- instead of dicomplexes thus far.[46] Examples of such complexes are collected in Scheme 16.

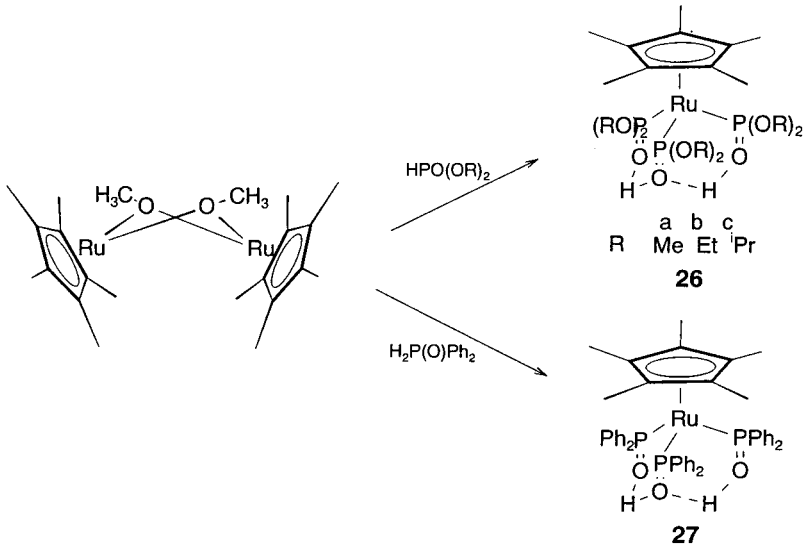
8. Generation and Reactions of Potent 12-VE Cp^*Ru^+ Cations

Among the most versatile transformations starting from **1** can be reckoned the generation of electrophilic solvent complexes $[Cp^*Ru(s)]^+$ **28**. The simplest method to generate these species is by protonation of **1** using a noncoordinating acid. Cations **28** obtained in this way are of varying stability depending on the solvent. When generated in e.g. acetone or nitromethane they appear to exist for some time in solution without decomposition, in CH_2Cl_2 they are less stable but more reactive; in acetonitrile the well-known solvent complex $[Cp^*Ru(NCCH_3)_3]^+$ [47] is formed. Lewis acid (BF_3·Et_2O) can be used instead

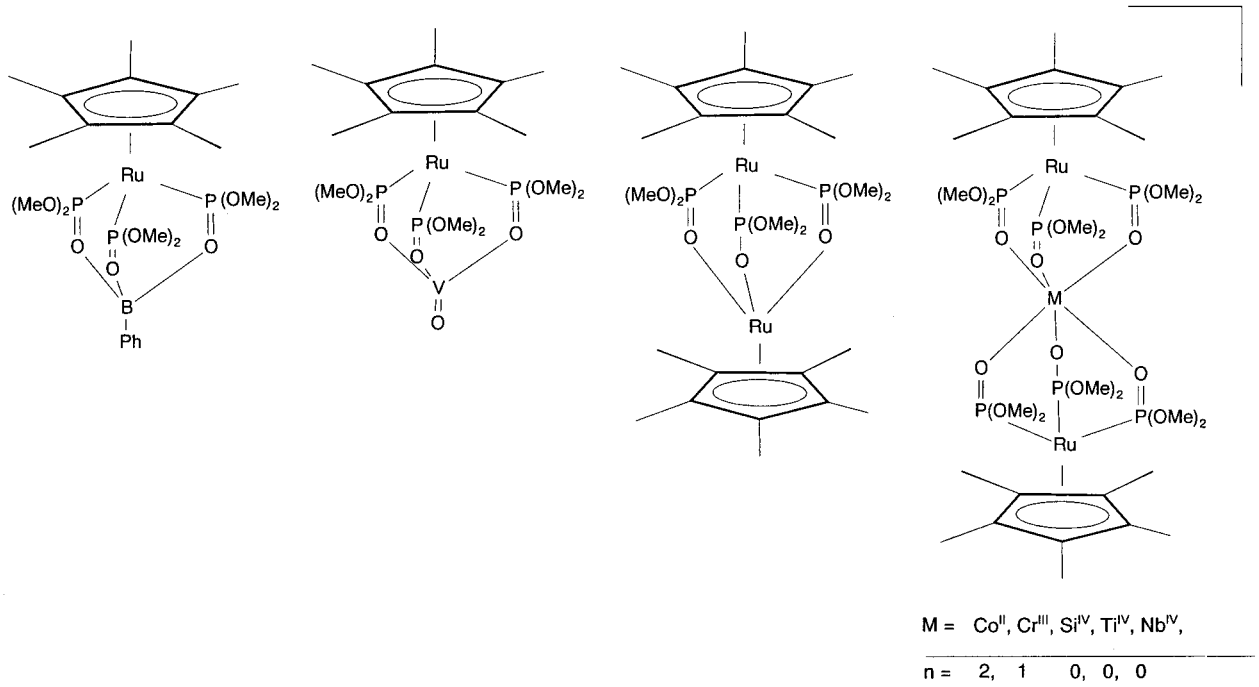
Scheme 14. Reaction of 1a with $P(OMe)_3$



Scheme 15. Preparation of Ru-Based Tripod Ligand



Scheme 16. Ru-Based Tripod Complexes

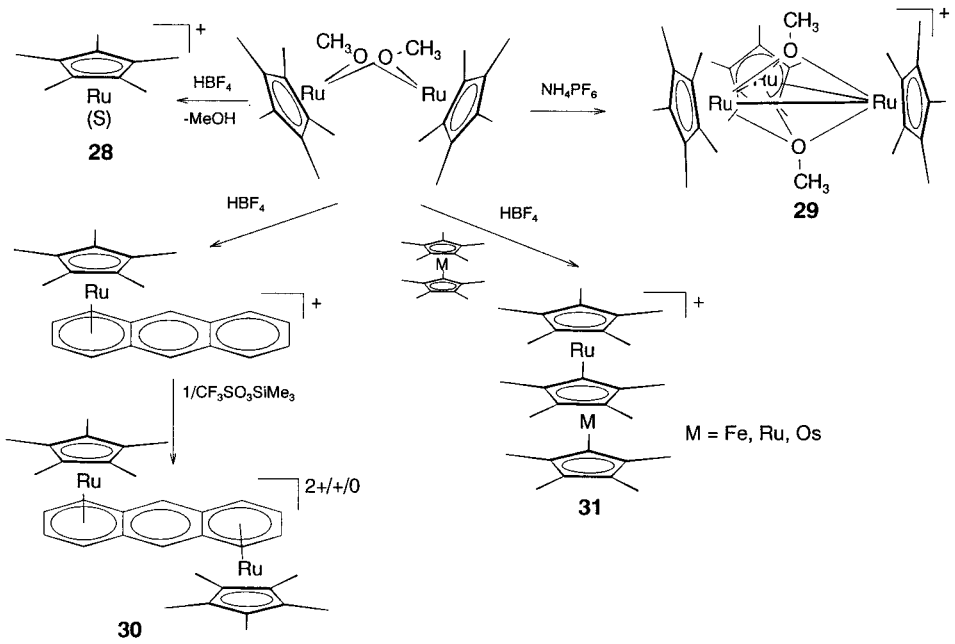


of Brønsted acid and in cases where acidic conditions are undesired $CF_3SO_3SiMe_3$, abstracting Me_3SiOMe, can be employed. Cations **28** are potent but *soft* electrophiles which are prone to complex to virtually any six-electron ligand and, moreover, have been found to generate such ligand systems from more saturated precursors by dehydrogenation and hydrogen transfer.

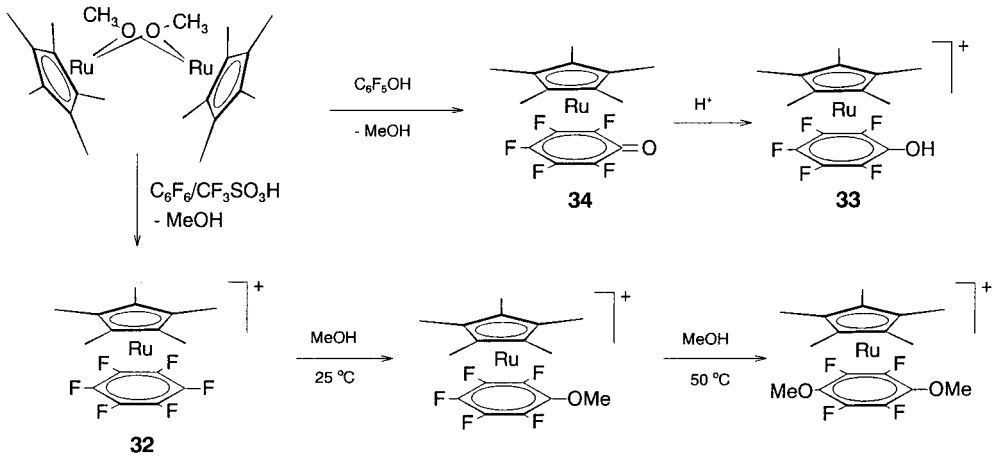
Treatment of **1** with the mild acid NH_4PF_6 in acetone in the absence of any potential ligand gave a trinuclear cationic cluster **29** which can be thought as being generated by attack of a Cp^*Ru^+ on **1**. X-ray structure determination of the cluster revealed a geometry nearly identical to **1** with respect to Ru−Ru bond lengths and Ru−O−Ru bond angles.[10] Similar triangular Ru−Ru−Ru clusters with S, S−*i*-Pr, and Cl atoms in apical position have been generated recently in the group of Hidai.[48]

