Regio- and Stereoselective Functionalization of *cyclo*-C_8 Compounds by Iterative Nucleophilic and Electrophilic Addition to Coordinated Cyclooctatetraene

Gerhard Lange,[a] Oliver Reimelt,[a] Lars Jessen,[a] and Jürgen Heck*[a]

Dedicated to Prof. Dr. Wolfgang Walter on the occasion of his 80th birthday

Keywords: Electrophilic additions / Hydrido complexes / Nucleophilic additions / Ruthenium / Cyclooctatetraene

The addition of various nucleophiles (Nu^1) to the cationic complex $[CpRu(\eta^6\text{-cot})]^+$ (**1**$^+$) has been performed and yielded the neutral complexes $CpRu(\eta^5\text{-}C_8H_8Nu^1)$ (**2**) [cot = cyclooctatetraene; Nu^1 = Me (**2a**), $CH(CO_2Me)_2$ (**2b**), CH=CH_2 (**2c**), C_6H_5 (**2d**), H (**2e**), D (**2f**), NMe_2 (**2g**), OMe, (**2h**), C≡C*t*Bu (**2i**)]. The nucleophiles Nu^1 add exclusively to the cot ring, and stereoselectively in the *exo* position with respect to the metal center. As evidenced by NMR spectroscopy the *cyclo*-C_8 ligand in **2c**, **2e**–**2i** is bound in a 1,2-η:5,6,7-η fashion in solution. The molecular structure analysis of **2c** [space group $P\bar{1}$, a = 757.9(1), b = 759.1(1), c = 1053.1(3) pm, α = 81.93(2), β = 80.22(1), γ = 88.73(1)°, V = 591.2(2) Å^3, Z = 2, R_{merge} = 0.0265] verifies the 1,2-η:5,6,7-η coordination mode of the *cyclo*-C_8 ligand in the solid state and shows the Nu^1 substituent to be in an *exo* position. For **2a** and **2b** a 1,2,3,4,5-η haptomer is also found, and this interconverts to the 1,2-η:5,6,7-η derivative in solution; in contrast, the *cyclo*-C_8 ligand of the phenyl derivative **2d** remains in the 1,2,3,4,5-η fashion. The protonation of the neutral complexes **2a**–**2d** by the addition of HBF_4 generates the new cationic products $[CpRu(\eta^6\text{-}C_8H_9Nu^1)]^+$ (**3**$^+$) [Nu^1 = Me (**3a**$^+$), $CH(CO_2Me)_2$ (**3b**$^+$), CH=CH_2 (**3c**$^+$), C_6H_5 (**3d**$^+$)]. When Nu^1 = $CH(CO_2Me)_2$ (**3b**$^+$) two different haptomers were isolated that exhibit 1,2-η:4,5,6,7-η and 1,2,3,4,5,6-η bonding modes, respectively. In solution the 1,2-η:4,5,6,7-η haptomer completely rearranges to the 1,2,3,4,5,6-η derivative. The crystal structure analysis of **3d**BF_4 [space group *Pbc*2(1), a = 1678.8(7), b = 1031.4(2), c = 981.8(2) pm, V = 1700.0(9) Å^3, Z = 4, R_{merge} = 0.032] confirms the 1,2-η:4,5,6,7-η bonding mode of the *cyclo*-C_8 ligand, which has also been indicated in solution. The second nucleophilic addition to the coordinated *cyclo*-C_8 ligand yields new neutral complexes that exist as two different haptomers depending on the steric demand of the two nucleophiles. The haptomer $CpRu(1,2,3,4,5\text{-}\eta\text{-}C_8H_9\text{-}6\text{-}Nu^1\text{-}8\text{-}Nu^2)$ (**4a**) is formed with Nu^1 = Nu^2 = $CH(CO_2Me)_2$ whereas with Nu^1 = Me, Nu^2 = $CH(CO_2Me)_2$ (**4b**) and Nu^1 = Nu^2 = Me (**4c**) the haptomer $CpRu(1,2\text{-}\eta\text{:}5,6,7\text{-}\eta\text{-}C_8H_9\text{-}4\text{-}Nu^1\text{-}8\text{-}Nu^2)$ is obtained. The protonation of **4a**–**4c** produces the cationic hydride species $[CpRu(H)(1,2,3,4,5\text{-}\eta\text{-}C_8H_9Nu^1Nu^2)]^+$ (**5**$^+$) [Nu^1 = Nu^2 = $CH(CO_2Me)_2$ (**5a**$^+$), Nu^1 = CH_3, Nu^2 = $CH(CO_2Me)_2$ (**5b**$^+$), Nu^1 = Nu^2 = Me (**5c**$^+$)] as indicated by the high-field shifted singlet for one proton below δ = −10 in the ^{1}H-NMR spectra. An X-ray structure analysis of a single crystal obtained from the protonation reaction of **4b** [space group $P2_1/c$, a = 1285.5(12), b = 1015.8(8), c = 1586.3(14) pm, β = 108.61(7)°, V = 1963(3) Å^3, Z = 4, R_{merge} = 0.0942] reveals a special disorder, the interpretation of which results in the structure determination of two independent complexes in a ratio of 59:41 differing by two hydrogen atoms in the formula. Both complexes are cations; one exhibits a disubstituted 1,2,3,4,5-η-bonded cyclooctadienyl ligand and an agostic interaction of the Ru center with a hydrogen atom at C5 of the *cyclo*-C_8 ligand (**5b**BF_4), whereas the second complex contains a cyclooctatriene ligand in a 1,2,3,4,5,6-η bonding mode without a metal hydride function (**6**BF_4). The coexistence of two different molecules in one single crystal that differ by two hydrogen atoms in addition to the agostic hydrogen atom in **5b**$^+$, points to an elimination of an H_2 molecule from **5b**$^+$ in the solid state to generate **6**$^+$. This suggestion is corroborated by the formation of a cationic complex **7**$^+$ as the main product in solution, which contains a *cyclo*-C_8 ligand without the malonate nucleophile [Nu^2 = $CH(CO_2Me)_2$], whereas a freshly prepared NMR sample only reveals **5b**$^+$ and **6**$^+$. In all of these products the Me nucleophile (Nu^1 = Me) is linked to a metal-coordinated carbon atom indicating an additional intramolecular hydrogen migration after the initial protonation.

Introduction

Nucleophilic addition to unsaturated organic ligands is very pertinent to synthetic organometallic chemistry.[1] Since this type of reaction displays pronounced stereo- and regioselectivity it is used in the synthesis of natural products.[2] More recent investigations demonstrate that this synthetic concept can be transferred to coordinated carbocycles like cyclooctatetraene,[3] which generates an access to multiple stereo- and regioselectively functionalized *cyclo*-C_8 ligands, and which may be of some importance in the synthesis of precursor compounds for *cyclo*-C_8 terpenoids.[4] In this paper we present results obtained from an iteratively applied reaction sequence of nucleophilic addition-protonation using different nucleophiles.

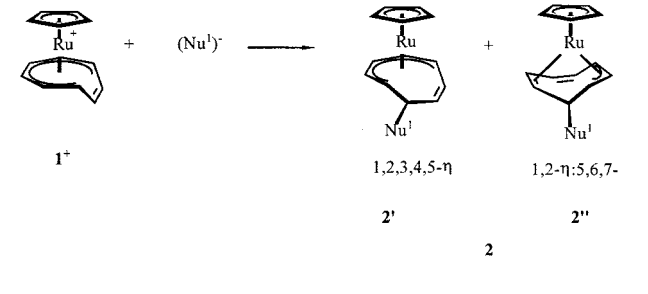
[a] Institut für Anorganische und Angewandte Chemie, Universität Hamburg,
Martin-Luther-King-Platz 6, 20146 Hamburg, Germany
Fax: (internat.) + 49-(0)40/42838-6945
E-mail: heck@chemie.uni-hamburg.de

  1434−1948/00/0909−1941 $ 17.50+.50/0

Results and Discussion

Primary Nucleophilic Addition

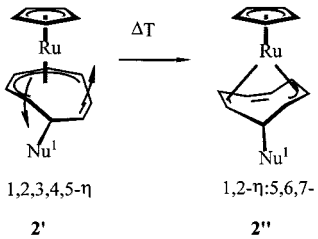
The initial nucleophilic addition to $[CpRu(\eta^6\text{-cot})]^+$ ($\mathbf{1}^+$) (Cp = cyclopentadienyl, cot = cyclooctatetraene) (Scheme 1) occurs exclusively at the cot ligand as predicted from the Davies−Green−Mingos rules.[5] In order to test the electrophilicity of the coordinated cot in $\mathbf{1}^+$, the charged heteronucleophiles OMe^- and NMe_2^- were also used; the nucleophilicity of neutral amines and phosphanes appeared to be too low to add to the cot ligand in $\mathbf{1}^+$.



Nu^1	Me	$CH(CO_2Me)_2$	$CH{=}CH_2$	C_6H_5	H	D	NMe_2	OMe	$C{\equiv}CtBu$
2	**a**	**b**	**c**	**d**	**e**	**f**	**g**	**h**	**i**

Scheme 1. Nucleophilic addition to $\mathbf{1}^+$

The assignment of the NMR signals can easily be performed by applying ^1H-^1H and ^1H-^{13}C correlation spectroscopy when the single proton signal of the nucleophile-bearing sp^3-carbon atom C8 is localized. When Nu^1 = Me or $CH(CO_2Me)_2$, two different isomers can be identified: in the isomer **2′** (e.g. **2a′** and **2b′**) the proton of the Nu^1-substituted carbon atom C8 couples with the vicinal protons of a coordinated and noncoordinated carbon−carbon double bond; in the second isomer **2′′** (e.g. **2a′′** and **2b′′**) the proton on C8 couples to protons of metal-bound carbon atoms only (Table 3). Since the number of metal-bound carbon atoms of the *cyclo*-C_8 ligands in both isomers are the same, and they only differ in the position of the coordinated carbon atoms in the *cyclo*-C_8 ring, we introduced the notation "hapticity isomers" or "haptomers".[6] Whereas haptomer **2a′** slowly rearranges in solution to **2a′′** at ambient temperature, the different haptomers of **2b** are sufficiently stable to be isolated separately.[6,7] ^1H-NMR experiments at T = 60 °C demonstrate a slow interconversion of **2b′** to **2b′′**. Apparently, the 1,2,3,4,5-η-haptomer **2′** is initially formed as the kinetically controlled product during the nucleophilic addition, and this gradually rearranges to the thermally more stable 1,2-η:5,6,7-η-haptomer **2′′** (Scheme 2).



Scheme 2. Proposed flip-flop mechanism for the 1,2,3,4,5-η/1,2-η:5,6,7-η haptomerism

For Nu^1 = $CH{=}CH_2$ (**2c**), H (**2e**), D (**2f**), NMe_2 (**2g**), OMe (**2h**), and $C{\equiv}CtBu$ (**2i**) the only isomer observed is the 1,2-η:5,6,7-η haptomer, a situation in contrast to **2d** (Nu^1 = C_6H_5), which has a 1,2,3,4,5-η structure as determined by NMR spectroscopy (see Table 3). No indications for a structural rearrangement in **2d** have been found. The reason for the interconversion of the haptomers **2a′** to **2a′′** and **2b′** to **2b′′** may be deduced from the steric demand of the nucleophile Nu^1. When sterically more crowded nucleophiles are used, such as a phenyl group or a substituted malonate $CR(CO_2Me)_2$ ($R \neq H$),[8] the 1,2,3,4,5-η haptomer is exclusively identified.

The influence of the steric demand of the nucleophile can also be rationalized by the crystal structure analysis of the vinyl derivative **2c**, which proves the 1,2-η:5,6,7-η coordination mode for **2c** in the solid state (Figure 1). The vinyl group is located in an *exo* position with respect to the metal center and opposite to the noncoordinating double bond. The carbon−carbon and ruthenium−carbon bonds are quite normal and are very similar to Ru−C bond lengths of pentadienyl−Ru moieties in open and semi-open ruthenocenes.[9] One exception is the Ru−C7 bond, which is elongated by more than 5 pm with respect to the other bond lengths between the Ru center and the metal-bound carbon atoms of the *cyclo*-C_8 ligand. Such a deviation of a Ru−C bond length in the vicinity to an sp^3-carbon atom from the mean value of other Ru−C bond lengths is found more often in (cyclooctatrienyl)ruthenium complexes.[10]

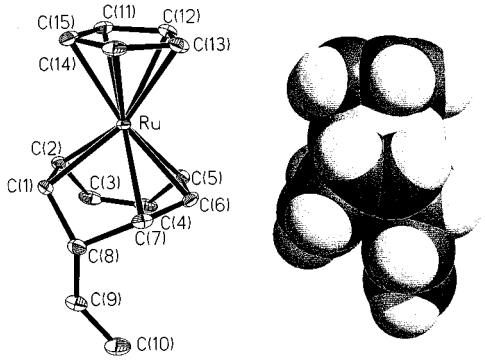


Figure 1. Molecular structure of **2c** (left: ORTEP plot, 30% thermal ellipsoids, the hydrogen atoms are omitted for clarity; right: space-filling model to illustrate the steric demand of the vinyl nucleophile and the noncoordinated double bond); selected bond lengths [pm]: Ru−C1 217.81(19), Ru−C2 219.0(2), Ru−C5 218.08(19), Ru−C6 215.74 (19), Ru−C7 224.3(2), C1−C2 142.3(3), C1−C8 154.2(3), C2−C3 149.1(4), C3−C4 132.2(4), C4−C5 149.5(3), C5−C6 143.2(3), C6−C7 138.9(3), C7−C8 153.1(3)

The most interesting structural features of **2c** concerning the formation of the different haptomers are the non-bond lengths between C8 and C9, and the carbon atom C3 of the non-coordinated double bond opposite to C8 and C9, which are 307.6(3) and 308.4(3) pm, respectively. The close proximity of these atoms to each other can be appreciated from the space-filling model shown in Figure 1. Larger nucleophiles would not allow the C3−C4 double bond to bend towards the nucleophile, and hence would favor the situation wherein C3 and C4 were kept in a metal-coordination mode.

