Ruthenium Tris(pyrazolyl)borate Complexes, 12[+] Cross Coupling of Acetylenes with Olefins – Formation of η^3-Butadienyl and η^2-Butadiene Complexes via a Metallacyclobutane Intermediate

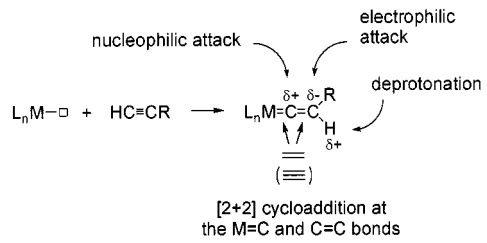
Christian Slugovc,[a] Kurt Mereiter,[b] Roland Schmid,[a] and Karl Kirchner,*[a]

Keywords: C–C coupling / Metallacycles / Metallacyclobutane / Ruthenium / Tripodal ligands / Vinylidene complexes

Selective coupling of olefins and terminal acetylenes is shown to be effected in the coordination sphere of Ru^{II} by the successive intermediacy of vinylidene and ruthenacyclobutane complexes. Subsequent deprotonation of one of the β-hydrogen atoms of the latter by NaOEt yields η^3-butadienyl complexes, while in the presence of Cl^- rearrangement takes place to give neutral η^2-butadiene complexes by a β-hydrogen elimination/reductive elimination sequence. [Ru(tp)(COD)Cl] and [Ru(tp){η^3-(*P,C,C*)-$Ph_2PCH{=}CHC(Ph){=}CH_2$}Cl] were the starting materials which were treated with HC≡CR (R = Ph, C_6H_9, ferrocenyl, CH_2Ph, *n*Bu). The η^3-butadienyl complexes are nucleophilic at the enynyl carbon atom reacting readily with the electrophiles H^+ and I_2 to give the corresponding η^2-butadienyl complexes. X-ray structures of representative products are given.

Introduction

The transition metal mediated transformation of acetylenic substrates is an important process in applied (organometallic) chemistry.[1] Particularly reactive are terminal alkynes which form, when exposed to a transition metal center, vinylidene complexes. This class of compounds exhibits a wide range of reactivity as illustrated in Scheme 1 including migratory insertions of alkyl, aryl, vinyl, alkynyl, and hydride ligands onto the electrophilic α-carbon atom of the vinylidene moiety.[2]



Scheme 1. Formation and common modes of reaction of vinylidene complexes

A rather rare example of C−C bond formation within a vinylidene complex is the cycloaddition of alkynes and olefins to the M=C bond giving metallacyclobutene and metallacyclobutane intermediates, respectively, which then polymerize through ring opening.[3] Although the underlying process is characteristic of early transition metals, we report here a facile C−C coupling reaction between olefins and terminal acetylenes proceeding via a ruthenacyclobutane[4] intermediate which finally converts into either η^3-butadienyl or η^2-butadiene complexes depending on the reaction conditions.[2c,5] In addition, we demonstrate that η^3-butadienyl complexes are nucleophilic at the enynyl carbon atom and react with electrophiles to give the corresponding functionalized η^2-butadiene complexes. A preliminary account of this work has already been published.[6]