If **28** is generated in the presence of an arene as a six-electron ligand $[Cp^*Ru(arene)]^+$ complexes are formed in high yield featuring a considerable variety of functionalities on the arene[49] (in fact the only case we are aware where the reaction of **28** with an arene failed to give the sandwich cation was with sterically encumbered hexaethylbenzene). The method is thus a versatile alternative for the synthesis of Cp*Ru(arene) complexes using $RuCl_3/C_5Me_5H$/arene,[50] $[Cp^*Ru(NCMe)_3]^+$,[47,51] $[Cp^*RuCl_2]_2$,[52] or **2**.[53] With this strategy it has been possible to place several Cp^*Ru^+ units on fused polyarenes as is depicted for the anthracene derivative **30** in Scheme 17, where alternative methods have given much lower yields.[54] In contrast to simple $Cp^*Ru(arene)^+$ cations these polyarene cations and, in particular dinuclear dications, are amenable to electrochemical reduction and have given the first 19-VE Ru sandwich complexes

Scheme 17. Generation and Reactions of the Cp*Ru$^+$ Fragment



Scheme 18. Cp*Ru Fluoroarene Complexes



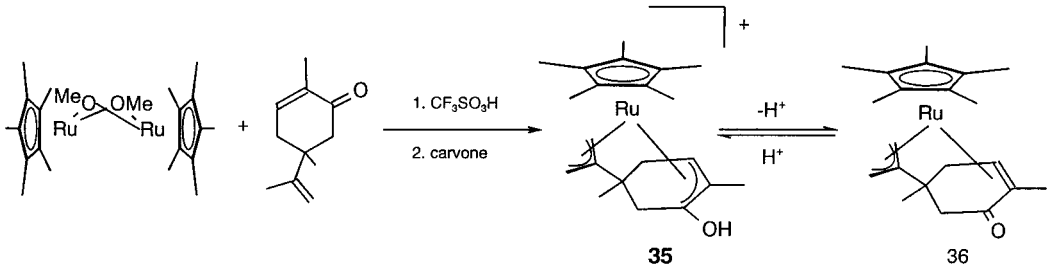
allowing the study of electronic interaction across polyarene systems.[52,54]

The Cp*Ru$^+$ unit is capable of dehydrogenating various cyclic olefins to (complexed) arenes depending on conditions. Cyclohexadiene is converted to benzene at −80 °C. Cyclohexene or methylcyclohexene give benzene and toluene respectively at ambient temperature to 80 °C.[55,56] Enones such as cyclohexenone also give mostly benzene, whereas 4,4-dimethylcyclohex-2-en-1-one in THF at 80 °C ended up in complexed 4-methylphenol.[57] Similarly chlorinated cyclohexanes were converted to benzene or chlorobenzenes along with trimeric clusters (Cp*Ru)$_3$-(μ-Cl)$_2$(μ-Y)(μ-C-Z) (Y = Cl, CO; Z = H, Cl).[57] Hydrogen, water, HCl, and methane respectively have been assayed by GC as accompanying products. Steroids featuring one double bond in the A or B ring (testosterone, progesterone, cholesterol, and dehydroisoandrosterone) are aromatized under forcing conditions (120−140 °C) with concomitant loss of the 18-methyl group.[58] The potential of **28** as a strong but soft lewis acid was further demonstrated by the group of Chaudret in reactions with linear olefins, which gave, apart from cyclization to the benzene sandwich, products of olefin oligomerization as well as metathesis.[59]

With **28** generated in the presence of group 8 metallocenes, Cp′$_2$M, tripledecker cations [Cp*Ru-Cp′MCp′]$^+$ (**31**) are obtained.[60] A reaction closely related to the ones just mentioned is the action of anhydrous $ZnCl_2$ on the acac derivative [Cp*Ru-(acac)]$_2$ (generated from **1** and acacH in high yield, section 11) in ether in the presence of a six-electron ligand, which has given cation complexes such as [Cp*Ru(cycloheptatriene)]$^+$ or [Cp*Ru(pyrrole)]$^+$.[61] Moreover was **28** shown to give Cp*Ru(thiophene)$^+$ with thiophene.[49]

A particular intriguing application of this technique consists in the synthesis of fluoroarene complexes. Thus C_6F_6, formerly attached to metal fragments only via metal atom synthesis, has been easily complexed to Cp*Ru$^+$ in this manner. The ensuing hexafluoroarene cationic sandwich **32** is susceptible to nucleophilic exchange of one or two fluorine atoms (in para position) by e.g. methanol at ambient temperature (Scheme 18). X-ray structure determination

Scheme 19



of the pentafluorophenol derivative [Cp*Ru(C_6F_5OH)] CF_3SO_3 (**33**) (formed by accidental hydrolysis of the hexafluorobenzene cation) which can be obtained alternatively from **1** and pentafluorophenol via the fluorinated oxocyclohexadienyl sandwich complex **34** revealed a hexahapto bonded fluoroarene ring with bond distances comparable to those of other Cp*Ru arene complexes.[62]

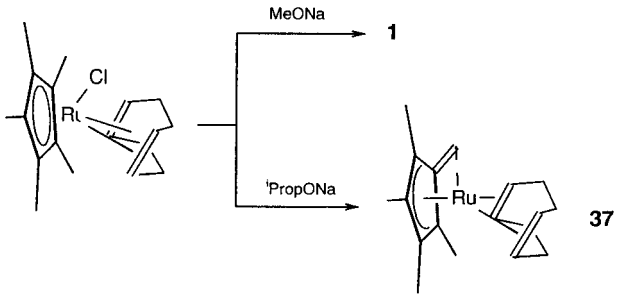
The strong preference of the 12 VE Cp*Ru^+ moiety to bind to carbon six-electron ligands is not restricted to cyclic π-systems. In our search for π-complexation with a high degree of *si/re* stereoselectivity (cf. section 12) we have reacted the naturally occurring cyclohexenone *carvone* with Cp*Ru^+ generated from **1a** and acid (Scheme 19). A bis-allyl complex **35** was produced, where hydrogen rearrangement has occurred in the ring as well as a dehydrogenation of the isopropenyl group. (Care has to be taken in the reaction not to bring the carvone in contact with the acid used to generate **28**, otherwise rapid aromatization to *carvacrole* and nonstereospecific complexation of the latter will ensue.[63]) The cation **35** is easily and reversibly deprotonated to the corresponding allyl enone complex **36**. According to NMR and confirmed by X-ray analysis **35** consists of one single diastereoisomer (or one enantiomer) which is also the case for **36**.[64]

9. Reactions with Olefins: C–H Activation and Dehydrogenation

As mentioned above, monoolefins do not generally add to **1** to form stable adducts, nor did diolefins or dienes react with **1** in the sense of adduct formation. To investigate the possible existence of a diolefin complex like Cp*Ru(COD)OR, the alkoxo analogue of the chloro complex Cp*Ru(1,5-COD)Cl, the latter was treated with alcoholates of varying size. Methanolate gave back **1a** with loss of the olefin. If bulkier alkoxides were used, HCl was elimiated between Ru and a methyl group of the Cp* ligand to give Ru(1,5-COD)(1,2,3,4-tetramethylfulvene) (**37**) (Scheme 20).[65] Unlike phosphines, with the weaker electron donation from a weaker σ-donor such as an olefin is counteracted by the OR π-donor at Ru to a such an extent as to prevent formation of stable Cp*Ru(OR)(olefin) complexes.

A stable alkoxo–olefin complex could be obtained only in the case of an olefinic alcohol as bridging alkoxide (Scheme 21).[66] Trying several butenols, pentenols, and hexenols the proper binding geometry was provided only with 3-butenol. Complex **38** thus formed is a dimer like **1** with two olefinic double

Scheme 20. Reaction of Cp*Ru(COD)Cl



bonds complexed cis to Ru. Again the geometry of the Ru–O–Ru–O rhombus was altered to almost planar with noninteracting Ru···Ru and rather long Ru–O distances (Table 2). Bond distances to olefinic carbons (2.16(1), 2.13(1) Å respectively) and bond lengths in coordinated C=C (1.42(1) Å) are indicative of a high degree of back-bonding.

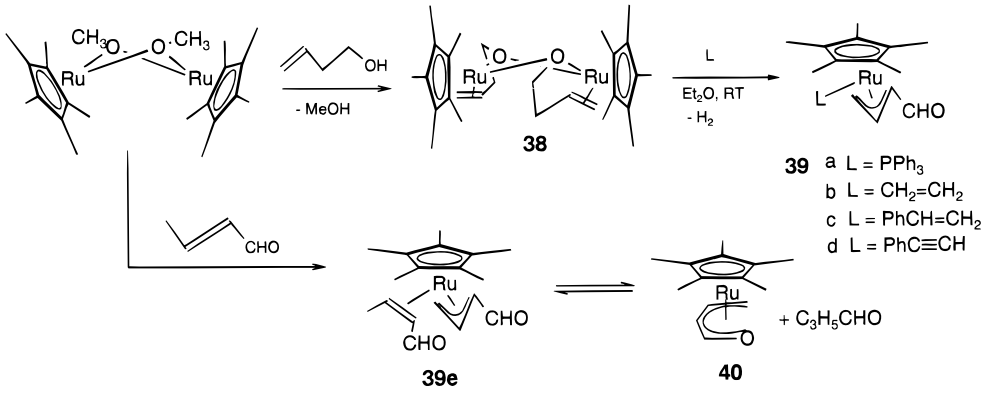
Treatment of the butene oxide complex **38** with different two-electron acceptor ligands L converted the olefinic alkoxide under dehydrogenation into an allyl aldehyde ligand generating complexes Cp*RuL(η^3-C_3H_4CHO), **39**.[66] In the case of PPh_3 the intermediate mononuclear phosphine butenoxide complex was isolated from the room temperature reaction, which subsequently dehydrogenated at 70 °C to **39a**.