To gain a deeper insight into the interconversion mechanism, hydride and deuteride addition from the borates $[BEt_3H]^-$ and $[BEt_3D]^-$ were performed and revealed the 1,2-η:5,6,7-η haptomers of **2e** (Nu = H) and **2f** (Nu = D). The NMR signals of the *endo* and *exo* protons of the sp^3-carbon atom (C8) in the *cyclo*-C_8 ligand of **2e** (Nu = H) are isochronic and show a triplet at δ = 2.87 due to the coupling with the two vicinal protons on C1 and C7, which are both quadruplets (Figure 2, A). The corresponding signal in the spectrum of **2f** (Nu = D, Figure 2, B) is now a doublet of doublets with similar coupling constants (J = 7.5 and 9.0 Hz). Each component is superimposed by a triplet caused by geminal coupling with the deuterium nucleus (J_{HD} = 1.7 Hz). Additionally, the integral of the signal at δ = 2.87 is only half that for **2e**. In agreement with this, the signals of the vicinal protons on C1 and C7 change their patterns to a triplet and a doublet of doublets, respectively, for **2f** (Table 3).

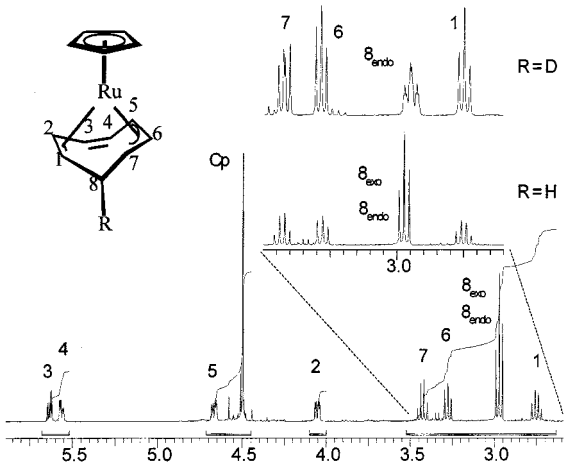
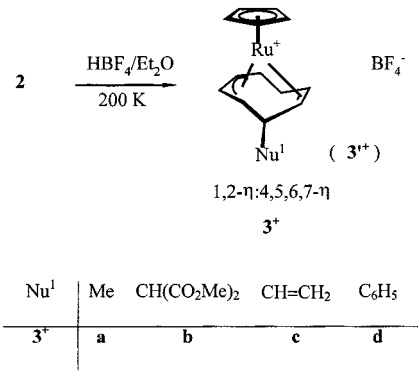


Figure 2. ^{1}H-NMR spectra of **2e** and **2f** illustrating the difference in the splitting pattern when the nucleophilic Nu^1 has changed from H^- to D^-

The ^{1}H-NMR spectra of **2e** and **2f** remain unchanged at temperatures up to 90 °C even after several days, which indicates that no hydrogen migration takes place. The thermal stability of the cyclooctatrienyl ligand in the Ru complexes **2f** is in sharp contrast to the corresponding iron complex, which demonstrates a complete scrambling of the deuterium atom under comparable conditions.[11] Therefore, assuming the *exo* addition of the hydride in strict analogy to the addition of any other nucleophile, the interconversion from the kinetically controlled 1,2,3,4,5-η product to the thermodynamically more stable 1,2-η:5,6,7-η haptomer is believed to be a flipping mechanism, as indicated in Scheme 2, rather than a hydrogen migration after the nucleophile has been added to the terminal carbon atom of the metal-coordinated part of the cot ligand.

First Protonation

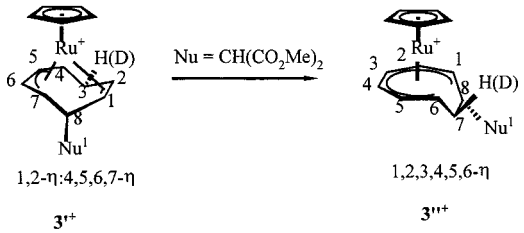
A second nucleophilic addition to the *cyclo*-C_8 ligand again requires a cationic complex. Therefore, some of the complexes of **2** were protonated with HBF_4 to yield the new cationic products $\mathbf{3}^+$ (Scheme 3) except for the cases where Nu^1 = NMe_2 (**2g**) and Nu^1= OMe (**2h**). The protonation of **2g** leads to a gradual cleavage of the NMe_2 group whereas for **2h** the methoxy group is completely split off. As evidenced by 1D- and 2D-NMR experiments the protonation of **2** occurs in position 3 of the *cyclo*-C_8 ligand to afford the cationic complex in a 1,2-η:4,5,6,7-η bonding mode ($\mathbf{3'}^+$, Scheme 3).



Scheme 3. Protonation of the cyclooctatrienyl complexes **2**

In order to ascertain the protonation site of the *cyclo*-C_8 ring (*exo* or *endo* with respect to the metal center) a protonation experiment was performed with **2b** [Nu^1 = $CH(CO_2Me)_2$] using a mixture of $DBF_4/HBF_4 \approx 4:1$. The comparison of the signal intensities in the ^{1}H-NMR spectra of the cationic product $\mathbf{3b}^+$ and its deuterated congener $\mathbf{3b}^+\mathbf{\text{-}D_1}$ clearly indicates position 3 as the site of the protonation (δ = 3.19) (Table 5). The resonance signal of the other proton of position 3 is found at δ = 1.99. Assuming that the anisotropy cone of diamagnetic sandwich compounds[12] also holds for the present Ru complexes, the signals of the protons in the *endo* position with respect to the metal center should be shifted downfield compared to the signal of the *exo* proton.[13] Conclusively, the protonation of **2** stereoselectively occurs in the *endo*-position with respect to the metal center, which is also in agreement with protonation experiments involving other sandwich compounds.[14] This stereoselectivity suggests a protonation of the metal center as a first step and a subsequent hydrogen migration to the *cyclo*-C_8 ligand.[14b]

The ^{1}H-NMR spectra of $\mathbf{3b}^+$ contain small signals due to a second isomer, which increase in intensity in the course of time. After 6 days at room temperature, the NMR signals of only one isomer are recorded and these correspond to the initial minor isomer, which was identified as the 1,2,3,4,5,6,-η haptomer. Apparently, the 1,2-η:4,5,6,7-η haptomer $\mathbf{3'}^+$ is converted into the 1,2,3,4,5,6,-η haptomer $\mathbf{3''}^+$ (Scheme 4). In addition to this haptotropic rearrangement it is evident from the ^{1}H-NMR spectra of $\mathbf{3b\text{-}D_1}^+$ that the *endo* proton on C3 of $\mathbf{3'}^+$ (δ = 3.19) has migrated to the *endo* position on C7 in $\mathbf{3''}^+$ (δ = 1.63) (Scheme 4). The position of this resonance still shows a distinct low-field shift compared to the signal of the other proton on C7 (δ =



Scheme 4. Proposed 1,5-hydrogen migration mechanism for the 1,2-η: 4,5,6,7-η/1,2,3,4,5,6-η haptomerism

−0.95, Table 5),[11,13] indicating the *endo* position of the deuterium atom.

It is interesting to note that the nature of the nucleophile does not consistently influence the hapticity of the eight-membered ligand. Whereas for $Nu^1 = CH(CO_2Me)_2$ the more stable isomer is the 1,2-η:5,6,7-η haptomer for the neutral complex **2b** and the 1,2,3,4,5,6-η haptomer for the cationic species **3b**$^+$, for $Nu^1 = C_6H_5$ the opposite is true: In **2d** the 1,2,3,4,5,-η bonding mode is favored, and upon protonation the coordination of the *cyclo*-C_8 ligand changes to the 1,2-η:4,5,6,7-η fashion in **3d**$^+$, a situation demonstrated by solution NMR studies and verified in the solid state structure (Figure 3).

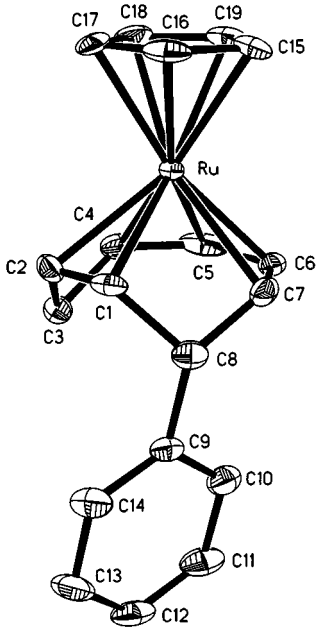
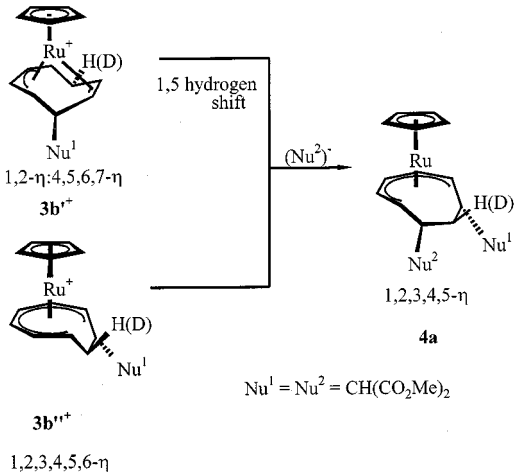


Figure 3. Molecular structure of **3d**BF_4 (ORTEP plot, 30% thermal ellipsoids, the hydrogen atoms and the counter ion are omitted for clarity); selected bond lengths [pm]: Ru−C1 228.1(4), Ru−C2 229.4(6), Ru−C4 226.5(6), Ru−C5 218.3(5), Ru−C6 220.7(5), C1−C2 135.8(8), C1−C8 150.7(7), C2−C3 150.7 (8), C3−C4 150.4(9), C4−C5 135.1(14), C5−C6 147.1(11), C6−C7 139.7 (10), C7−C8 153.7(8), C8−C9 154.9(6)

The crystal structure analysis of the phenyl derivative **3d**BF_4 reveals a η^6-coordination mode for the *cyclo*-C_8 ligand, wherein the noncoordinated carbon atoms of the eight-membered ring, C3 and C8, protrude from the plane of the metal-bound carbon atoms in an *exo* position with respect to the metal center. The non-bond lengths between C3 and C8, and C3 and C9 are 308.4(8) and 308.2(9) pm, respectively, which indicates a close proximity of the two sp^3-carbon atoms of the *cyclo*-C_8 ligand. A sterically more demanding nucleophile at C8 may push the C3 position to the metal center, thus inducing a metal−hydrogen interaction that could be a first step in the metal-assisted 1,5-hydrogen migration as found in **3b**$^+$ (see Scheme 4). The metal−carbon bond lengths in **3d**$^+$ are slightly elongated in comparison to the corresponding bond lengths of the neutral complex **2c** due to the positive charge in **3d**$^+$, which reduces the metal−ligand back donation. Accordingly, the C1−C2 bond length in **3d**$^+$ [135.5(8) pm] is distinctly shorter than the corresponding bond length in **2c** [142.3 (3) pm]. Also in agreement with the reduced metal−ligand back donation is the bond length alternation in the metal-bound butadiene part of the *cyclo*-C_8 ligand: C4−C5 135.1(14) pm, C5−C6 147.1(11) and C6−C7 139.7(10) pm.[15]

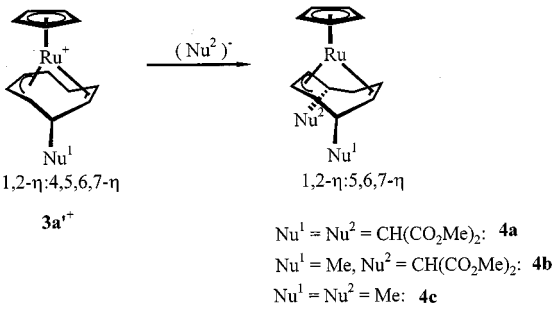
Second Nucleophilic Addition

The second nucleophilic addition can in principle give rise to two isomeric products depending on the type of haptomer used for this reaction. However, earlier attempts have already demonstrated that for $Nu^1 = CH(CO_2Me)_2$ the addition of the second nucleophile [$Nu^2 = CH(CO_2Me)_2$] only gives rise to the 6,8-bifunctionalized cyclooctadienyl complex **4a**[6] regardless of whether the starting haptomer is **3b**$'^+$ or **3b**$''^+$. The nucleophilic addition to mixtures of partially deuterated **3b**$'^+$ and **3b**$''^+$ yielded **4a** only with the deuterium atom exclusively in *endo* position at C7. Hence, **3b**$'^+$ has to rearrange to haptomer **3b**$''^+$ by a 1,5-hydrogen migration before the second nucleophilic addition occurs (Scheme 5).[6]



Scheme 5. Nucleophilic addition to **3b**$^+$

This outcome contrasts the result of the second nucleophilic addition [Nu^2 = Me, $CH(CO_2Me)_2$] to complexes with Nu^1 = Me, which occurs exclusively in the 4-position of the cyclooctatriene ligand of **3a**$^+$ (Scheme 6).