A related olefin activation was observed if **1** was reacted with croton aldehyde giving **39e**, L = MeCH=CHCHO.[67] An equilibrium between the allylic adduct **39e** and the oxadienyl complex **40** is manifest in the NMR. Such Ru oxadienyl complexes are known but have been isolated only with stabilizing Me groups in 2,4 position.[68]

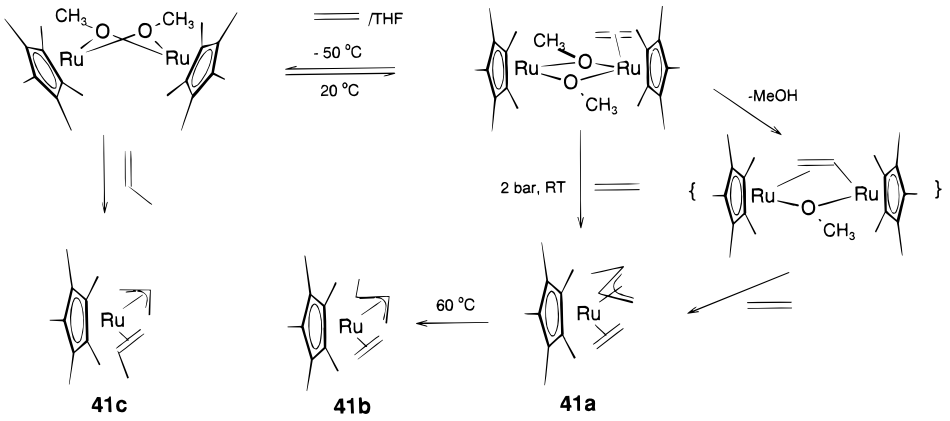
As has been mentioned above, ethylene adds reversibly to **1** at low temperature. When solutions containing **1** and excess ethylene are kept at ambient temperature the *syn-exo* isomer **41a** was isolated (Scheme 22). The thermodynamically more stable *syn-endo* form **41b** formed on heating **41a** to 60 °C. Propene, in a similar reaction, gave the allyl propene complex **41c**.[69]

In the case of ethylene, coupling of two molecules of ethylene in the Ru coordination sphere has taken place, whereas propylene obviously forms the allyl simply by dehydrogenation. Although direct coupling of two ethylene molecules at Ru and subsequent dehydrogenation of the butene is a mechanistic possibility, a more plausable alternative is the coordination of but one ethylene and elimination of methanol to form a σ-vinyl intermediate. The small amount of polyethylene observed in the reaction can

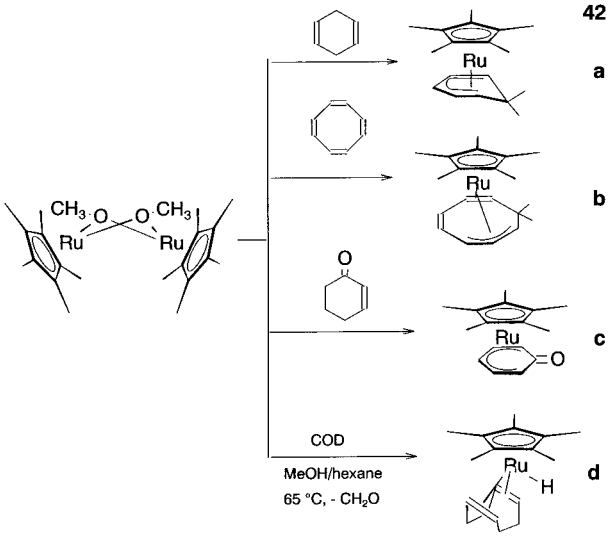
Scheme 21. Formation and Reaction of Butenol Complex



Scheme 22. Reaction of 1 with Ethylene and Propylene



Scheme 23. Reaction of 1 with Cyclic Olefins



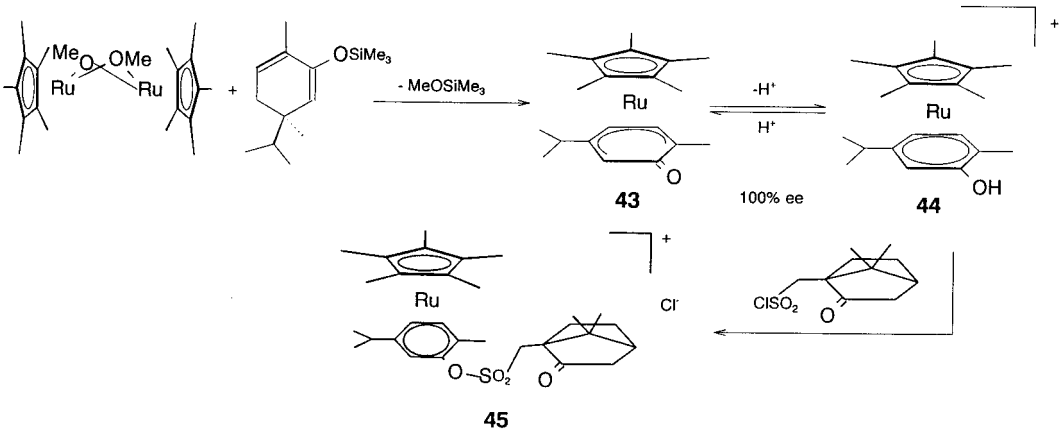
originate from this stage, whereas isomerization of the primary insertion product of ethylene into the Ru−vinyl bond leads to the allyl complex.

Similarly reactions assembled in Scheme 23 proceed smoothly at ambient temperature where the cycloolefinic ligand is dehydrogenated or hydrogenated so as to provide the proper hapticity for an 18 VE sandwich complex. Cyclohexadiene is converted to the cyclohexadienyl ligand in **42a**, whereas cyclooctatetraene is hydrogenated to give **42b**. Even cyclohexenone is aromatized to the oxocyclohexadienyl complex **42c**, the same that was obtained, albeit in lower yield, from deprotonation of the phenol cation complex **51** (section 10). The reaction in this case was conducted using cyclohexenone/Ru about 2:1 where the excess cyclic olefin is hydrogenated. The initial formation of methanol can be detected if the reactions are monitored by ^{1}H NMR (shift of the OMe signal from 4.8 to 3.5 ppm). Thus, **1** or its analogues in every instance transforms dienes and activated olefins into the five-electron ligands needed to complete the 13-VE shell of a neutral Cp*Ru fragment via hydrogen transfer to OMe, eventually to excess olefin if more than one hydrogen atom has to be removed. Evidently, 1,5-cyclooctadiene sets too high a barrier for dehydrogenative aromatization, thus stabilization through hydride formation as an alternative occurs. (Note, however, conversion of 1,5-COD to complexed cyclohexatriene with the cation fragment **28**.)

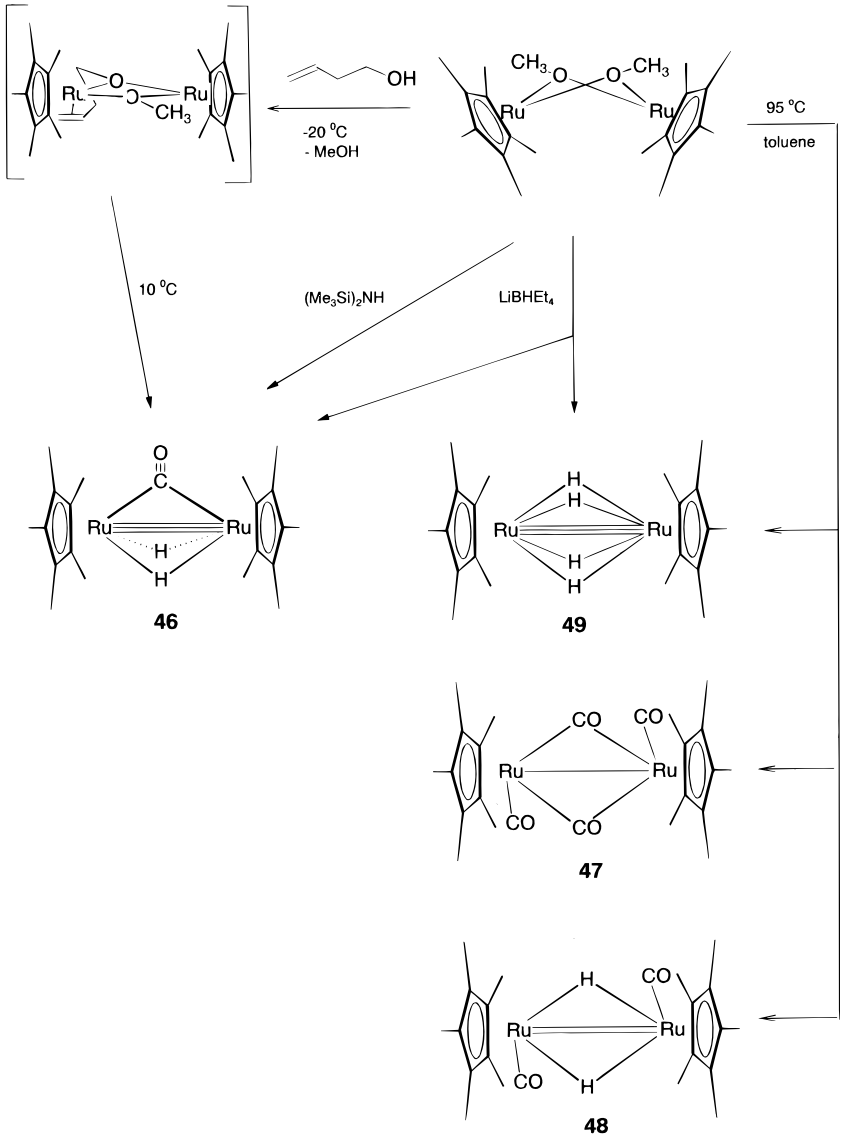
Mechanistically hydrogen transfer from an allylic or even a vinylic (viz. ethylene) position to the metal followed by transfer to an oxygen or a second olefin is the most plausible assumption to explain these reactions.

This dehydrogenative complexation has found application in the reaction of **1** with the silylenol ether derived from *7-dihydrocarvone* as depicted in Scheme 24. Different from the reaction of the natural carvon featuring the exocyclic double bond, in this case dehydrogenation occurred only in the six-membered ring yielding the oxacyclohexadienyl complex **43** or, after protonation, the phenol cation **44**. Derivatization at the oxygen with *(S)*-camphonesulfonyl chloride to give a *(S)*-camphonesulfonyl ester **45** revealed

Scheme 24. Transformation of Central into Planar Chirality in Dehydrogenative Complexation of Dihydrocarvone Silylenol Ether



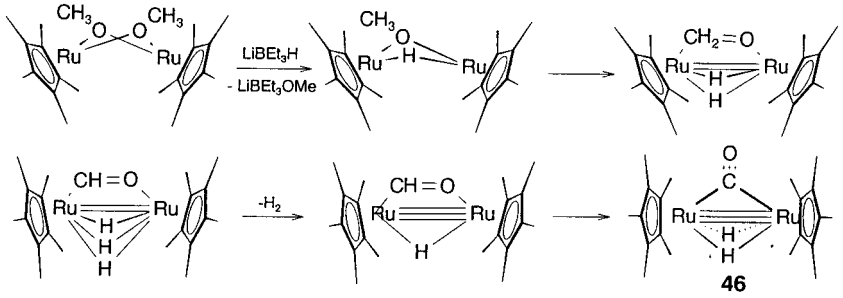
Scheme 25. Decomposition of 1 to Carbonyl Hydrides and Hydride Complexes



the presence of but one diastereoisomer, that means fully enantioselective complexation, where the attack of the Cp*Ru moiety is governed by the isopropyl group and the central chirality at this carbon has been transformed completely into planar chirality of the π-complex.

During the synthesis of the butenoxide complex **38**[66] we had made the observation that the exchange reaction between **1** and 3-butenol had to be run at the lowest possible temperature where the system reacted (−20 °C), otherwise decomposition into a different product was the main reaction. However,

Scheme 26. Formation of 46 by Nucleophilic Substitution of OMe for H



after crystallization the compound turned out to be reasonably stable at ambient temperature even in solution. The product formed at higher temperature in this and many other reactions was a dimeric carbonyl hydride $Cp^*Ru(\mu\text{-}CO)(\mu\text{-}H)_2RuCp^*$ (**46**) which had previously been obtained in low yield from the photolysis of $[Cp^*Ru(\mu\text{-}CO)_2]_2$ in the presence of hydrogen.[70] This compound has been found to be formed under a wide variety of conditions e.g. when **1** was treated with pentenol or hexenenol, with amino alcohols or with phenylacetylene. All these reagents bind to **1** or exchange the OMe group in **1a** (as can be seen from a color change on mixing the reagents) but insufficiently stabilize the dimeric structure. It was found that also thermolysis of **1** at 95 °C in toluene gave **46** as the principal decomposition product along with smaller quantities of hydrido dicarbonyl **48** and dicarbonyl **47** (Scheme 25).[66]

A high yield synthesis for **46** was found when **1** was reacted with $(Me_3Si)_2NH$. Labeling of the OMe group as $O^{13}CD_3$ and running the reaction with $(Me_3Si)_2NH$ revealed that both, bridging hydrogen and CO in **46** derive from the bridging OMe group.[71]

The various reactions leading to **46** have one feature in common: an addition product is formed that counteracts O−Ru π-bonding but is not strong enough to stabilize the dimer. Alternatively, one OMe bridge is substituted for a bridging group that has no or insufficient π-donating capabilities. In the course of the synthesis of **38** it is the monosubstitution product with one OMe and one O-butenyl group in the bridge which is believed to decompose into **46**.

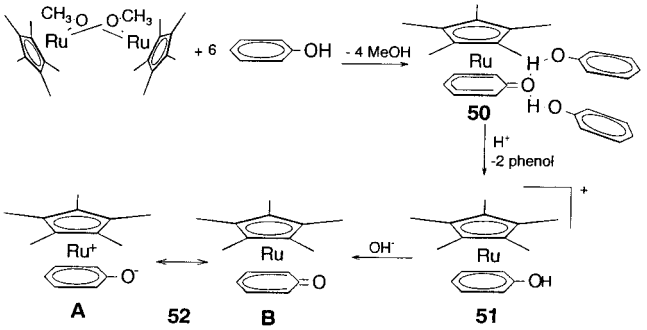
The hypothesis is further corroborated by the products found from treatment of **1** with hydride ($LiBH_4$, $LiBHEt_3$). A molar ratio of $LiBHEt_3$ to **1** as 1:1, sufficient to substitute one OMe group from the dimer, gave mostly **46**, whereas with excess hydride reagent the known dinuclear tetrahydride $Cp^*Ru(\mu\text{-}H)_4RuCp^*$ [72] (**49**) was formed in high yield. (Compounds **46** and **49** are isostructural with nearly identical lattice parameters and near identical Ru−Ru distances.[71,73]) Note that in the former case using hydride and **1a** deuterium labeled in the OMe group, bridging hydrogen in **46** still contains deuterium. A possible mechanism for the formation of **46** with hydride as the nucleophile is given in Scheme 26. A similar mechanism has been suggested for the reaction of $Ru(H)Cl(PPh_3)_3$ with NaOMe leading to $Ru(H)_2(CO)(PPh_3)_3$ via the nonisolated methoxide $Ru(H)(OMe)(PPh_3)_3$.[74]

10. Phenol Complexes, σ- vs π-Complexation

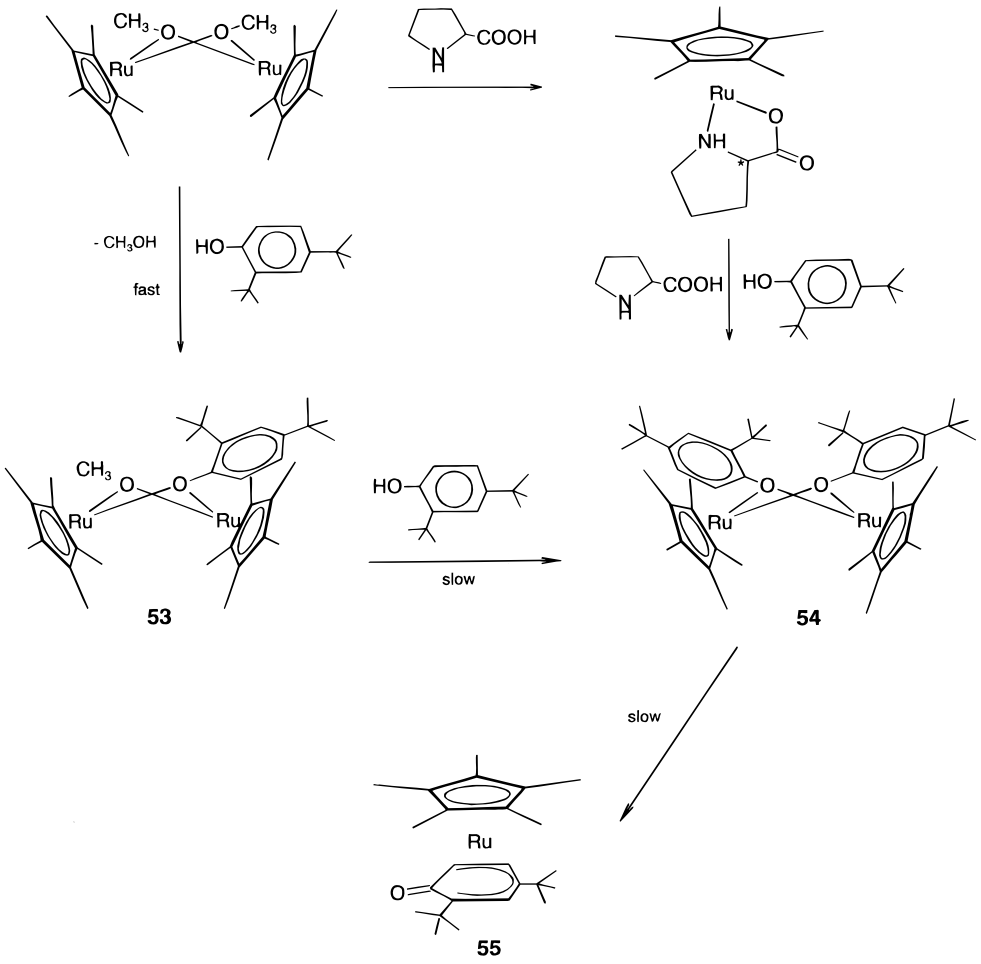
Phenol and phenol derivatives can be anticipated to complex to Cp*Ru in two ways: (i) as a bridging alcohol (designated σ-complex) or (ii) in a sandwich-like fashion either as oxacyclohexadienyl or in the protonated form as π-complexed phenol. The enhanced acidity of phenol ($pK_a \cong 12$) in comparison to aliphatic alcohols ($pK_a = 15-20$) would favor σ-complexation, according to the rule established for aliphatic alcohols, whereas the high propensity of the Cp*Ru moiety to bind arenes as six-electron ligands argues for π-complexation. Under acid conditions the latter complexation as cationic $[Cp^*Ru(phenol)]^+$ is to be expected, without extra acid both possibilities have to be considered.