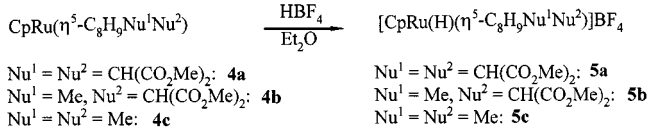


Scheme 6. Nucleophilic addition to **3a**$^+$

The ^{1}H- and ^{13}C-NMR spectra clearly demonstrate the low local symmetry (C_1) of the cyclooctadienyl ligand in **4b** [Nu^1 = Me, Nu^2 = $CH(CO_2Me)_2$] and **4c** (Nu^1 = Nu^2 = Me), in which the number of signals corresponds to the number of hydrogen and carbon atoms in the eight-membered ring in each case, whereas the NMR spectra of **4a** contain considerably fewer signals due to the C_s symmetry of the *cyclo*-C_8 ligand (Table 6). By means of ^{1}H-^{1}H and ^{1}H-^{13}C correlation spectra the different signals for **4b** and for **4c** can be assigned unequivocally and confirm the products **4b** and **4c** as 4,8-bifunctional cyclooctadienyl complexes.

Second Protonation

The bifunctionalized cyclooctadienyl complexes **4a**, **4b** and **4c** are easily protonated by the addition of HBF_4 to their ether solutions at low temperature. The products precipitate as light yellow solids and can be isolated by filtration (Scheme 7).

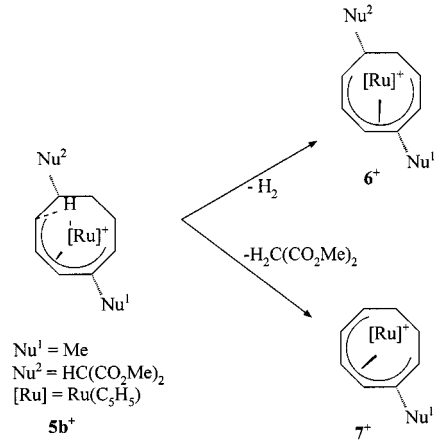


Scheme 7. Protonation of the cyclooctadienyl complexes **4a**−**4c**

In contrast to the first protonation, the second one gives rise to ruthenium complexes with a metal−hydride function as shown by the high-field shift of singlets from δ = −10.4 to −10.6 in the ^{1}H-NMR spectra.[16] No indication is found for the scrambling of proton positions that was observed in electronically related compounds like the protonated (cyclopentadienyl)(3-methylpentadienyl)ruthenium complex.[17,18] For **5a**$^+$ [Nu^1 = Nu^2 = $CH(CO_2Me)_2$] and **5c**$^+$ (Nu^1 = Nu^2 = Me) the ^{1}H-NMR spectra are similar to those of **4a** and **4c** apart from an overall distinct low-field shift of the signals for the metal-coordinated C−H units, which is due to the cationic nature of the complexes, and the hydrido signal at δ < −10 (Table 7). The coordination mode of the *cyclo*-C_8 ligand is therefore assumed to remain unchanged upon protonation of **4a** and **4c**. However, in solution the ^{1}H-NMR spectra provide evidence for a slow decomposition of the products, which form different Ru complexes that were not characterized further in the cases of **5a**$^+$ and **5c**$^+$.

The ^{1}H-NMR spectrum of a freshly prepared sample of the protonated product of **4b** [Nu^1 = Me, Nu^2 = $CH(CO_2Me)_2$] indicates the existence of two different species and displays remarkable differences to the spectrum of the precursor complex. The signal due to the Me substituent in the neutral complex **4b** appears as a doublet at δ = 0.96 in accordance with the Me signals of **4c** (δ = 1.02 and 1.20). The corresponding Me signals of the protonated species of the starting complex **4b** are observed as singlets, which are low-field shifted to δ = 2.32 for the major component (**5b**$^+$) and even to δ = 2.62 for the minor one (**6**$^+$). In contrast, the position of the corresponding Me signals in **5c**$^+$ does not differ significantly from that in the starting complex **4c**. The lack of a ^{1}H-^{1}H coupling for the Me substituent in **5b**$^+$ and **6**$^+$, as well as the distinct low-field shift of the Me signals, point to a metal coordination of the Me-substituted carbon atom in **5b**$^+$ and **6**$^+$. Therefore, in **5b**$^+$ and **6**$^+$ a hydrogen migration had to occur on the *cyclo*-C_8 ligand upon protonation.

The most striking difference between the ^{1}H-NMR spectra of **5b**$^+$ and **6**$^+$ is the lack of the hydrido signal at δ ≈ −10 for the minor product **6**$^+$. A careful analysis of the ^{1}H,^{1}H-COSY spectrum also proves that **6**$^+$ contains two hydrogen atoms less than **5b**$^+$. On keeping the solution of the NMR sample under an inert gas, a further product **7**$^+$ can be identified as a cationic cyclooctatriene complex without the malonate substituent (Table 7). The former malonate nucleophile can be identified in the ^{1}H-NMR spectrum as a free methyl malonate (δ = 3.36 and 3.70). The signals due to complexes **6**$^+$ and **7**$^+$ both grow in the course of time, whereas the signals due to **5b**$^+$ vanish. Hence, the hydride complex **5b**$^+$ decomposes in solution under cleavage of dihydrogen or methyl malonate (Scheme 8). Most interestingly, the formation of **5b**$^+$ and **6**$^+$ has been observed in a single crystal analysis.



Scheme 8. Elimination of H_2 and $H_2C(CO_2Me)_2$ from the cationic complex **5b**$^+$ in solution

Suitable crystals for an X-ray structure analysis of the protonation product of **4b** [Nu^1 = Me, Nu^2 = $CH(CO_2Me)_2$] were obtained from a dichloromethane/diethyl ether solution. The determination of the molecular structure was successful on the assumption of a disorder of the two cationic complexes in a ratio of 59:41, which differ

in the *cyclo*-C_8 ligands. Attempts were made to separate the carbon atoms C1, C5, C7, and C8 of the *cyclo*-C_8 ligands in different split positions. However, this procedure was only successful for C8. The positions of C1, C5, and C7 do not vary sufficiently in the two species to be calculated in different split positions. The best fit could be obtained by taking into account two cationic species, one bearing a 1,2,3,4,5-η-cyclooctadienyl ligand (**5b**$^+$, 59%) and the other a 1,2,3,4,5,6-η-cyclooctatriene ligand (**6**$^+$, 41%) (Figure 4).

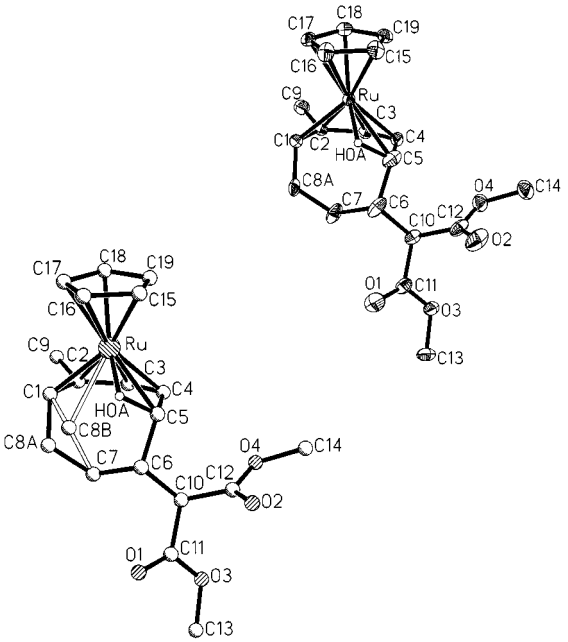
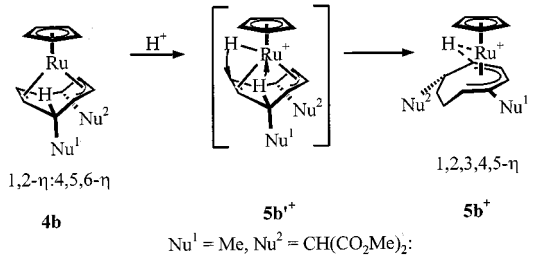


Figure 4. Molecular structures of **5b**BF_4 and **6**BF_4 as obtained from the X-ray crystal structure analysis of the protonation product of **4b**; top: **5b**BF_4 (ORTEP plot, 30% thermal ellipsoids, the anion and all H atoms except the H^- are omitted for clarity); bottom: superposition of **5b**BF_4 and **6**BF_4 (note the difference in the notation of C8A, C8B; C8A belongs to **5b**$^+$ and C8B to **6**$^+$); selected bond lengths [pm]: Ru−C1 217.7(7), Ru−C2 219.7(7), Ru−C3 220.8(7), Ru−C4 213.5(8), Ru−C5 227.3(8), Ru−C8A 246(2), Ru−H0A 173(13), C1−C2 140.8(10), C2−C3 144.0(10), C3−C4 143.8(10), C4−C5 147.6(13), C5−C6 151.0(12), C6−C7 151.8(11), C7−C8A 147.4(13), C7−C8B 152.0(10), C1−C8A 159.3(16), C1−C8B 143.6(9), C5−H0A 129(13)

The most prominent structural feature of **5b**$^+$ is the agostic hydrogen atom H0A between the Ru center and C5. The position of this hydrogen atom was found from the difference electron map. The Ru−H0A distance is 173(12) pm and the distance between C5 and H0A is calculated to be 129(13) pm. In accordance with the agostic hydrogen atom at C5, the Ru−C1−C4 bond lengths are distinctly shorter than the bond length between the Ru center and C5 [213.5(8)−220.8(7) pm vs. 227.3(8) pm]. The carbon−carbon bond length between C4 and C5, which is linked to the agostic hydrogen atom, seems to be elongated [147.6(13) pm] compared to the other carbon−carbon distances [140.8(10)−144.0(10) pm] of the metal-coordinated entity of the *cyclo*-C_8 ligand. Hence, the structural data of **5b**$^+$ much resemble those of the electronically related protonated (cyclopentadienyl)(3-methylpentadienyl)ruthenium.[18]

Another important result from the structure determination of **5b**$^+$ is the position of the first nucleophile (Nu^1 = Me) on the *cyclo*-C_8 ligand: the Me group is directly linked to the metal-bound carbon atom C2, as already indicated by the ^{1}H-NMR study. The carbon atoms C6, C7, and C8 are not metal-coordinated and are sp^3-hybridized with $Nu^2 = CH(CO_2Me)_2$ at C6.

Conclusively, the formation of **5b**$^+$ upon protonation of **4b** requires more than a simple protonation of the metal center, as evidenced for **5a**$^+$ and **5c**$^+$. Compound **4b** may first be protonated at the metal center to give the metal−hydride function (Scheme 9). Subsequently, the hydrogen atom could migrate to position 1 of the *cyclo*-C_8 ligand and, more or less simultaneously, the hydrogen atom at C3 migrates to the metal center leading to a 1,2,3,4,5-η coordination mode of the *cyclo*-C_8 ligand with the first nucleophile Me linked to a metal-coordinated carbon atom; the hydrogen atom at the metal center forms an agostic bond to C5. The formation of **6**$^+$ can be explained by the elimination of a hydrogen molecule from **5b**$^+$. It is worth mentioning that the dehydrogenated product **6**$^+$ is the only by-product when the crystalline material is freshly dissolved for an NMR sample, whereas the decomposition product **7**$^+$ is preferentially formed in solution (Scheme 8).