Whereas **28** (as a MeOH solvate) reacts with phenol to the cationic phenol sandwich **51**,[49] the methoxo complex **1**, when reacted with phenol in ether,[49c] required 3 mol of phenol per Cp*Ru for complete reaction. The reaction product had the composition $Cp^*RuC_6H_5O{\cdot}2C_6H_5OH$ where extra phenol is released neither in solution nor in vacuo or by chromatography. Determination of the molecular structure disclosed a π-complexed *planar* oxocyclohexadienyl ligand in **50** where two phenol molecules are firmly hydrogen bonded to the oxygen. C−O bond distance in the oxocyclohexadienyl is 1.284(7) Å, intermediate between a single and a double bond. The most intriguing feature of the structure is the planarity of the oxocyclohexadienyl at variance with other examples of $\eta^{5/6}$-oxocyclohexadienyls, in particular the 2,6-di-*t*-Bu derivative, obtained from **2** with 2,6-di-*tert*-butylphenolate.[9] A rationale for this exception is the high stabilization of the zwitterionic oxy cation A in Scheme 27 through hydrogen bonding which leads to perfect η^6-coordination and as a conse-

Scheme 27. Phenol and Oxocyclohexadienyl Complexes Derived from 1



Scheme 28. Phenolic σ-Complexes



quence to planarity of the cyclohexadienyl. Hydrogen bonding to the oxygen of late transition metal alkoxo complexes is not uncommon and one closely related example is provided by an intramolecular H-bond in the chelating phenolphosphine complex Cp*Ru(η^2-*P,O*-PPh_2-1-(2-OC_6H_4))(PPh_2-1-(2-HOC_6H_4)).[75]

On protonation, **50** gives the cationic phenol complex [Cp*Ru(η^6-phenol)]$^+$ **51**. The neutral, phenol free, oxocyclohexadienyl complex **52** can be obtained by action of base on either **50** or **51**. It has, however, proved difficult to extract it from aqueous solution due to a strong tendency for hydration. The complex is best obtained from treatment of **1** with cyclohexenone in hexane (see section 9) which gives the compound in high yield and anhydrous form. This is indicated by a chemical shift difference between aromatic protons (benzene-d_6), a measure for the participation of form B, much greater than in samples obtained from the phenol complex by deprotonation.

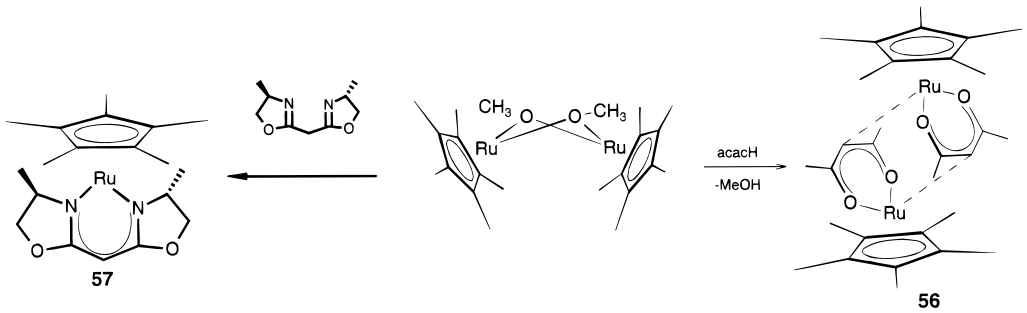
Variation of the phenol to include salicylic aldehyde or α-keto derivatives opens a further bonding possibility, i.e., chelating σ-complexation through two oxygen atoms such as in the acetylacetone complex (see section 11). In any case π-complexes were formed exclusively either as an η^6-arene or as an η^5-cyclohexadienyl sandwich. Even perfluorinated phenols did complex as π-arenes (see section 8).

The first phenolic σ-complex was detected recently[76] when 2,4-di-*tert*-butylphenol was used as a ligand. Reaction of the Li-phenolate with Cp*Ru(proline) (see section 12) surprisingly gave the characteristic cherry red, air-sensitive solution of a Cp*Ru(OR) dimer. NMR exchange experiments between **1a** and 2,4-di-*tert*-butylphenol then showed the stepwise formation of first mixed Cp*Ru(μ-OMe)(μ-2,4-di-*tert*-butylphenol)RuCp* **53** and successively Cp*Ru(μ-2,4-di-*tert*-butylphenol)$_2$ RuCp* **54**, the latter slowly rearranging to the sandwich complex **55**. Compound **53** has been characterized by X-ray structure analysis and exhibits a geometry very similar to the one found for **1a**.

Further experiments using **1a** and various substituted phenols in benzene-d_6[76] revealed σ-bridged intermediates for e.g. 2-methyl-4-isopropylphenol (carvacrole) and even for unsubstituted phenol prior to the formation of the π-oxocyclohexadienyl complex. In these latter cases, however, σ-complexes cannot be isolated due to relatively fast rearrangement into π-complexes.

The finding may be rationalized (post festum!) as follows: the π-complex, whether cationic phenol or neutral oxocyclohexadienyl, appears to be the thermodynamic more stable isomer for any derivative. Two bulky substituents in ortho position of the phenolic arene strongly destabilize the σ-phenol complex due to steric interference of the "downward" pointing *t*-Bu group with the Cp* methyl groups in the folded geometry (Scheme 28). As a matter of fact,

Scheme 29. Formation and Structure of the acac Complex



2,4,6-tri-*tert*-butylphenol did not react with **1a**. If only one *tert*-butyl group is present in the ortho position this can point into the empty space "upside" giving little steric interference but still helping to rise the kinetic barrier for $\sigma \rightarrow \pi$ rearrangement.

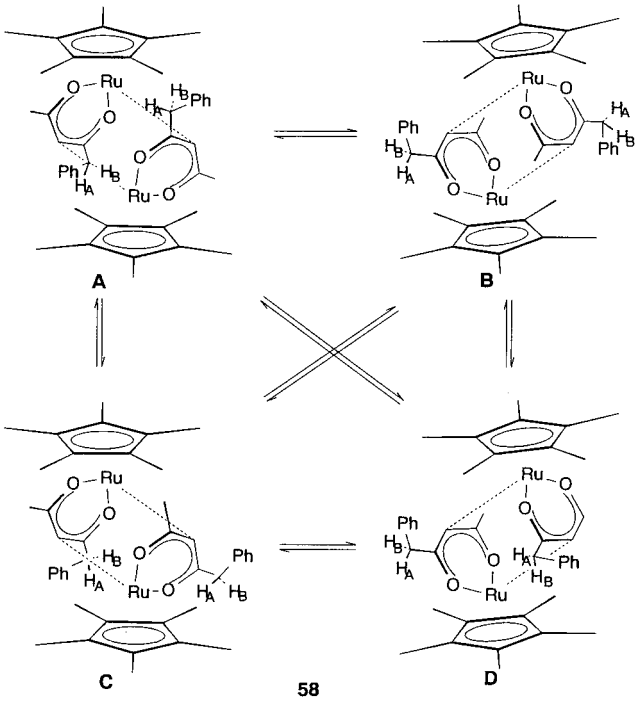
11. Chelating Ligand Derivatives

A further modification of the motive [Cp*Ru(OR)]$_2$ consists of the introduction of β-diketonate anions such as acac$^-$ or similar monoanionic bidentate ligands (acetic acid ester, malonic acid ester a.o.) featuring two oxygen (or other heteroatom) binding sites (Scheme 29). In fact, **1** reacts smoothly with acacH to give a complex Cp*Ru(acac)[77] **56**, which by X-ray structure analysis has been shown to be a dimer in the solid state where the two molecules are interlinked by two long Ru−C bonds of 2.42 Å to the central acac C atom.[78] We recently obtained an analogous complex **57** featuring the C_2-symmetric chiral ligand methyl(bis-5-methyltetrahydrooxazol). In this compound Me groups at the tetrahydrooxazole,[79] which should be diastereotopic in a dimer, show a single absorption in the NMR (toluene-d_8, see below) down to low temperature. We therefore, in this case, suggest a monomeric complex in solution.