Scheme 9. Proposed mechanism for the formation **5b**$^+$

In a final step, the *cyclo*-C_8 ligand should be cleaved to yield stereo- and regioselectively functionalized cyclooctadiene compounds. This operation was successfully performed for **5a**$^+$ [$Nu^1 = Nu^2 = CH(CO_2Me)_2$][6] by the addition of a coordinating solvent (MeCN) to a suspension of **5a**$^+$ in diethyl ether, whereas for the methylated derivative **5b**$^+$ the cleavage of the corresponding cyclooctadiene failed. Alternatively, the cleavage of the *cyclo*-C_8 ligand was attempted by a protonation of the complexes **4b** and **4c** in the presence of a large excess of acetonitrile. As a result the cationic half-sandwich complex $[CpRu(MeCN)_3]^+$ could be recovered and this is the starting material for the synthesis of $[CpRucot]^+$ (**1**$^+$). However, the organic products of this reaction have not yet been characterized. The reaction conditions for a straight cleavage of the stereoselectively functionalized cyclooctadiene ligand are currently being investigated. Successful decomplexations of η^4-coordinated cyclooctatetraene and cyclooctadienes by photochemical and thermal methods have been reported previously.[19]

Conclusions

In this study we have shown that iterative nucleophilic and electrophilic additions to coordinated cyclooctatetraene

are useful tools for the synthesis of stereo- and regioselectively bifunctionalized *cyclo*-C_8 ligands. As demonstrated, the regioselectivity at the different stages of the nucleophilic additions and protonation reactions is controlled by the steric demand of the nucleophiles. Two different mechanisms for the rearrangements are proposed: (i) a flip-flop mechanism in which the product of the first nucleophilic addition changes from the kinetically controlled 1,2,3,4,5-η haptomer to the thermodynamically more stable 1,2-η:5,6,7-η haptomer (Scheme 2) in cases of small nucleophiles and (ii) a 1,5-hydrogen migration caused by the first protonation, which causes a rearrangement of the 1,2-η:4,5,6,7-η haptomer to the 1,2,3,4,5,6-η derivative [Nu^1 = $CH(CO_2Me)_2$] or vice versa when Nu^1 = Ph (see Scheme 5). A third rearrangement can be observed after the second protonation and leads to **5b**$^+$ [Nu^1 = Me, Nu^2 = $CH(CO_2Me)_2$], since the hydrogen atom of the carbon atom bearing Nu^1 is cleaved and a new sp^3-carbon atom is formed, as illustrated in Scheme 9 for **5b**$^+$. The cleavage of the desired *cyclo*-C_8 ligand was successful for the case where Nu^1 = Nu^2 = $CH(CO_2Me)_2$ but as yet has proved unsuccessful when Nu^1 = Nu^2 = Me and Nu^1 = Me, Nu^2 = $CH(CO_2Me)_2$. However, efforts to synthesize stereo- and regioselectively bifunctionalized cyclooctadienes through iterative nucleophilic and electrophilic additions will be continued due to the fact that it is a simple and hence attractive procedure to achieve more intricate organic reactions towards *cyclo*-C_8 terpenoids.

Experimental Section

All reactions were carried out under N_2 and all solvents were saturated with N_2. THF, Et_2O, hexane, and toluene were freshly distilled from the appropriate alkali metal or metal alloy. Dichloromethane was dried with CaH_2 and distilled under N_2. − NMR: Bruker AM 360 and Varian Gemini 200. − IR (Nujol mull, KBr cells): FT-IR 1720X (Perkin−Elmer). − EI-MS (70 eV): Finnigan MAT 311 A, Heraeus CHN-O-Rapid; Institut für Anorganische und Angewandte Chemie, Universität Hamburg. − [CpRu(η^6-cot)]PF_6 (**1**PF_6),[20] the sodium salts of the malonic ester[21] and lithium dimethylamide[22] were synthesized as described. Methyllithium as 5% solution in diethyl ether was purchased from Merck©, Li[BEt_3H] as a 1 M solution in THF from Aldrich and HBF_4 as a 54% solution in diethyl ether from Fluka.

X-ray Crystal Structure Analysis: Determination of the cell parameters and collection of the reflection intensities were performed with a Hilger & Watts [**2c**, **3d**BF_4] or Enraf−Nonius CAD4 [**5b**BF_4] four-circle diffractometer (see Table 1). SHELXS-86[23] was used for structure solving with direct methods and SHELXL-97[24] for structure refinement (refinement on F^2) (for crystallographic details see Table 1).

Crystal Structure Refinement of 2c: Hydrogen atoms on the Cp ring and on C8 were fixed in idealized positions. Positions of all other H atoms were refined free with equal C−H bond lengths in the sets of H1;H2;H5;H6;H7;H3;H4;H9 and H10a;H10b using the SADI operation. Thermal parameters of all protons were attached to the corresponding C atoms with a factor of 1.2.

Crystal Structure Refinement of 3d: Protons on the Cp and the phenyl ring, and on C3 and C8 were fixed in idealized positions. Positions of all other H atoms were refined free with equal C−H bond lengths using the SADI operation. Thermal parameters of all H atoms were attached to the corresponding C atoms with a factor of 1.2.

Crystal Structure Refinement of 5d: H atoms on the Cp ring and on C6, C8A, C9, C10, C13, and C14 were fixed in idealized positions. Positions of all other H atoms (except the agostic hydrogen atom) were refined free with C−H bond lengths fixed to 99 pm for H1, H3, H4, H5, H71, and H72, H71 and H72 were further fixed to equal distances to the vicinal C atoms C6 and C8A. Thermal parameters of all H atoms were attached to the corresponding C atoms with a factor of 1.5 for methyl and 1.2 for all others. The agostic hydrogen atom HOA was refined free in position and its thermal parameter set to 1.5 times the parameter of the Ru center. The site occupation factors for the disordered atoms were refined as a free variable.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-137491 (**2c**), -137492 (**3d**BF_4), and -137493 (**5b**BF_4 and **6**BF_4). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

General Procedure for the Synthesis of Compounds 2a−2i: A solution of the nucleophile in THF (or diethyl ether for Nu^1 = Me) was added dropwise to a suspension of **1** in 50 mL of THF or diethyl ether. The solvent was removed under reduced pressure, the residue was extracted with hexane or diethyl ether, and the extract filtered through Celite. After removal of the solvent, the product was normally obtained as a pale yellow oil. For more preparative details see Table 2, for ^{1}H- and ^{13}C-NMR data see Table 3.

(η^5-Cyclopentadienyl)(1,2,3,4,5-η-8-*exo*-methylcyclooctatrien-6-yl)ruthenium(II) (2a′): $C_{14}H_{16}Ru$ (285.37): calcd. C 58.93, H 5.65; found C 58.94, H 5.38.

(η^5-Cyclopentadienyl)(1,2-η:5,6,7-η-8-*exo*-methylcyclooctatrien-3-yl)ruthenium(II) (2a′′): IR (Nujol): $\tilde{\nu}$ = 1652 (C=C) cm^{-1}. − EI-MS (70 eV); *m/z* (%): 285 (91) [M$^+$], 270 (20) [M$^+$ − CH_3], 259 (100) [$CpRuC_7H_7^+$], 245 (58) [$CpRuC_6H_6^+$], 231 (1) [$CpRuC_5H_5^+$], 218 (2) [$CpRuC_4H_4^+$], 205 (2) [$CpRuC_3H_3^+$], 192 (2) [$CpRuC_2H_2^+$], 179 (1) [CpRuCH$^+$], 166 (23) [CpRu$^+$]. − $C_{14}H_{16}Ru$ (285.37): calcd. C 58.93, H 5.65; found C 58.62, H 5.69.

[1,2-η:5,6,7-η-8-*exo*-Bis(methoxycarbonyl)methylcyclooctatrien-3-yl](η^5-cyclopentadienyl)ruthenium(II) (2b′′): IR (Nujol): $\tilde{\nu}$ = 1733 (C=O), 1651 (C=C) cm^{-1}. − EI-MS (70 eV); *m/z* (%): 401 (91) [M$^+$], 375 (87) [M − $C_2H_2^+$], 283 (22) [M − $CO_2CH_3^+$], 270 (46) [M − $CH(CO_2CH_3)^+$], 258 (11) [M − $CH(CO_2CH_3)_2^+$], 245 (100) [$CpRuC_7H_7^+$], 232 (5) [$CpRuC_5H_5^+$], 167 (34) [CpRu$^+$], 104 (41) [$C_8H_8^+$], 101 (40) [Ru$^+$]. − $C_{18}H_{20}O_4Ru$ (401.45): calcd. C 53.86, H 5.02; found C 54.12, H, 5.18.

[1,2,3,4,5-η-8-*exo*-Bis(methoxycarbonyl)methylcyclooctatrien-6-yl]-(η^5-cyclopentadienyl)ruthenium(II) (2b′): The separation of **2b′** from the haptomer **2b′′** was performed by column chromatography (Al_2O_3/5% H_2O, toluene/diethyl ether = 1:1). Only **2b′** could be isolated.

(η^5-Cyclopentadienyl)(1,2-η:5,6,7-η-8-*exo*-vinylcyclooctatrien-3-yl)-ruthenium(II) (2c): Yellow crystalline product. − IR (Nujol): $\tilde{\nu}$ = 1656 (C=C_{free}), 1631 (C=C_{vinyl}) cm^{-1}. − EI-MS (70 eV); *m/z* (%): 297 (100) [M$^+$], 283 (18) [M − CH_2^+], 271 (98) [M − $C_2H_3^+$], 245

Table 1. Crystallographic details for **2c**, **3d**BF_4, and **5b**BF_4

Compound	**2c**	**3d**BF_4	**5b**BF_4
Empirical formula	$C_{15}H_{16}Ru$	$C_{19}H_{19}BF_4Ru$	$C_{19}H_{25}BF_4O_4Ru$
Molecular mass	297.35	435.22	505.27
T [K]	173(2)	173(2)	173(2)
Space group	$P\bar{1}$	$Pbc2(1)$	$P2(1)/c$
a [Å]	7.5790(10)	16.788(7)	12.855(12)
b [Å]	7.5910(10)	10.314(2)	10.158(8)
c [Å]	10.531(3)	9.818(2)	15.863(14)
α [°]	81.93(2)		
β [°]	80.220(10)		108.61(7)
γ [°]	88.730(10)		
V [Å^3]	591.2(2)	1700.0(9)	1963(3)
Z	2	4	4
$\rho_{calcd.}$[gcm^{-1}]	1.670	1.700	1.710
μ [mm^{-1}]	1.293	0.961	7.024
Crystal size [mm]	0.3 × 0.2 × 0.1	0.3 × 0.2 × 0.04	0.2 × 0.3 × 0.5
2θ range [°]	60.13	55.13	152.79
No. collected intensities	4181	4189	4319
No. observed intensities[a]	3239	1930	2895
No. of parameters	176	246	294
GooF (F^2, all data)	1.075	1.108	1.034
R_{merge} (all data)	0.0265	0.0322	0.0942
$R1$ (obs. data)	0.0234	0.0287	0.0562
$wR2$ (all data)	0.0588	0.0762	0.1577
max/min transmission	0.793/−0.934	1.382/−0.479	3.100/−3.277
Diffractometer	Hilger&Watts[b]	Hilger&Watts[b]	CAD4[c]

[a] Observation criterion $I > 4\sigma(I)$. − [b] Equipped with graphite-monochromized Mo-K_α radiation. − [c] Equipped with graphite-monochromized Cu-K_α radiation.

Table 2. Reacion conditions for the first nucleophilic addition

1 [mg /mmol]	MNu[1]	MNu[1] [mg/mmol]	T[a] [°C]	Solvent for reaction	Solvent for extraction	Product	Yield [mg (%)]
904.0/2.18	LiMe	53/2.41	r.t.	Et_2O	hexane	**2a**	495 (80)
748.0/1.8	$NaCH(CO_2Me)_2$	286/1.8	−78	THF	Et_2O	**2b**	410 (57)
582.0/1.4	$BrMgCH{=}CH_2$	131/1.4	r.t.	THF	hexane	**2c**	243 (58)
335.0/0.81	$BrMgC_6H_5$	2700/14	r.t.	Et_2O	hexane	**2d**	182 (65)
248.0/0.6	$LiB(C_2H_5)_3H$	64/0.6	−78	THF	hexane	**2e**	140 (87)
489.0/1.18	$LiB(C_2H_5)_3D$	125/1.2	−78	THF	hexane	**2f**	273 (85)
169.0/0.41	$LiN(Me)_2$	21/0.41	r.t.	THF	hexane	**2g**	100 (78)
295.0/0.7	NaOMe	38/0.7	−30	Et_2O	hexane	**2h**	143 (67)
181.0/0.44	LiC≡C*t*Bu	38/0.44	−78	THF	hexane	**2i**	90 (61)

[a] Reaction temperature, r.t.: room temperature.

(50) [$CpRuC_6H_6^+$], 167 (98) [$CpRu^+$], 102 (12) [Ru^+]. − $C_{15}H_{16}Ru$ (297.36): calcd. C 60.59, H 5.42; found C 60.21, H 5.59.

(η^5-Cyclopentadienyl)(1,2,3,4,5-η-8-*exo*-phenylcyclooctatrien-6-yl)ruthenium(II) (2d): Yellow powder. − IR (KBr): $\tilde{\nu}$ = 3078, 3051 (C−$H_{arom.}$), 3007, 2940 (C−$H_{aliph.}$), 1669 (C=C_{free}), 1595 (C=$C_{arom.}$) cm^{-1}. − EI-MS (70 eV); *m*/*z* (%): 347 (6) [M^+], 321 (7) [$CpRuC_{12}H_{11}^+$], 245 (3) [$CpRuC_6H_6^+$], 219 (100) [$CpRuC_4H_4^+$], 199 (22) [$CpRuC_2H_2^+$], 167 (9) [$CpRu^+$], 105 (7) [$C_8H_8^+$], 101 (3) [Ru^+]. − $C_{19}H_{18}Ru$ (347.44): calcd. C 65.69, H 5.22; found C 65.39, H 5.29.

(1,2-η:5,6,7-η-Cyclooctatrien-3-yl)(η^5-cyclopentadienyl)ruthenium(II) (2e): IR (Nujol): $\tilde{\nu}$ = 1645 (C=C) cm^{-1}. − EI-MS (70 eV); *m*/*z* (%): 271 (93) [M^+]. − $C_{13}H_{14}Ru$ (271.21): calcd. C 57.55, H 5.20; found C 57.57, H 5.30.

(η^5-Cyclopentadienyl)(1,2-η:5,6,7-η-8-*exo*-dimethylaminocyclooctatrien-3-yl)ruthenium (II) (2g): Yellow powder. − IR (Nujol): $\tilde{\nu}$ = 1657 (C=C), 1263 (C−N) cm^{-1}. − EI-MS (70 eV); *m*/*z* (%): 314 (100) [M^+], 300 (13) [M − CH_3^+], 285 (10) [M − $(CH_3)_2^+$], 271 (44) [M − $N(CH_3)_2^+$]. − $C_{15}H_{19}NRu$ (314.42): calcd. C 57.31, H 6.09, N 4.46; found C 57.53, H 6.06, N 4.24.

(Cyclopentadienyl)(1,2-η:5,6,7-η-8-*exo*-methoxycyclooctatrien-3-yl)ruthenium(II) (2h): Yellow powder. − IR (Nujol): $\tilde{\nu}$ = 1652 (C=C), 1225 (C−O) cm^{-1}. − EI-MS (70 eV); *m*/*z* (%): 301 (31) [M^+], 271 (16) [$CpRuC_8H_8^+$], 258 (8) [$CpRuC_7H_7^+$], 245 (18) [$CpRuC_6H_6^+$], 232 (5) [$CpRuC_5H_5^+$], 167 (27) [$CpRu^+$], 104 (54) [$C_8H_8^+$]. − $C_{14}H_{17}ORu$ (302.38): calcd. C 55.80, H 5.35; found C 55.83, H 5.55.

(Cyclopentadienyl)[1,2-η:5,6,7-η-8-*exo*-(3′,3′-dimethylbutyn-1′-yl)-cyclooctatrien-3-yl]ruthenium(II) (2i): IR (Nujol): $\tilde{\nu}$ = 1651 (C=C) cm^{-1}. − EI-MS (70 eV); *m*/*z* (%): 351 (71) [M^+], 336 (9) [M − CH_3^+], 322 (20) [M − $(CH_3)_2^+$], 306 (5) [M − $(CH_3)_3^+$], 292 (14) [M − $C(CH_3)_3^+$], 269 (5) [M − $C{\equiv}CC(CH_3)_3^+$]. − $C_{19}H_{20}Ru$ (349.46): calcd. C 64.93, H 6.31; found C 64.45, H 6.33.

General Procedure of the First Protonation: Compound **2** was dissolved in diethyl ether (50 mL) and allowed to react with HBF_4, which was dissolved in diethyl ether, at −78 °C. After warming to

Table 3. NMR data of the cyclooctatrienyl complexes **2a**−**2i**

2a′: ^{1}H NMR: δ = 4.50 (s, 5 H, Cp), 1.21 (d, $^3J_{8,Me}$ = 7.2 Hz, 3 H, Me), 3.96 (dd, $^3J_{1,8}$ = 5.5 Hz, $^3J_{1,2}$ = 9.0 Hz, 1 H, 1-H), 4.24 (dd, 1 H, 2-H), 5.56 (dd, $^3J_{2,3}$ = $^3J_{3,4}$ = 6.0 Hz, 1 H, 3-H), 4.51 (m, 1 H, 4-H), 3.70 (dd, $^3J_{4,5}$ = $^3J_{5,6}$ = 7.8 Hz, 1 H, 5-H), 5.78 (m, 1 H, 6-H), 5.29 (dd, $^3J_{6,7}$ = 12.5 Hz, $^3J_{7,8}$ = 2.7 Hz, 1 H, 7-H), 2.43 (m, 1 H, 8-H).
2a′′: ^{1}H NMR (C_6D_6): δ = 4.43 (s, 5 H, Cp), 0.89 (d, $^3J_{8,CH3}$ = 7.5 Hz, 3 H, Me), 2.93 (dd, $^3J_{1,8}$ = 8.0 Hz, 1 H, 1-H), 3.91 (dd, $^3J_{1,2}$ = 8.0 Hz, 1 H, 2-H), 5.65 (dd, $^3J_{2,3}$ = 2.4 Hz, 1 H, 3-H), 5.42 (dd, $^3J_{3,4}$ = 6.0 Hz, 1 H, 4-H), 4.63 (dd, $^3J_{5,6}$ = 8.0 Hz, $^3J_{4,5}$ = 3.4 Hz, 1 H, 5-H), 3.40 (m, 2 H, 6-H, 8-H), 3.78 (dd, $^3J_{7,8}$ = 9.3 Hz, $^3J_{6,7}$ = 7.4 Hz, 1 H, 7-H); [$CD_3C(O)CD_3$]: δ = 4.75 (s, 5 H, Cp), 0.64 (d, $^3J_{8,CH3}$ = 7.6 Hz, 3 H, Me), 2.99 (dd, $^3J_{1,8}$ = $^3J_{1,2}$ = 8.3 H, 1 H, 1-H), 3.83 (m, 2 H, 2-H, 7-H), 5.43 (dd, $^3J_{2,3}$ = 2.5 Hz, $^3J_{3,4}$ = 5.8 Hz, 1 H, 3-H), 5.22 (dd,$^3J_{4,5}$ = 3.2 Hz, 1 H, 4-H), 4.55 (dd, $^3J_{5,6}$ = 7.7 Hz, 1 H, 5-H), 3.50 (t, $^3J_{6,7}$ = 7.7 Hz, 1 H, 6-H), 3.40 (m, 1 H, 8-H). − ^{13}C{^{1}H} NMR (C_6D_6): δ = 79.5 (Cp), 24.1 (Me), 26.4 (C1), 68.2 (C2), 135.6 (C3), 134.2 (C4), 64.1 (C5), 77.3 (C6), 34.3 (C7), 34.0 (C8).
2b′: ^{1}H NMR (C_6D_6): δ = 4.43 (s, 5 H, Cp), 3.38 (s, 3 H, Me), 3.27 (s, 3 H, Me), 4.41 (m, 1 H, 1-H), 4.30 (dd, $^3J_{1,2}$ = 6.7 Hz, $^3J_{2,3}$ = 9.3 Hz, 1 H, 2-H), 5.51 (m, 2 H, 3-H, 6-H), 4.10 (dd, $^3J_{3,4}$ = 5.7 Hz, $^3J_{4,5}$ = 8.2 Hz, 1 H, 4-H), 3.66 (dd, $^3J_{5,6}$ = 8.2 Hz, 1 H, 5-H), 5.89 (m, 1 H, 7-H), 3.74 (m, 1 H, 8-H), 3.31 (d, $^3J_{8,9}$ = 11 Hz, 1 H, 9-H). − ^{13}C{^{1}H} NMR: δ = 79.6 (s, Cp), 169.3, 168.9 (C=O), 51.7, 51.6 (Me), 39.1 (C1), 75.5 (C2), 99.5 (C3), 76.4 (C4), 40.4 (C5), 129.3 (C6), 126.6 (C7), 43.2 (C8), 40.4 (C9).
2b′′: ^{1}H NMR (C_6D_6): δ = 4.34 (s, 5 H, Cp), 3.34 (s, 6 H, Me), 2.95 (dd, $^3J_{1,2}$ = $^3J_{1,8}$ = 8.0 Hz, 1 H, 1-H, H), 3.86 (dd, $^3J_{2,3}$ = 2.6 Hz, 1 H, 2-H), 5.73 (dd, $^3J_{3,4}$ = 6.0 Hz, 1 H, 3-H), 5.44 (dd, $^3J_{4,5}$ = 3.4 Hz, 1 H, 4-H), 4.57 (dd, $^3J_{5,6}$ = 8.1 Hz, 1 H, 5-H), 3.38 (dd, $^3J_{6,7}$ = 7.4 Hz, 1 H, 6-H), 3.90 (dd, $^3J_{7,8}$ = 9.2 Hz, 1 H, 7-H), 4.48 (m, 1 H, 8-H), 4.00 (d, $^3J_{1,9}$ = 12.1 Hz, 1 H, 9-H). − ^{13}C{^{1}H} NMR: δ = 80.5 (s, Cp), 169.3, 168.9, 167.3 (s, C=O), 58.3 (s, Me), 23.5 (C1), 68.5 (C2), 136.6 (C3), 134.7 (C4), 65.3 (C5), 78.4 (C6), 31.4 (C7), 40.3 (C8), 52.1 (C9).
2c: ^{1}H NMR (C_6D_6): δ = 4.45 (s, 5 H, Cp), 5.59 (m, 1 H, 9-H), 4.96 (dd, $^2J_{10,11}$ = 2.1 Hz, $^3J_{9,10}$ = 10.3 Hz, 1 H, 10-H), 4.77 (dd, $^3J_{9,11}$ = 17.4 Hz, 1 H, 11-H), 2.91 (dd, $^3J_{1,2}$ = $^3J_{1,8}$ = 7.8 Hz, 1 H, 1-H), 3.93 (dd, $^3J_{2,3}$ = 2.4 Hz, 1 H, 2-H), 5.54 (dd, $^3J_{3,4}$ = 5.9 Hz, 1 H, 3-H), 5.29 (dd, $^3J_{4,5}$ = 3.4 Hz, 1 H, 4-H), 4.63 (dd, $^3J_{5,6}$ = 7.5 Hz, 1 H, 5-H), 3.45 (dd, $^3J_{6,7}$ = 7.5 Hz, 1 H, 6-H), 3.75 (dd, $^3J_{7,8}$ = 7.5 Hz, 1 H, 7-H), 4.03 (m, 1 H, 8-H). − ^{13}C{^{1}H} NMR: δ = 79.8 (Cp), 144.6 (C9), 110.2 (C10), 24.2 (C1), 67.9 (C2), 135.3 (C3), 134.3 (C4), 64.7 (C5), 76.7 (C6), 30.1 (C7), 42.3 (C8).
2d: ^{1}H NMR (C_6D_6): δ = 7.70 (m, 1 H, *p*-Ph), 6.91 (m, 2 H, *m*-Ph), 7.08 (m, 2 H, *o*-Ph), 4.49 (s, 5 H, Cp), 4.13 (dd, $^3J_{1,8}$ = 5.6 Hz, $^3J_{1,2}$ = 8.8 Hz, 1 H, 1-H), 4.00 (dd, $^3J_{2,3}$ = 5.8 Hz, 1 H, 2-H), 5.57 (dd, $^3J_{3,4}$ = 5.8 Hz, 1 H, 3-H), 4.56 (dd, $^3J_{4,5}$ = 7.8 Hz, 1 H, 4-H), 3.69 (dd, $^3J_{5,6}$ = 7.8 Hz, 1 H, 5-H), 5.87 (dd, $^3J_{6,7}$ = 10.6 Hz, 1 H, 6-H), 5.43 (dd, $^3J_{7,8}$ = 2.7 Hz, 1 H, 7-H), 3.81 (m, 1 H, 8-H). − ^{13}C{^{1}H} NMR: δ = 79.5 (Cp), 149.0, 129.7, 126.1 (Phenyl-C), 39.8 (C1), 75.5 (C2), 99.5 (C3), 49.5 (C4), 30.2 (C5), 132.9 (C6), 131.6 (C7), 45.8 (C8).
2e: ^{1}H NMR (C_6D_6): δ = 4.40 (s, 5 H, Cp), 2.65 (m, 1 H, 1-H), 3.96 (dd, $^3J_{1,2}$ = 7.5 Hz, $^3J_{2,3}$ = 2.1 Hz, 1 H, 2-H), 5.46 (dd, $^3J_{3,4}$ = 6.1 Hz, 1 H, 3-H), 5.54 (dd, $^3J_{4,5}$ = 3.2 Hz, 1 H, 4-H), 4.57 (dd, $^3J_{5,6}$ = 7.5 Hz, 1 H, 5-H), 3.18 (dd, $^3J_{6,7}$ = 7.5 Hz, 1 H, 6-H), 3.33 (m, 1 H, 7-H), 2.87 (m, 2 H, 8_{endo}-H, 8_{exo}-H). − ^{13}C{^{1}H} NMR: δ = 79.6 (Cp), 12.4 (C1), 66.8 (C2), 135.0 (C3), 132.3 (C4), 63.4 (C5), 74.2 (C6), 21.7 (C7), 22.6 (C8).
2f: ^{13}C{H} NMR: δ = 22.6 (t, $^1J_{C,D}$ = 20.3 Hz, C7).
2g: ^{1}H NMR (C_6D_6): δ = 4.47 (s, 5 H, Cp), 1.99 (s, 6 H, Me), 2.86 (dd, $^3J_{1,2}$ = $^3J_{1,8}$ = 7.7 Hz, 1 H, 1-H), 3.52 (dd, $^3J_{2,3}$ = 2.3 Hz, 1 H, 2-H), 5.61 (dd, $^3J_{3,4}$ = 5.9 Hz, 1 H, 3-H), 5.43 (dd, $^3J_{4,5}$ = 3.3 Hz, 1 H, 4-H), 4.65 (dd, $^3J_{5,6}$ = 7.9 Hz, 1 H, 5-H), 3.19 (dd, $^3J_{6,7}$ = 7.8 Hz, 1 H, 6-H), 3.93 (dd, $^3J_{7,8}$ = 7.8 Hz, 1 H, 7-H), 3.63 (dd, 1 H, 8-H). − ^{13}C{^{1}H} NMR: δ = 79.9 (Cp), 39.8 (Me), 27.5 (C1), 67.4 (C2), 134.1 (C3), 132.9 (C4), 65.8 (C5), 78.5 (C6), 66.5 (C7), 34.1 (C8).
2h: ^{1}H NMR (C_6D_6): δ = 4.36 (s, 5 H, Cp), 3.02 (s, 3 H, Me), 2.99 (dd, $^3J_{1,2}$ = 7.9 Hz, $^3J_{1,8}$ = 7.3 Hz, 1 H, 1-H), 4.06 (dd, $^3J_{2,3}$ = 2.4 Hz, 1 H, 2-H), 5.68 (dd, $^3J_{3,4}$ = 6.0 Hz, 1 H, 3-H), 5.41 (dd, $^3J_{4,5}$ = 3.6 Hz, 1 H, 4-H), 4.68 (dd, $^3J_{5,6}$ = 7.8 Hz, 1 H, 5-H), 3.63 (dd, $^3J_{5,6}$ = $^3J_{6,7}$ = 7.8 Hz, 1 H, 6-H), 3.77 (dd, $^3J_{7,8}$ = 8.0 Hz, 1 H, 7-H), 4.56 (dd, $^3J_{1,8}$ = 7.3 Hz, 1 H, 8-H). − ^{13}C{^{1}H} NMR: δ = 79.8 (Cp), 50.8 (Me), 24.8 (C1), 67.8 (C2), 134.7 (C3), 132.6 (C4), 65.9 (C5), 76.0 (C6), 35.6 (C7), 30.1 (C8).
2i: [$CD_3C(O)CD_3$]: δ = 4.78 (s, 5 H, Cp), 1.18 (s, 9 H, Me), 2.97 (dd, $^3J_{1,2}$ = $^3J_{1,8}$ = 8.0 Hz, 1 H, 1-H), 3.91 (dd, $^3J_{2,3}$ = 2.4 Hz, 1 H, 2-H), 5.39 (dd, $^3J_{3,4}$ = 5.9 Hz, 1 H, 3-H), 5.15 (dd, $^3J_{4,5}$ = 3.2 Hz, 1 H, 4-H), 4.62 (dd, $^3J_{5,6}$ = 7.9 Hz, 1 H, 5-H), 3.45 (dd, $^3J_{6,7}$ = 6.9 Hz, 1 H, 6-H), 3.76 (dd, $^3J_{7,8}$ = 9.4 Hz, 1 H, 7-H), 4.08 (dd, $^3J_{7,8}$ = 9.4 Hz, 1 H, 8-H). − ^{13}C{^{1}H} NMR [$CD_3C(O)CD_3$]: δ = 80.4 (Cp), 30.0 (Me), 21.5 (C1), 69.0 (C2), 135.9 (C3), 133.5 (C4), 65.1 (C5), 75.9 (C6), 31.4 (C7), 66.9 (C8).