The derivative Cp*Ru(Phacac)[80] (**58**), due to the bent conformation around Ru in the dimer, has diastereotopic benzylic hydrogen atoms in a frozen conformation. Two possible dynamic processes, depicted in Scheme 30, interconvert these protons H_A and H_B. The horizontal processes corresponds to dissociation into monomers and reformation of the dimer. Since the monomer probably has a planar C_{2v} configuration[81] or may undergo rapid inversion at the metal, benzylic protons will be statistically interchanged in this automerization. Dissociation and reclosure of the dimer can further lead to cis/trans isomers, vertical arrows in Scheme 30, with respect to the benzylic group in the dimer. Both processes are observable in VT NMR with rate constants depending critically on the solvent.

In toluene splitting of the benzylic protons into a symmetrical AB pattern occurs at about −60 °C. At still lower temperature further splitting of the signals, in particular of the ortho protons of the phenyl group due to freezing out of the vertical equilibrium is evident. Although coalescence temperatures for both processes are different, due to the smaller shift difference within the cis/trans isomers, the barrier is identical within the limits of error and amounts to 43 kJ/mol (E_a). Molecular weight determination in toluene has confirmed the dimer in this solvent,

Scheme 30. Interconversion of Isomers in 57

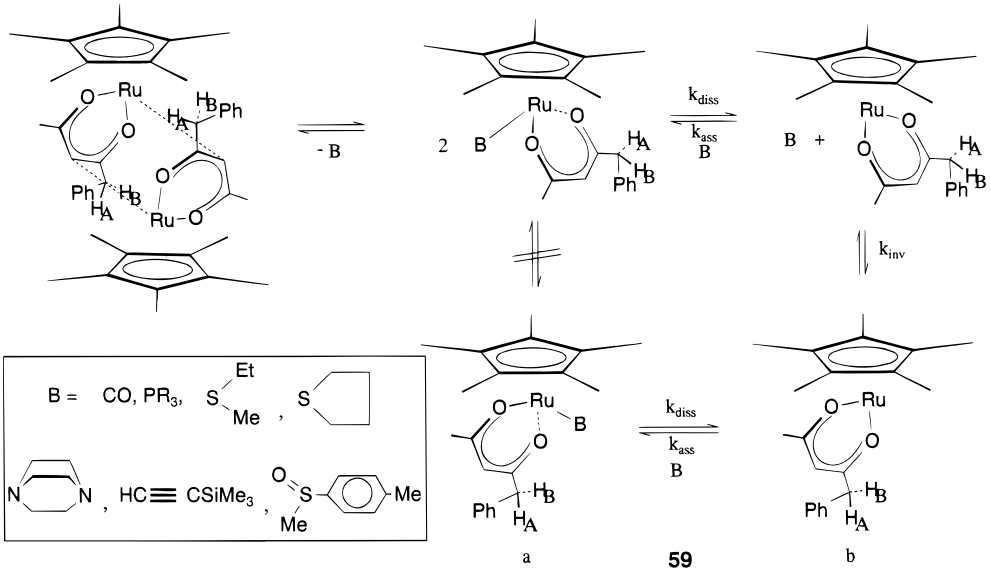


thus the measured barrier to inversion reflects the energy of dissociation into monomers which may be roughly equated to twice the Ru−C_2 bond energy in the dimer.

In CH_2Cl_2, a sharp AB pattern for benzylic protons, visible at low temperature, persists up to −10 °C when the compound starts to decompose in this solvent. We interpret this behavior as evidence for cleavage into monomers stabilized by coordination of the solvent. Similar complexes with CH_2Cl_2 had been identified in closely related [CpRe(PR_3)(NO)]$^+$.[82]

In addition to CH_2Cl_2 a selection of donor/acceptor molecules B, have been added to **58**. In each case the barrier for interconversion of benzylic protons rises with respect to the base free toluene solution, indicating adduct formation with B. As outlined in Scheme 31, B cleaves the dimer into monomeric adducts **59a**. However, since inversion of the Phacac ring leading to interchange of benzylic protons is restricted to the base free monomer **59b** the inversion barrier in these systems depends on the association equilibrium and reflects the strength of the adduct. Using a slight excess of B over the stoichiometry of a 1:1 adduct allows independent monitoring of the adduct equilibrium. Adduct strength falls in the order B = PPh_3 ≈ CO > THT ≈ MeSEt > 3-NC-

Scheme 31. Adduct Formation and Inversion of 58



pyridine > DABCO. Notably π-acceptor bases such as PPh_3 and CO coordinate with relatively strong bonding to the unsaturated Cp*Ru(acac), whereas pure σ-donors, such as the diazabicyclooctane form relatively weak adducts.

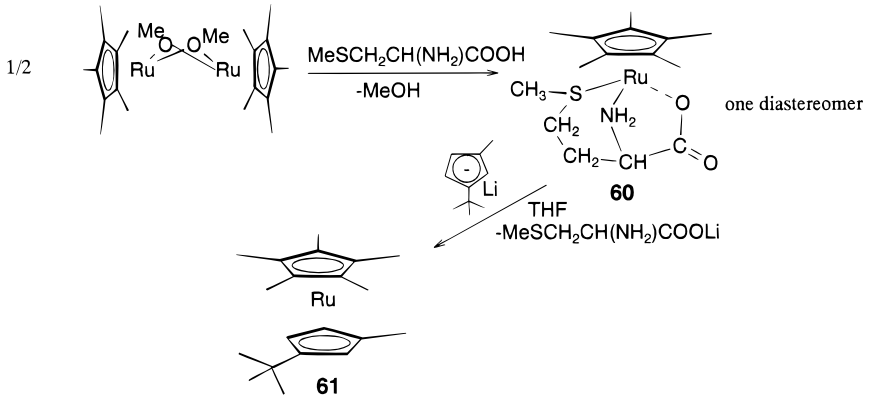
Adducts **59a** with symmetrical bases are enantiomers where the inversion process corresponds to epimerization. Those with unsymmetrical bases are diastereomers and, due to rapid equilibria at ambient temperature, the frozen structures observed in the NMR at low temperature are diastereomeric mixtures and directly indicate the degree of diastereoselectivity in the base addition.

12. Precursors for Enantioselective π-Complexation

The unique ability of **1** to react with σ-ligands of low proton acidity has opened the way to Cp*RuL_σ complexes which would be difficult to obtain by other routes. Whereas reaction with simple carboxylic acids has never led to isolable products, amino acids, e.g. methionine and proline by reaction of **1a** with the acid gave isolable complexes of composition Cp*Ru(amino acid) which do not contain further coligands. According to NMR methionine is bound through three atoms, O, N, S making Ru formally coordinatively saturated. Although no crystal structure is yet available (crystals obtained were heavily disordered) when starting from enantiomerically pure amino acid, the NMR shows only one set of signals, indicating the formation of one single diastereoisomer (note that for methionine there could be four diastereoisomers for each enantiomer of the amino acid due to two possible arrangements around Ru and a new chiral center created at S on complexation). This means that configuration of the amino acid determines all other configurations of the complex. In the case of proline, where only two binding sites are available, the complex Cp*Ru(proline) is coordinatively unsaturated. The yellow, air-sensitive (pyrophoric!) crystals obtained from THF are soluble only in coordinating solvents such as acetonitrile. In methanol an equilibrium with **1** and free amino acid exists. This behavior suggests that the complex may be a polymer in the solid with additional bonding of the metal to a carboxylic oxygen of a neighbor molecule. The stereochemistry in that case is less well-defined, we assume, however, predominance of one diastereoisomer.

These amino acid complexes could be utilized to demonstrate an enantioselective π-complexation. Cyclopentadienylation of Cp*Ru(amino acid), e.g. **60**,

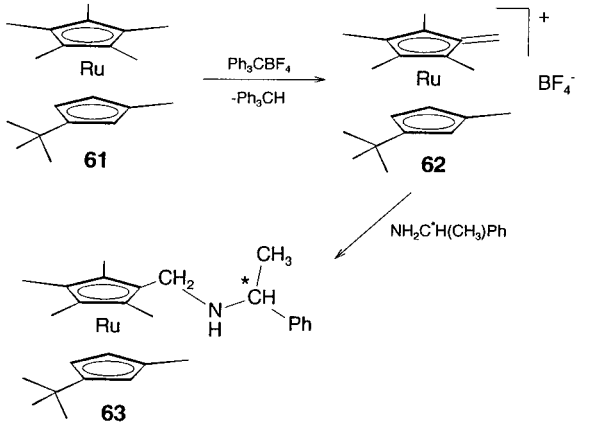
Scheme 32. Enantioselective Synthesis of Planar Chiral Ruthenocens



using a prochiral cyclopentadienide with substituents differing in size, occurs under very mild conditions (around −20 °C) and leads to ruthenocenes, e.g. **61**, with planar chirality in high enantiomeric excess (Scheme 32). This reaction seems to be the first demonstration of such an enantioselective π-complexation where chemical and optical yields are in a practical range.[83] A problem in this particular case has been the determination of the optical purity. It was solved by a derivatization reaction. Ruthenocenes featuring a Cp* ligand undergo facile hydride abstraction to fulvene cations **62**.[84] It was found that even in the presence of methyl groups at the other ring, hydride abstraction is confined to the Cp* ligand giving one single fulvene in all cases. These cationic fulvene complexes are amenable for addition of nucleophiles at the exocyclic C=CH$_2$ group to regenerate a ruthenocene.[84]

By using the readily available α-phenylethylamine (as the (*S*) enantiomer), stable diasteromers **63** are formed which show doubling of NMR signals due to diastereoisomerism at Ru (Scheme 33). In the most

Scheme 33



favorable case, where 1-*tert*-butyl-3-methylindenyl was used as the prochiral Cp, >95% optical induction was established by NMR integration. By using this methodology it was assessed that the other enantiomer of the amino acid induces the other enantiomer of the ruthenocene with the same cyclopentadienide.

Absolute configuration of a chiral ruthenocene was determined via X-ray structure of the fulvene salt [(Ru(C$_5$Me$_4$CH$_2$)(1-*tert*-butyl-3-methylindenyl)]BF$_4$ derived from it.

13. Conclusion

The body of reactions outlined in this account, all originating from the methoxo complex **1** or derivatives directly derived from it characterize a system of, in its kind unprecedented, synthetic versatility. Due to the coordinatively unsaturated character of the dinuclear parent compound which is reasonably stable at its own but is readily attacked by electrophiles and nucleophiles of all kinds, this wealth of transformations generally proceed under very mild reaction conditions. In comparison to the reactivity of other comparable unsaturated transition metal fragments such as Cp$_2$M, M = Ti, Zr, Hf, or cations such as Cp*Rh^{2+}, L$_2$Rh$^+$, and L$_2$(Pt,Pd)$^{2+}$ (although not isolable as such) where the reaction chemistry is dominated to a large extent by the formation and elaboration of all kinds of M−C bonds, **1** has been mostly used in connection with O, S, N, and X heteroatom ligands. Although the chemistry of **1** with alkenes and alkynes has perhaps not been fully explored, the lack of stable monoolefin complexes at one hand and the ready formation of heteroatom complexes on the other indicates a certain preference of the Cp*Ru$^+$ fragment for these latter. This particular feature, exemplified in a spectacular way by amino acid complexes **60**, allows the a facile entry into other reactive Cp*Ru σ-ligand half-sandwich complexes which marks, not confined to Ru, one of the exciting and rapidly developing areas in transition metal chemistry.

14. Acknowledgments

Achievements collected in this article, as far as work from our own laboratory is concerned, are due to a number of dedicated and enthusiastic co-workers: Janusz Kossakowski, Byung-Sun Kang, Hong Wang, Andreas Hörnig, Christian Rietmann, Thomas Rüther, Karin Bücken, and Roland Pasch. Toward all of them I want to express my warmest thanks for their endurance and collaborativity. Certainly most of the work would have remained fragmentary without the invaluable help of our crystallographer Uli Englert and co-workers. The work was generously supported by repeated loans of RuCl$_3$ from Johnson Matthey. Support by the Deutsche Forschungsgemeinschaft, Bonn, and the Fonds der Chemischen Industrie, Frankfurt, Main is gratefully acknowledged.

15. References

(1) (a) Poliakoff, M.; Weitz, E. *Adv. Organomet. Chem.* **1986**, *25*, 277. (b) Long, C. In *The chemistry of the metal−carbon bond*; Hartley, F. R., Ed., Wiley: New York, 1989; Vol. 5, p 31ff. (c) Whittlesey, M. K.; Perutz, R. N.; Virrels, I. G.; George, M. W. *Organometallics* **1997**, *16*, 268.
(2) (a) Vaska, L. *Chem. Ind. (London)* **1963**, 1402. (b) La Plata, S. J.; Ibers, J. A. *Inorg. Chem.* **1965**, *4*, 778. (c) Skapski, A. C.; Troughton, P. G. H. *J. Chem. Soc., Chem. Commun.* **1968**, 1230.
(3) (a) Tilley, T. D.; Heyn, R. H. *J. Chem. Soc., Chem. Commun.* **1988**, 278. (b) Arliguie, T.; Bordo, C.; Chaudret, B.; Devilliers, J.; Poilblanc, R. *Organometallics* **1989**, *8*, 1308.
(4) Joslin, F. L.; Johnson, M. P.; Mague, J. T.; Roundhill, D. M. *Organometallics* **1991**, *10*, 2781−94.
(5) de la Jara Leal, A.; Tenoria, M. J.; Puerta, M. C.; Valerga, P. *Organometallics* **1995**, *14*, 3839.
(6) Ogasawara, M.; Macgregor, S. A.; Streib, W. E.; Folting, K.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1996**, *118*, 10189.
(7) Lindner, E.; Pautz, S.; Haustein, M. *Coord. Chem. Rev.* **1996**, *155*, 145.
(8) Koelle U.; Kossakowski, J. *J. Chem. Soc., Chem. Commun.* **1988**, 549.
(9) Loren, S. D.; Campion, B. K.; Heyn, R. H.; Tilley, T. D.; Bursten, B. E.; Luth, K. W. *J. Am. Chem. Soc.* **1989**, *111*, 4712.
(10) Koelle, U.; Kossakowski, J.; Boese, R. *J. Organomet. Chem.* **1989**, *378*, 449.
(11) Koelle, U.; Rietmann, Chr.; Englert, U. *J. Organomet. Chem.* **1992**, *423*, C20.
(12) Kee, T. P.; Park, L. Y.; Robbins, J.; Schrock, R. R. *J. Chem. Soc., Chem. Commun.* **1991**, 121.
(13) Blake, R. E., Jr.; Heyn, R. H.; Tilley, T. D. *Polyhedron* **1992**, *11*, 709.
(14) (a) Poulton, J. T.; Folting, K.; Streib, W. E.; Caulton, K. G. *Inorg. Chem.* **1992**, *31*, 3190. (b) Johnson, T. J.; Folting, K.; Streib, W. E.; Martin, J. D.; Huffmann, J. C.; Jackson, S. A.; Eisenstein, O.; Caulton, K. G. *Inorg. Chem.* **1994**, *33*, 488.