room temperature, the mixture was filtered and the residue washed several times with diethyl ether. The yellow residue was dissolved in dichloromethane, the product was precipitated with diethyl ether and dried under vacuum. For more preparative details see Table 4, for ^{1}H- and ^{13}C-NMR data see Table 5.

Table 4. Reaction conditions of the protonation reaction of **2a**−**2d**, **2g**, and **2h**

Starting material	Nu[1]	mg [mmol]	HBF_4 [ml]	Product BF_4 salts	Yield [mg (%)]
2a	Me	361.0 (1.27)	0.2	**3a**$^+$	433 (91)
2b	$CH(CO_2Me)_2$	652.0 (1.6)	0.23	**3b**$^+$	724 (91)
2c	$CH=CH_2$	162.0 (0.54)	0.07	**3c**$^+$	173 (72)
2d	C_6H_5	78.0 (0.23)	0.03	**3d**$^+$	76 (76)
2g	NMe_2	98.0 (0.31)	0.04	**1**$^+$ + **3e**$^+$	n.d.[a]
2h	OMe	63.0 (0.21)	0.03	**1**$^+$	75 (93)

[a] n.d. = not determined.

(η^5-Cyclopentadienyl)(1,2-η:4,5,6,7-η-8-*exo*-2-methylcycloocta-1,4,6-triene)ruthenium(II) Tetrafluoroborate (3aBF_4): IR (Nujol): $\tilde{\nu}$ = 1035 (BF_4) cm^{-1}. − EI-MS (70 eV); *m/z* (%): 286 (73) [M − BF_4^+], 271 (31) [M − BF_4 − CH_3^+], 259 (89) [$CpRuC_7H_8^+$], 245 (26) [$CpRuC_6H_6^+$], 232 (43) [$CpRuC_5H_5^+$], 217 (12) [$CpRuC_4H_4^+$], 205 (6) [$CpRuC_3H_3^+$], 191 (14) [$CpRuC_2H_2^+$], 179 (9) [$CpRuC_1H_1^+$], 167 (84) [$CpRu^+$], 143 (15) [$C_3H_3Ru^+$], 114 (11) [$C_1H_1Ru^+$], 105 (25) [$C_8H_9^+$], 104 (11) [$C_8H_8^+$], 102 (10) [Ru^+]. − $C_{14}H_{17}BF_4Ru$ (373.16): calcd. C 45.06, H 4.59; found C 44.35, H 5.40.

[1,2-η:4,5,6,7-η-8-*exo*-Bis(methoxycarbonyl)methylcycloocta-1,4,6-triene](η^5-cyclopentadienyl)ruthenium(II) Tetrafluoroborate (3b′BF_4): IR (Nujol): $\tilde{\nu}$ = 1733 (C=O), 1252−1156 (C−O), 1048 (BF_4) cm^{-1}. − EI-MS (70 eV); *m/z* (%): 401 (18) [M − BF_4^+], 343 (30) [M − BF_4 − $(CO_2CH_3)^+$], 282 (36) [M − BF_4-$(CO_2CH_3)_2^+$], 272 (12) [$CpRuC_8H_8^+$], 258 (16) [$CpRuC_7H_7^+$], 245 (18) [$CpRuC_6H_6^+$], 167 (76) [$CpRu^+$]. − $C_{18}H_{21}BF_4O_4Ru$ (489.27): calcd. C 44.19, H 4.33; found C 43.49, H 4.38.

(η^5-Cyclopentadienyl)(1,2-η:4,5,6,7-η-8-*exo*-vinylcycloocta-1,4,6-triene)ruthenium(II) Tetrafluoroborate (3cBF_4): IR (Nujol): $\tilde{\nu}$ = 1633 (C=C_{vinyl}), 1050 (BF_4) cm^{-1}. − EI-MS (70 eV); *m/z* (%): 297 (6) [M − BF_4^+], 271 (10) [$CpRuC_8H_8^+$], 196 (8) [$CpRuC_2H_2^+$], 178 (6) [$CpRuC_1H_1^+$], 167 (18) [$CpRu^+$]. − $C_{15}H_{17}BF_4Ru$ (385.20): calcd. C 46.78, H 4.45; found C 46.31, H 4.44.

(η^5-Cyclopentadienyl)(1,2-η:4,5,6,7-η-8-*exo*-phenylcycloocta-1,4,6-triene)ruthenium(II) Tetrafluoroborate (3dBF_4): IR (Nujol): $\tilde{\nu}$ = 1597, 1569 (C=C_{phenyl}), 1075 (BF_4) cm^{-1}. − EI-MS (70 eV); *m/z*

Table 5. NMR data of the protonated complexes **3a$^+$**−**3i$^+$**, obtained from [D$_6$]acetone solutions

3a$^+$: ^{1}H NMR: δ = 5.54 (s, 5 H, Cp), 0.70 (d, $^3J_{8,CH3}$ = 7.6 Hz, 3 H, Me), 3.79 (dd, $^3J_{1,2}$ = $^3J_{1,8}$ = 8.5 Hz, 1 H, 1-H), 3.67 (m, 1 H, 2-H), 3.13 (m, 1 H, 3$_{endo}$-H), 2.11 (m, 1 H, 3$_{exo}$-H), 4.49 (m, 1 H, 4-H), 5.66 (dd, $^3J_{4,5}$ = $^3J_{5,6}$ = 8.1 Hz, 1 H, 5-H), 5.57 (m, 1 H, 6-H), 4.84 (dd, $^3J_{7,8}$ = $^3J_{6,7}$ = 9.8 Hz, 1 H, 7-H), 3.56 (m, 1 H, 8-H). − ^{13}C{^{1}H} NMR: δ = 84.2 (Cp), 19.1 (Me), 32.7 (C-1), 39.6 (C-2), 21.5 (C-3), 33.2 (C-4), 91.6 (C-5), 90.6 (C-6), 45.1 (C-7), 27.8 (C-8).
3b′$^+$: ^{1}H NMR: δ = 5.59 (s, 5 H, Cp), 3.72 (s, 3 H, Me), 3.67 (s, 3 H, Me), 3.92 (dd, $^3J_{1,8}$ = $^3J_{7,8}$ = 8.1 Hz, 1 H, 1-H), 3.63 (m, 1 H, 2-H), 3.22 (m, 1 H, 3$_{endo}$-H), 1.81 (m, 1 H, 3$_{exo}$-H), 4.56 (m, 1 H, 4-H), 5.81 (dd, $^3J_{5,6}$ = $^3J_{4,5}$ = 8 Hz, 1 H, 5-H), 5.60 (m, 1 H, 6-H), 4.79 (dd, $^3J_{7,8}$ = $^3J_{6,7}$ = 9.8 Hz, 1 H, 7-H), 4.17 (m, 1 H, 8-H), 3.09 (d, $^3J_{8,9}$ = 12.4 Hz, 1 H, 9-H); (CD$_3$CN): δ = 5.35 (s, 5 H, Cp), 3.79 (s, 3 H, Me), 3.74 (s, 3 H, Me), 3.76 (dd, 1 H, 1-H), 3.27 (m, 1 H, 2-H), 3.17 (m, 3 H, 3$_{endo}$-H), 1.70 (m, 1 H, 3$_{exo}$-H), 4.35 (m, 1 H, 4-H), 5.51 (dd, 1 H, 5-H), 5.28 (m, 1 H, 6-H), 3.60 (dd, 1 H, 7-H), 4.10 (m, 1 H, 8-H), 2.95 (d, 1 H, 9-H). − ^{13}C{^{1}H} NMR: δ = 83.8 (Cp), 52.1 (Me), 167.7 (C=O), 35.6 (C1), 52.3 (C2), 18.0 (C3), 32.3 (C4), 90.6 (C5), 90.9 (C6), 41.4 (C7), 33.2 (C8), 55.2 (C9).
3b′$^+$-D$_1$: ^{13}C{^{1}H} NMR: δ = 17.6 (t, $^1J_{C,D}$ = 24.6 Hz, C3).
3b′′$^+$: ^{1}H NMR: δ = 5.67 (s, 5 H, Cp), 3.73 (s, 3 H, Me), 3.65 (s, 3 H, Me), 6.11 (dd, $^3J_{1,8}$ = 9.7 Hz, $^3J_{1,2}$ = 3.6 Hz, 1 H, 1-H), 5.43 (m, 2 H, 2-H, 6-H), 6.96 (dd, $^3J_{2,3}$ = $^3J_{3,4}$ = 8.4 Hz, 1 H, 3-H), 6.84 (dd, $^3J_{4,5}$ = 6.3 Hz, 1 H, 4-H), 6.26 (dd, $^3J_{5,6}$ = 6.3 Hz, 1 H, 5-H), 1.63 (m, 1 H, 7$_{endo}$-H), −0.95 (m, 1 H, 7$_{exo}$-H), 3.92 (m, 1 H, 8-H), 3.40 (d, $^3J_{8,9}$ = 8.3 Hz, 1 H, 9-H). − ^{13}C{^{1}H} NMR: δ = 87.2 (Cp), 52.3 (Me), 86.7 (C1), 85.7 (C2), 105.6 (C3), 95.5 (C4), 83.3 (C5), 78.01 (C6), 28.3 (C7), 32.3 (C8), 58.0 (C9).
3b′′-D$_1$: ^{13}C{^{1}H} NMR: δ = 27.1 (t, $^1J_{C,D}$ = 20.3 Hz, C7).
3c$^+$: ^{1}H NMR: δ = 5.57 (s, 5 H, Cp), 5.45 (m, 1 H, CH$_{vinyl}$), 4.91 (m, 1 H, CH$_{2,vinyl}$), 4.81 (m, 1 H, CH$_{2,vinyl}$), 3.95 (dd, $^3J_{1,2}$ = $^3J_{1,8}$ = 7.4 Hz, 1 H, 1-H), 3.62 (m, 1 H, 2-H), 2.95 (m, 1 H, 3$_{endo}$-H), 2.01 (m, 1 H, 3$_{exo}$-H), 4.41 (m, 1 H, 4-H), 5.50 (m, 1 H, 5-H), 5.75 (m, 1 H, 6-H), 4.67 (m, 1 H, 7-H), 4.20 (m, 1 H, 8-H). − ^{13}C{^{1}H} NMR: δ = 84.0 (Cp), 140.0 (CH$_{vinyl}$), 118.5 (CH$_{2,vinyl}$), 32.9 (C1), 33.1 (C2), 17.8 (C3), 36.8 (C4), 90.6 (C5), 92.6 (C6), 41.4 (C7), 37.2 (C8).
3d$^+$: ^{1}H NMR: δ = 5.62 (s, 5 H, Cp), 7.25 (m, 2 H, *m*-Ph), 7.14 (m, 1 H, *p*-Ph), 7.04 (m, 2 H, *o*-Ph), 4.37 (dd, $^3J_{1,2}$ = $^3J_{1,8}$ = 8.8 Hz, 1 H, 1-H), 3.64 (m, 1 H, 2-H), 2.63 (m, 1 H, 3$_{endo}$-H), 0.70 (m, 1 H, 3$_{exo}$-H), 4.32 (m, 1 H, 4-H), 5.77 (dd, $^3J_{4,5}$ = $^3J_{5,6}$ = 8.1 Hz, 1 H, 5-H), 5.91 (dd, $^3J_{6,7}$ = 9.3 Hz, 1 H, 6-H), 4.94 (dd, $^3J_{7,8}$ = 9.3 Hz, 1 H, 7-H), 4.84 (m, 1 H, 8-H). − ^{13}C{^{1}H} NMR: δ = 84.2 (Cp), 141.0, 129.1, 127.0, 124.8 (Phenyl-C), 31.9 (C1), 32.5 (C2), 38.5 (C2), 17.9 (C3), 37.6 (C4), 90.5 (C5), 93.0 (C6), 41.9 (C7), 38.5 (C8).
3e$^+$: ^{1}H NMR: δ = 5.76 (s, 5 H, Cp), 2.96 (s, 6 H, Me), 6.08 (m, 1 H, 1-H), 5.86 (dd, $^3J_{1,2}$ = $^3J_{2,3}$ = 8.9 Hz, 1 H, 2-H), 7.10 (dd, $^3J_{3,4}$ = 8.9 Hz, 1 H, 3-H), 6.94 (m, 1 H, 4-H), 6.42 (dd, $^3J_{4,5}$ = $^3J_{5,6}$ = 5.5 Hz, 1 H, 5-H), 5.13 (m, 1 H, 6-H), 2.17 (m, 1 H, 7$_{endo}$-H), −0.61 (m. 1 H, 7$_{exo}$-H), 4.90 (m, 1 H, 8-H).