(15) Bickford, C. C.; Johnson, T. J.; Davidson, E. R.; Caulton, K. G. *Inorg. Chem.* **1994**, *33*, 1080.
(16) (a) Tilley, T. D.; Grubbs, R. H.; Bercaw, J. E. *Organometallics* **1984**, *3*, 274. (b) Oshima, N.; Suzuki, H.; Moro-oka, Y. *Chem. Lett.* **1984**, 1161. (c) Koelle, U.; Kossakowski, J.; Klaff, N.; Wesemann, L.; Englert, U.; Herberich, G. E. *Angew.* Chem., Int. Ed. Engl. **1991**, *30*, 690.
(17) Koelle, U.; Kossakowski, J. *Inorg. Synth.* **1992**, *29*, 225.
(18) Hoernig, A.; Englert, U.; Koelle, U. *J. Organomet. Chem.* **1993**, *453*, 255.
(19) Suzuki, H.; Kakigano, T.; Igarashi, M.; Usui, A.; Noda, K.; Oshima, M.; Tanaka, M.; Moro-oka, Y. *Chem. Lett.* **1993**, 1707.
(20) Rauchfuss, T. B.; Rodgers, D. P. S.; Wilson, S. R. *J. Am. Chem. Soc.* **1986**, *108*, 3114.
(21) Koelle, U.; Kossakowski, J. *J. Organomet. Chem.* **1989**, *362*, 383.
(22) Fagan, P. J.; Mahoney, W. S.; Calabrese, J. C. *Organometallics* **1990**, *9*, 1843.
(23) Koelle, U.; Kang, B.-S.; Englert, U. *J. Organomet. Chem.* **1991**, *420*, 227.
(24) Campion, B. K.; Heyn, R. H.; Tilley, T. D. *Organometallics* **1990**, *9*, 1106.
(25) Le Floch, P. L.; Mansuy, S.; Ricard, L.; Mathey, F.; Jutand, A.; Amatore, C. *Organometallics* **1996**, *15*, 3267.
(26) Wang, M. H.; Englert, U.; Koelle, U. *J. Organomet. Chem.* **1993**, *453*, 127.
(27) Gemel, C.; Mereiter, K.; Schmid, R.; Kirchner, K. *Organometallics* **1997**, *16*, 5601.
(28) Takahashi, A.; Mizobe, Y.; Matsuzaka, H.; Dev, S.; Hidai, M. *J. Organomet. Chem.* **1993**, *456*, 243.
(29) (a) Mashima, K.; Mikami, A.; Nakamura, A. *Chem. Lett.* **1992**, 1473. (b) Mashima, K.; Kaneyoshi, H.; Kaneko, S.; Mikami, A.; Tani, K.; Nakamura, A. *Organometallics* **1997**, *16*, 1016.
(30) Koelle, U.; Pasch, R. Unpublished data.
(31) Hoernig, A.; Englert, U.; Koelle, U. *J. Organomet. Chem.* **1994**, *464*, C25.
(32) Hoernig, A.; Rietmann, Chr.; Englert, U.; Wagner, T.; Koelle, U. *Chem. Ber.* **1993**, *126*, 2609.
(33) Koelle, U.; Hoernig, A.; Englert, U. *J. Organomet. Chem.* **1992**, *438*, 309.
(34) Chaudret, B.; Duteil, A.; He, X. D. *J. Organomet. Chem.* **1990**, *391*, C45.
(35) Johnson, T. J.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1992**, *114*, 2725.
(36) Koelle, U.; Kang, B.-S. Unpublished data.
(37) Takahashi, A.; Mizobe, Y.; Hidai, M. *J. Organomet. Chem.* **1995**, *496*, 109.
(38) Dev, S.; Mizobe, Y.; Hidai, M. *Inorg. Chem.* **1990**, *29*, 4797.
(39) (a) Nishio, M.; Matsuzaka, H.; Mizobe, Y.; Tanase, T.; Hidai, M. *J. Chem. Soc., Chem. Commun.* **1993**, 375. (b) Matsuzaka, H.; Hirayama, Y.; Nishio, M.; Mizobe, Y.; Hidai, M. *Organometallics* **1993**, *12*, 36. (c) Matsuzaka, H.; Koizumi, H.; Takagi, Y.; Nishio, M.; Hidai, M. *J. Am. Chem. Soc.* **1993**, *115*, 10396. (d) Nishio, M.; Matsuzaka, H.; Mizobe, Y.; Tanase, T.; Hidai, M. *Organometallics* **1994,** *13*, 4214. (e) Matsuzaka, H.; Takagi, Y.; Ishii, Y.; Nishio, M.; Hidai, M. *Organometallics* **1995**, *14*, 2153.
(40) Koelle, U.; Rietmann, Chr.; Tjoe, J.; Wagner, T.; Englert, U. *Organometallics* **1995**, *14*, 103.
(41) Kuwata, S.; Mizobe, Y.; Hidai, M. *Inorg. Chem.* **1994**, *33*, 3619.
(42) Koelle, U.; Rüther, Th.; Kläui, W. *J. Organomet. Chem.* **1992**, 426, 99.
(43) (a) Bryndza, H. E.; Calabrese, J. C.; Marsi, M.; Roe, D. C.; Tam, W.; Bercaw, J. E. *J. Am. Chem. Soc.* **1986**, *108*, 4805. (b) Newman, L. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 5314. (c) Bryndza, H. E.; Tam, W. *Chem. Rev.* **1988**, *88*, 1163.
(44) Koelle, U.; Rüther, Th.; Englert, U.; Le Navror, N.; Kläui, W. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 991.
(45) Kläui, W. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 627.
(46) Koelle, U.; Rüther, T.; Englert, U. *Inorg. Chem.*, in press.
(47) (a) Gill, T. P.; Mann, K. R. *Organometallics* **1982**, *1*, 485. (b) Schrenk, J. L.; McNair, A. M.; McCormick, F. B.; Mann, K. R. *Inorg. Chem.* **1986**, *25*, 3501.
(48) Hashizume, K.; Mizobe, Y.; Hidai, M. *Organometal*ics **1995**, *14*, 5367.
(49) (a) Chaudret, B.; He, X.; Huang, Y. *J. Chem. Soc., Chem. Commun.* **1989**, 1844. (b) He, X. D.; Chaudret, B.; Dahan, F.; Huang, Y.-S. *Organometallics* **1991**, *10*, 970. (c) Koelle, U.; Wang, M. H.; Raabe, G. *Organometallics* **1991**, *10*, 2573.
(50) Kaganovich, V. S.; Kudinov, A. R.; Rybinskaya, M. I. *Izvest. Akad. Nauk. Engl. Transl.* **1986**, 456.
(51) (a) McNair, A. M.; Mann, K. R. *Inorg. Chem.* **1986**, *25*, 2519. (b) Moriarty, R. M.; Ku, Y.-Y.; Gill, U. S. *Organometallics* **1988**, *7*, 660. (c) Kudinov, A. R.; Petrovskii, P. V.; Struchkov, Yu. T.; Yanovskii, A. I.; Rybinskaya, M. I. *J. Organomet. Chem.* **1991**, *421*, 91.
(52) Chávez, I.; Cisternas, A.; Otero, M.; Román, E.; Müller, U. *Z. Naturforsch. B* **1990**, *45*, 658.
(53) (a) Fagan, P. J.; Ward, M. D.; Caspar, J. V.; Calabrese, J. C.; Krusic, P. J. *J. Am. Chem. Soc.* **1988**, *110*, 2981. (b) Fagan, P. J.; Ward, M. D.; Calabrese, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 1698. (c) Chaudret, B.; Jalon, F. *J. Chem. Soc., Chem. Commun.* **1988**, 711.
(54) Koelle, U.; Wang, M. H. *Organometallics* **1990**, *9*, 195.
(55) Rondon, D.; Chaudret, B.; He, X.-D.; Labroue, D. *J. Am. Chem. Soc.* **1991**, *113*, 5671.
(56) Chaudret, B.; Dahan, F.; He, X. D. *J. Chem. Soc., Chem. Commun.* **1990**, 1111.
(57) Rondon, D.; He, X.-D.; Chaudret, B. *J. Organomet. Chem.* **1992**, *433*, C18.
(58) (a) Urbanos, F.; Fernandez-Baeza, J.; Chaudret, B. *J. Che*m. Soc., Chem. Commun. **1991**, 1739. (b) Urbanos, F.; Halcrow, M. A.; Fernandez-Baeza, J.; Dahan, F.; Labroue, D.; Chaudret, B. *J. Am. Chem. Soc.* **1993**, *115*, 3484. (c) Halcrow, M. A.; Urbanos, F.; Chaudret, B. *Organometallics* **1993**, *12*, 955.
(59) Carreno, R.; Chaudret, B.; Labroue, D.; Sabo-Etienne, S. *Organometallics* **1993**, *12*, 13.
(60) Herberich, G. E.; Englert, U.; Marken, F.; Hofmann, P. *Organometallics* **1993**, *12*, 4039.
(61) Koelle, U.; Rietmann, Chr. Unpublished results.
(62) Koelle, U.; Hoernig, A.; Englert, U. *Organometallics* **1994**, *13*, 4064.
(63) Carreno, R.; Urbanos, F.; Dahan, F.; Chaudret, B. *New. J. Chem.* **1994**, *18*, 449.
(64) Koelle, U.; Pasch, R.; Ganter, B.; Englert, U. *Organometallics* **1997**, *16*, 3950.
(65) Koelle, U.; Kang, B.-S.; Thewalt, U. *J. Organomet. Chem.* **1990**, *386*, 267.
(66) Koelle, U.; Kang, B.-S.; Thewalt, U. *Organometallics* **1992**, *11*, 2893.
(67) Koelle, U.; Pasch, R. Unpublished results.
(68) Schmidt, Th.; Goddard, A. *J. Chem. Soc., Chem. Commun.* **1991**, 1427.
(69) Koelle, U.; Kang, B.-S.; Spaniol, T.; Englert, U. *Organometallics* **1992**, *11*, 249.
(70) Forrow, N. J.; Knox, S. A. R. *J. Chem. Soc., Chem. Commun.* **1984**, 679.
(71) Koelle, U.; Kang, B.-S.; Thewalt, U. *Organometallics* **1991**, *10*, 2569.
(72) (a) Suzuki, H.; Omori, H.; Lee, D. W.; Yoshida, Y.; Moro-oka, Y. *Organometallics* **1988**, *7*, 2243. (b) Suzuki, H.; Omori, H.; Moro-oka, Y. *Organometallics* **1988**, *7*, 2579. (c) Omori, H.; Suzuki, H.; Take, Y.; Moro-oka, Y. *Organometallics* **1989**, *8*, 2270. (d) Suzuki, H.; Kakigano, T.; Igarashi, M.; Tanaka, M.; Moro-oka, Y. *J. Chem. Soc., Chem. Commun.* **1991**, 283. (e) Takao, T.; Yoshida, S.; Suzuki, H. *Organometallics* **1995**, *14*, 3855.
(73) Marsh, R. E. *Organometallics* **1988**, *8*, 1583.
(74) Chaudret, B.; Cole-Hamilton, D. J.; Nohr, R. S.; Wilkinson, G. *J. Chem. Soc.*, Dalton Trans. **1977**, 1546.
(75) Canestrari, M.; Chaudret, B.; Dahan, F.; Huang, Y.-S.; Poilblanc, R. *J. Chem. Soc.*, Dalton Trans. **1990**, 1179.
(76) Bücken, K.; Koelle, U.; Pasch, R.; Ganter, B. *Organometallics* **1996**, *15*, 3095.
(77) Koelle, U.; Kossakowski, J.; Raabe, G. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 773.
(78) Smith, M. E.; Hollander, F. J.; Andersen, R. A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1294.
(79) Koelle, U.; Pasch, R. Unpublished results.
(80) Koelle, U.; Rietmann, Chr.; Raabe, G. *Organometallics* **1997**, *16*, 3273.
(81) Ward, T. R.; Schafer, O.; Daul, C.; Hofmann, P. *Organometallics* **1997**, *16*, 3207.
(82) Fernández, J. M.; Gladysz, J. A. *Organometallics* **1989**, *8*, 207. Merrifield, J. H.; Strouse, C. E.; Gladysz, J. A. *Organometallics* **1982**, *1*, 1204.
(83) Koelle, U.; Bücken, K.; Englert, U. *Organometallics* **1996**, *15*, 1376.
(84) Koelle, U.; Grub, J. *J. Organomet. Chem.* **1985**, *289*, 133.

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