(%): 347 (8) [M − BF$_4^+$], 321 (8) [M − (C$_2$H$_2$)-BF$_4^+$], 167 (10) [CpRu$^+$]. − C$_{19}$H$_{19}$BF$_4$Ru (435.26): calcd. C 52.43, H 4.40; found C 51.82, H 4.58.

Second Nucleophilic Addition

[1,2,3,4,5-η-6,8-*exo*,*exo*-Bis{bis(methoxycarbonyl)methyl}-cyclooctadienyl](η^5-cyclopentadienyl)ruthenium(II) (4a): To a suspension of **3b**BF$_4$ (645 mg, 1.3 mmol) in THF (50 mL) was added a solution of NaCH(CO$_2$CH$_3$)$_2$ (223 mg, 1.45 mmol) in THF (20 mL) at room temperature. The solvent was removed under reduced pressure, the residue was extracted with toluene and the extract was filtered through Celite. After removal of the solvent, the product **4a** was obtained as a yellow powder. Yield: 558 mg (79%). For ^{1}H- and ^{13}C-NMR data see Table 6. − IR (KBr): $\tilde{\nu}$ = 2988 (C−H$_{arom.}$), 2947, 2923 (C−H$_{aliph.}$), 1729 (C=O), 1228 (C−O) 6cm^{-1}. − EI-MS (70 eV); *m*/*z* (%): 532 (11) [M$^+$], 402 (35) [M − CH(CO$_2$CH$_3$)$_2^+$], 343 (47) [M − CH(CO$_2$CH$_3$)$_2$ − (CO$_2$CH$_3$)], 283 (33) [CpRuC$_9$H$_{11}^+$], 272 (19) [CpRuC$_8$H$_8^+$], 258 (8) [CpRuC$_7$H$_7^+$], 245 (20) [CpRuC$_6$H$_6^+$], 167 (44) [CpRu$^+$], 101 (78) [Ru$^+$], 59 (100) [C$_2$H$_3$O$_2^+$]. − C$_{23}$H$_{28}$O$_8$Ru (533.58): calcd. C 51.78, H 5.29; found C 51.63, H 5.60.

[1,2-η:5,6,7-η-4-*exo*-Bis(methoxycarbonyl)methyl-8-*exo*-methyl-cyclooctadienyl](η^5-cyclopentadienyl)ruthenium(II) (4b): To a suspension of **3a**BF$_4$ (298 mg, 0.8 mmol) in THF (30 mL) was added a solution of NaCH(CO$_2$CH$_3$)$_2$ (123 mg, 0.8 mmol) in THF (20 mL). The solvent was removed under reduced pressure, the residue was extracted with toluene and the extract filtered through Celite. After removal of the solvent, the product **4b** was obtained as a green oil. Yield: 200 mg (60%). For ^{1}H- and ^{13}C-NMR data see Table 6. − IR (Nujol): $\tilde{\nu}$ = 1754, 1732 (C=O), 1253, 1139 (C−O) cm^{-1}. − EI-MS (70 eV); *m*/*z* (%): 416 (19) [M$^+$], 357 (9) [M − CO$_2$CH$_3^+$], 297 (8) [M − (CO$_2$CH$_3$)$_2^+$], 285 (68) [M − CH(CO$_2$CH$_3$)$_2^+$], 270 (11) [CpRuC$_8$H$_8^+$], 259 (55) [CpRuC$_7$H$_7^+$], 245 (16) [CpRuC$_6$H$_6^+$], 232 (11) [CpRuC$_5$H$_5^+$], 217 (10) [CpRuC$_4$H$_4^+$], 204 (4) [CpRuC$_3$H$_3^+$], 191 (8) [CpRuC$_2$H$_2^+$], 178 (6) [CpRuCH$^+$], 167 (58) [CpRu$^+$], 105 (29) [C$_8$H$_8^+$], 101 (97) [Ru$^+$]. − C$_{19}$H$_{24}$O$_4$Ru (417.50): calcd. C 54.67, H 5.79; found C 55.24, H 6.03.

Table 6. ^{1}H- and ^{13}C-NMR data of the products of the second nucleophilic addition (**4a**−**4c**)

4a: ^{1}H NMR (C$_6$D$_6$): δ = 4.45 (s, 5 H, Cp), 3.37, 3.35 (s, 12 H, Me), 3.84 (dm, $^3J_{1,2}$ = $^3J_{4,5}$ = 8.0 Hz, 2 H, 1-H, 5-H), 4.01 (dd, $^3J_{1,2}$ = $^3J_{4,5}$ = 8.0 Hz, $^3J_{2,3}$ = $^3J_{3,4}$ = 6.1 Hz, 2 H, 2-H, 4-H), 5.63 (t, $^3J_{2,3}$ = $^3J_{3,4}$ = 6.1 Hz, 1 H, 3-H), 2.83 (m, 2 H, 6-H, 8-H), 1.30 (m, 1 H, 7$_{endo}$-H), 0.19 (m, 1 H, 7$_{exo}$-H), 3.41 (d, $^3J_{6,9}$ = $^3J_{8,9'}$ = 7 Hz, 2 H, 9-H, 9′-H); [CD$_3$C(O)CD$_3$]: δ = 4.85 (s, 5 H, Cp), 3.68, 3.62 (s, 12 H, Me), 3.64 (m, 2 H, 1-H, 5-H), 4.15 (dd, 2 H, 2-H, 4-H), 6.01 (t, 1 H, 3-H), 2.36 (m, 2 H, 6-H, 8-H), 0.83 (d, 1 H, 7$_{endo}$-H), −0.18 (m, 1 H, 7$_{exo}$-H), 3.19 [d, 2 H, C*H*(CO$_2$Me)$_2$]. ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ = 80.2 (Cp), 61.6 (Me), 169.1, 168.8 (C=O), 44.1 (C1, C5), 72.3 (C2, C4), 103.1 (C3), 42.9 (C6, C8), 27.8 (C7), 51.6 (C9).
4a-D$_1$: ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ = 27.4 (t, $^1J_{C,D}$ = 17.4 Hz, C-7).
4b: ^{1}H NMR (C$_6$D$_6$): δ = 4.38 (s, 5 H, Cp), 0.96 (d, $^3J_{8,CH3}$ = 7.6 Hz, 3 H, Me), 3.43 (s, 3 H, OMe), 3.32 (s, 3 H, OMe), 2.95 (dd, $^3J_{1,8}$ = $^3J_{1,2}$ = 8.1 Hz, 1 H, 1-H), 3.51 (m, 1 H, 2-H), 1.38 (m, 1 H, 3$_{exo}$-H), 2.11 (m, 1 H, 3$_{endo}$-H), 4.14 (m, 1 H, 4-H), 4.78 (dd, $^3J_{4,5}$ = 5.3 Hz, 1 H, 5-H), 2.70 (dd, $^3J_{5,6}$ = 9.0 Hz, 1 H, 6-H), 3.70 (dd, $^3J_{7,8}$ = $^3J_{6,7}$ = 9.0 Hz, 1 H, 7-H), 3.38 (m, 1 H, 8-H), 3.55 (d, $^3J_{4,9}$ = 5.8 Hz, 1 H, 9-H). − ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ = 79.4 (Cp), 168.8, 168.7 (C=O), 51.8 (OMe), 24.6 (Me), 26.6 (C1), 61.3 (C2), 29.1 (C3), 55.4 (C4), 66.6 (C5), 73.7 (C6), 42.8 (C7), 35.3 (C8), 60.0 (C9).
4c: ^{1}H NMR: δ = 4.44 (s, 5 H, Cp), 1.20 (d, $^3J_{8,CH3}$ = 6.8 Hz, Me), 1.02 (d, $^3J_{4,CH3}$ = 7.6 Hz, 3 H, Me), 2.99 (dd, $^3J_{1,8}$ = 8.0 Hz, 1 H, 1-H), 3.60 (dd, $^3J_{2,3}$ = 16 Hz, $^3J_{1,2}$ = 8.0 Hz, 1 H, 2-H), 1.23 (m, 1 H, 3$_{exo}$-H), 1.92 (m, 1 H, 3$_{endo}$-H), 3.43 (m, 1 H, 4-H), 4.56 (m, 1 H, 5-H), 2.66 (dd, $^3J_{5,6}$ = 9.5 Hz, 1 H, 6-H), 3.78 (dd, $^3J_{7,8}$ = $^3J_{6,7}$ = 9.0 Hz, 1 H, 7-H), 3.34 (m, 1 H, 8-H). − ^{13}C{^{1}H} NMR: δ = 79.0 (Cp), 33.3, 23.9 (Me), 24.4 (C1), 62.9 (C2), 26.0 (C3), 52.9 (C4), 72.9 (C5), 74.1 (C6), 41.3 (C7), 35.3 (C8).

Table 7. ^{1}H-NMR data of the protonated complexes **5a$^+$**−**5c$^+$**, **6$^+$**, and **7$^+$**

5a$^+$: ^{1}H NMR (CD_2Cl_2): δ = 5.52 (s, 5 H, Cp), 3.76 (s, 6 H, Me), 3.72 (s, 6 H, Me), −10.6 (s, 1 H, Ru-H), 3.85 (dd, $^3J_{1,8} = {}^3J_{1,2} = {}^3J_{4,5} = {}^3J_{5,6}$ = 4.0 Hz, 2 H, 1-H, 5-H), 5.58 (m, 2 H, 2-H, 4-H), 7.05 (t, $^3J_{2,3} = {}^3J_{3,4}$ = 6.9 Hz, 3-H), 2.66 (m, 2 H, 6-H, 8-H), 1.24 (m, 7_{endo}-H), 0.27 (m, 1 H, 7_{exo}-H), 3.36 (d, $^3J_{6,9} = {}^3J_{8,9'}$ = 6.7 Hz, 2 H, 9-H, 9′-H).
5b$^+$: ^{1}H NMR (CD_2Cl_2): δ = 5.41 (s, 5 H, Cp), 3.76, 3.66 (s, 6 H, OMe), 3.34 [d, $^3J_{6,CH}$ = 6.7 Hz, 1 H, C*H*(CO_2Me)$_2$], 2.27 (s, 3 H, Me), 4.01 (m 1 H, 1-H), 6.92 (d, $^3J_{3,4}$ = 6.7 Hz, 1 H, 3-H), 5.41 (m, 1 H, 4-H), 5.42 (m, 1 H, 5-H), 3.84 (m, 1 H, 6-H), 1.32 (m, 1 H, 7_{endo}-H), 0.34 (m, 1 H, 7_{exo}-H), 2.49 (m, 1 H, 8_{endo}-H), 1.84 (m, 1 H, 8_{exo}-H), −10.41 (s, 1 H, Ru-H).
5c$^+$: ^{1}H NMR (CD_2Cl_2): δ = 5.36 (s, 5 H, Cp), 0.69 (d, $^3J_{8,CH3}$ = 7.6 Hz, 3 H, Me), 1.07 (d, $^3J_{4,CH3}$ = 6.8 Hz, 3 H, Me), 4.34 (m, 1 H, 1-H), 3.59 (m, 1 H, 2-H), 3.06 (m, 1 H, 3_{endo}-H), 2.08 (m, 1 H, 3_{exo}-H), 2.23 (m 1 H, 4-H), 5.32 (m, 1 H, 5-H), 5.30 (m, 1 H, 6-H), 4.67 (m, 1 H, 7-H), 3.48 (m, 1 H, 8-H), −10.47 (s, 1 H, Ru-H).
6$^+$: ^{1}H NMR (CD_2Cl_2): δ = 5.43 (s, 5 H, Cp), 5.18 (m, 1 H, 1-H), 6.06 (d, $^3J_{1,2}$ = 7.9 Hz, 1 H, 2-H), 6.70 (d, $^3J_{4,5}$ = 8.8 Hz, 1 H, 4-H), 5.26 (dd, $^3J_{5,6}$ = 9.7 Hz, 1 H, 5-H), 5.85 (dm, $^3J_{5,6}$ = 9.7 Hz, 1 H, 6-H), 3.74 (m, 1 H, 7-H), 1.58 (m, 1 H, 8_{endo}-H), −0.85 (m, 1 H, 8_{exo}-H), 2.62 (s, 3 H, Me), 3.21 [d, $^3J_{7,CH(CO2Me)2}$ = 7.4 Hz, 1 H, C*H*(CO_2Me)$_2$], 3.75 [s, 6 H, CH(CO_2*Me*)$_2$].
7$^+$: ^{1}H NMR (CD_2Cl_2): δ = 5.30 (s, 5 H, Cp), 5.94 (m, 1 H, 1-H), 5.40 (m, 1 H, 3-H), 6.65 (m, 1 H, 4-H), 6.58 (m, 1 H, 5-H), 5.48 (m, 1 H, 6-H), 1.58 (m, 1 H, 7_{endo}-H), −0.45 (tdd, $^3J_{7exo,8endo}$ = 4.6 Hz, $^3J_{6,7exo}$ = 9.1 Hz, $^2J_{7exo,7endo}$ = 13.4 Hz, 7_{exo}-H), 2.70 (m, 1 H, 8_{endo}-H), 2.14 (m, 1 H, 8_{exo}-H), 2.63 (s, 3 H, *Me*)

(η^5-Cyclopentadienyl)(1,2-η:5,6,7-η-4,8-*exo*,*exo*-dimethylcyclooctadienyl)ruthenium(II) (4c): Methyllithium (1.29 mL, 2.1 mmol of a 5% solution in diethyl ether) was added to a suspension of **3a**BF_4 (770 mg, 2.06 mmol) in diethyl ether (40 mL). The solvent was removed under reduced pressure, the residue extracted with hexane and the extract filtered through Celite. After removal of the solvent, the product **4c** was obtained as a green oil. Yield: 593 mg (96%). For ^{1}H- and ^{13}C-NMR data see Table 6. − IR (Nujol): $\tilde{\nu}$ = 1620 (C=$C_{arom.}$) cm^{-1}. − EI-MS (70 eV); *m*/*z* (%): 300 (100) [M^+], 285 (64) [$M - CH_3^+$], 273 (43) [$CpRuC_8H_9^+$], 259 (57) [$CpRuC_7H_7^+$], 245 (13) [$CpRuC_6H_6^+$], 230 (9) [$CpRuC_5H_5^+$], 167 (57) [$CpRu^+$]. − $C_{15}H_{20}Ru$ (301.42): calcd. C 59.78, H 6.69; found C 59.68, H 6.52.

Protonation of the Cyclooctadienyl Complexes 4a−4c: The procedure for the protonation was performed as described for the protonation of **2** (vide supra). For ^{1}H-NMR data see Table 7.

{1,2,3,4,5-η-6,8-*exo,exo*-Bis[bis(methoxycarbonyl)methyl]-cyclooctadienyl}(η^5-cyclopentadienyl)hydridoruthenium(II) Tetrafluoroborate (5aBF_4): 613 mg of 4a, 0.22 mL of HBF_4 solution (54% solution in diethyl ether), 40 mL of diethyl ether, T = −65 °C. Yield: 581 mg (81%) of a yellow powder. − IR (KBr): $\tilde{\nu}$ = 3117 (C−$H_{arom.}$), 2956 (C−$H_{aliph.}$), 1732 (C=O), 1244 (C−O), 1058 (BF_4) cm^{-1}. − $C_{23}H_{29}BF_4O_4Ru$ (557.40): calcd. C 44.10, H 4.52; found C 44.13, H 4.69.

{1,2,3,4,5-η-6-*exo*-[Bis(methoxycarbonyl)methyl]-2-methylcyclooctadienyl}(η^5-cyclopentadienyl)hydridoruthenium(II) Tetrafluoroborate (5bBF_4): 137 mg (0.49 mmol) of 4b, 0.06 mL of HBF_4 solution (54% in diethyl ether), 60 mL diethyl ether, T = −70 °C. Yield: 168 mg (64%) of a yellow crystalline material. − IR (Nujol): $\tilde{\nu}$ = 1756 (C=O), 1232 (C−O), 1057 (BF_4) cm^{-1}. − EI-MS (70 eV); *m*/*z* (%): 418 (8) [$M - BF_4^+$], 357 (8) [$M - BF_4$-$(CO_2CH_3)_2^+$], 285 (18) [$M - BF_4$-$CH(CO_2CH_3)_2^+$], 259 (18) [$CpRuC_7H_7^+$], 232 (20) [$CpRuC_5H_5^+$], 167 (40) [$CpRu^+$]. − $C_{19}H_{25}BF_4O_4Ru$ (505.32): calcd. C 45.17, H 4.99; found C 44.72, H 4.96.

(η^5-Cyclopentadienyl)(1,2-η:5,6,7-η-4,8-*exo*,*exo*-dimethylcyclooctadienyl)hydridoruthenium(II) Tetrafluoroborate (5cBF_4): 214 mg (0.71 mmol) of **4c**, 0.1 mL of HBF_4 solution (54% in diethyl ether), 45 mL of diethyl ether, T = −78 °C. Yield: 190 mg (69%) of a yellow powder. − IR (Nujol): $\tilde{\nu}$ =1048 (BF_4) cm^{-1}. − $C_{15}H_{21}BF_4Ru$ (389.21): calcd. C 46.29, H 5.44; found C 45.14, H 5.30.

Acknowledgments

This work was supported by the Deutsche Forschungsgemeinschaft (DFG, HE 1309/2). We thank the BASF AG for a donation of cyclooctatetraene and the DEGUSSA AG for a donation of $RuCl_3$.

[1] [1a] A. J. Pearson, S. Mallik, R. Mortezali, M. W. D. Perry, R. J. Shively, Jr., W. J. Youngs, *J. Am. Chem. Soc.* **1990**, *112*, 8034−8041. − [1b] A. J. Pearson, *Acc. Chem. Res.* **1980**, *13*, 463. − [1c] A. J. Pearson, S. K. Kole, J. Yoon, *Organometallics* **1986**, *5*, 2075−2081. − [1d] A. J. Birch, B. M. R. Bandora, K. Chamberlain. B. Chauncey, P. Dahler, A. I. Day, I. D. Jenkins, L. F. Kelley, T. C. Knor, G. Kretschmer, A. J. Liepa, A. S. Narula, W. D. Raverty, E. Rizzardo, C. Sell, G. R. Stephenson, D. J. Thompson, D. H. Williamson, *Tetrahedron* **1981**, *37*, suppl. 1, 5289−5302. − [1e] L. A. P. Kane-Maguire, E. D. Honig, D. A. Sweigart, *Chem. Rev.* **1984**, *84*, 525−543. − [1f] P. S. Bratermann, in: *Reactions of Coordinated Ligands*, Plenum, New York, **1986**. − [1g] B. M. Trost, T. R. Verhoeven, in: *Comprehensive Organometallic Chemistry* (Eds.: G. Wilkinson, F. G. A. Stone, E. W. Abel), Pergamon, New York, **1982**, vol. 8, p. 799−938. − [1h] A. J. Pearson, *Comprehensive Organometallic Chemistry*, Pergamon, New York, **1982**, vol. 8, p. 939−1011. − [1i] J. W. Faller, K.-H. Chao, *Organometallics* **1984**, *3*, 927−932.

[2] [2a] G. R. Stephenson, in: *Organic Synthesis via Organometallics* (Eds.: K. H. Dötz and R. W. Hoffmann), Verlag Friedrich Vieweg and Sohn, Braunschweig, Germany, **1991**. − [2b] H. J. Knölker, R. Boese, K. Hartmann, *Angew. Chem.* **1989**, *101*, 1745−1747; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 2. − [2c] H.-J. Knölker, M. Bauermeister, D. Bläser, R. Boese, J.-B. Pannek, *Angew. Chem.* **1989**, *101*, 225−227; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 223. − [2d] A. J. Pearson, *Pure Appl. Chem.* **1983**, *55*, 1767. − [2e] M. Rosenblum, J. C. Watkins, *J. Am .Chem. Soc.* **1990**, *112*, 6316−6322. − [2f] I. M. Palotai, G. R. Stephenson, L. A. P. Kane-Maguire, *J. Organomet. Chem.* **1987**, *319*, C5-C10.

[3] P. T. Beurskens, W. P. Bosman, H. C. Brussaard, J. Heck, R. J. M. Klein Gebink, M. Maters, J. M. M. Smits, *J. Organomet. Chem.* **1994**, *469*, 197−203.

[4] M. A. Patane, N. A. Petasis, *Tetrahedron* **1992**, *48*, 5757−5821.

[5] S. G. Davies, M. L. H. Green, D. M. P. Mingos, *Tetrahedron* **1978**, *34*, 3047−3077.

[6] J. Heck, G. A. Lange, O. Reimelt, *Angew. Chem.* **1998**, *110*, 533−535; *Angew. Chem. Int. Ed.* **1998**, *37*, 520−522.

[7] O. Reimelt, Diploma Thesis, Universität Hamburg, **1998**.

[8] O. Reimelt, J. Heck, unpublished results.

[9] R. D. Ernst, R. Gleiter, J. C. Green, I. Hyla-Kryspin, G. Sergson, L. Stahl, M. L. Ziegler, *Organometallics* **1989**, *8*, 298−306; R. D. Ernst, *Acc. Chem. Res.* **1985**, *18*, 56−62.

[10] P. J. Harris, J. A. K. Howard, S. A. R. Knox, R. J. McKinney, R. P. Philipps, F. G. A. Stone, P. Woodward, *J. Chem. Soc., Dalton Trans.* **1978**, 403−416.

[11] M. Damen, E. T. K. Haupt, J. Heck, M. Maters, B. Voss, *Organometallics* **1995**, *14*, 44−48.

[12] C. Elschenbroich, J. Koch, J. Schneider, B. Spangenberg, P. Schiess, *J. Organomet. Chem.* **1986**, *317*, 41−54.

[13] M. Brookhart, Y. H. Hong, S. K. Noh, F. J. Timmers, *Organometallics* **1988**, *7*, 2458−2465.

[14] [14a] B. F. G. Johnson, J. Lewis, D. J. Yarrow, *J. Chem. Soc., Dalton Trans.* **1972**, 2084−2089. − [14b] B. Buchmann, U. Pian-

tini, W. von Philipsborn, A. Salzer, *Helv. Chem. Acta* **1987**, *70*, 1487−1506.
[15] A. C. Ontko, J. F. Houlis, R. C. Schnabel, D. M. Roddick, *Organometallics* **1998**, *17*, 5467−5476; B. E. Mann, G. A. Sun, *J. Organomet. Chem.* **1998**, *551*, 21−26.
[16] F. M. Conroy-Lewis, S. J. Simpson, *J. Chem. Soc., Chem. Commun.* **1987**, 1675−1676; E. Cesarotti, C. White, *J. Organomet. Chem.* **1985**, *287*, 123−125.
[17] D. N. Cox, R. Roulet, *J. Chem. Soc., Chem. Commun.* **1989**, 175−176.
[18] W. Trakarnpruk, I. Hyla-Kryspin, A. M. Arif, R. Gleiter, R. D. Ernst, *Inorg. Chim. Acta* **1997**, *259*, 197−202.
[19] [19a] J. L. Schrenk, K. R. Mann, *Inorg. Chem.* **1986**, *25*, 1906−1908. − [19b] K. Itoh, K. Masuda, T. Fukahori, K. Nakano, K. Aoki, H. Nagashima, *Organometallics* **1994**, *13*, 1020−1029. − [19c] M. E. Cucullu, L. Luo, S. P. Nolan, P. J. Fagan, N. L. Jones, J. C. Calabrese, *Organometallics* **1995**, *14*, 289−296.
[20] [20a] M. C. Baird, R. A. Zelonka, *Can. J. Chem.* **1972**, *50*, 3063−3072. − [20b] M. C. Baird, R. A. Zelonka, *J. Organomet. Chem.* **1972**, *44*, 383−389. − [20c] T. A. Stephenson, D. A. Tocher, *Org. Synth., Coll. Vol.* **1986**, *III*, 99−103. − [20d] T. P. Gill, K. R. Mann, *Organometallics* **1982**, *1*, 485−488.
[21] A. J. Pearson, *J. Chem. Soc., Perkin Trans. 1* **1977**, 2069−2077.
[22] L. Brandsma, H. D. Verkruijsse, *Preparative Polar Organometallic Chemistry*, vol. 1, Springer-Verlag, Berlin, Heidelberg, New York, **1987**.
[23] G. M. Sheldrick, *SHELXS-86*, Universität Göttingen, Deutschland, **1986**.
[24] G. M. Sheldrick, *SHELXL-97*, Universität Göttingen, Deutschland, **1997**.

Received February 10, 2000
[I00045]