Results and Discussion

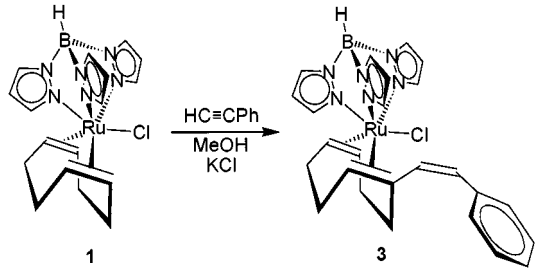
In an attempt to prepare the cationic vinylidene complex $[Ru(tp)(COD)(=C=CHPh)]^+$ (tp = hydrido(trispyrazolyl)-borate, COD = 1,5 cyclooctadiene), [Ru(tp)(COD)Cl] (**1**) has been treated with HC≡CPh in boiling MeOH. A polar medium has been chosen to allow for better ionization of the chloride to facilitate the opening of a coordination site. We[7] and others[8] have already shown that protic solvents favor cationic vinylidene complexes. However, no such complex was formed and basically unchanged **1** was obtained, together with polymeric materials[9] and a small amount of a new complex identified as [Ru(tp){(1,2-η;5,6-η)-1-[(*Z*)-3-phenyl-1-ethenyl]cyclooctadiene}Cl] (**3**). In the presence of excess KCl (6 equiv.) the formation of polymeric compounds is largely suppressed to afford **3**, isolated in 74% yield (Scheme 2). Characterization of **3** was by a combination of elemental analysis, and ^{1}H- and $^{13}C\{^1H\}$-NMR spectroscopy. Characteristic solution ^{1}H-NMR-spectroscopic data for **3** include two doublets at δ = 6.82 and 6.58 with a coupling constant $^3J_{HH}$ = 11.7 Hz, consistent with a (*Z*) arrangement of the double bond. All other resonances are unremarkable. The structural identity of **3** was unequivocally proven by X-ray crystallography. The result is depicted in Figure 1 with selected bond lengths and angles reported in the caption. The overall structure of **3** is similar

[+] Part 11: C. Slugovc, K. Mauthner, M. Kacetl, K. Mereiter, R. Schmid, K. Kirchner, *Chem. Eur. J.* **1998**, *4*, 2043.

[a] Institute of Inorganic Chemistry, Vienna University of Technology,
Getreidemarkt 9/153, A-1060 Vienna, Austria
Fax: (internat.) + 43-1/58801-15399
E-mail: kkirch@mail.zserv.tuwien.ac.at
[b] Institute of Mineralogy, Crystallography, and Structural Chemistry, Vienna University of Technology,
Getreidemarkt 9/171, A-1060 Vienna, Austria

  1434−1948/99/0707−1141 $ 17.50+.50/0

to that of Ru(tp)(COD)Br and related complexes containing the $[Ru(tp)(COD)]^+$ fragment.[10]



Scheme 2. Reaction of **1** with HC≡CPh in the presence of excess KCl

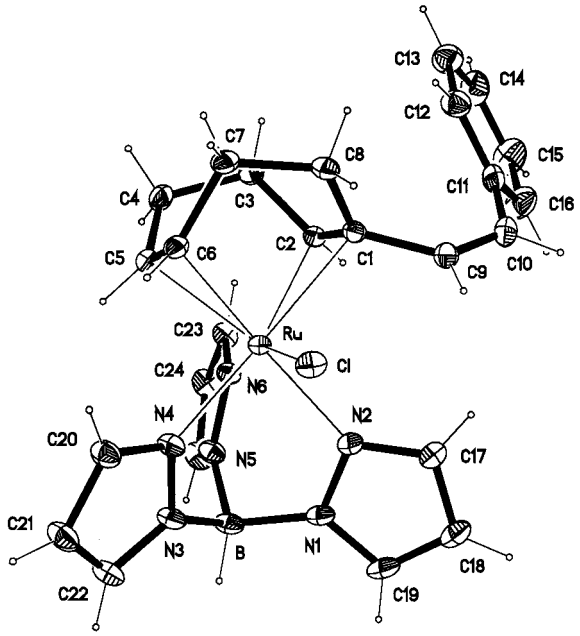
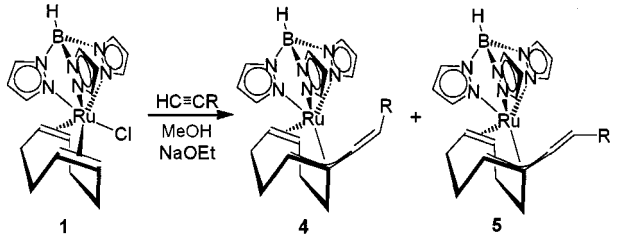


Figure 1. Structural view of **3**; selected bond lengths [Å] and angles [°]: Ru−N(2) 2.163(1), Ru−N(4) 2.121(1), Ru−N(6) 2.166(1), Ru−C(1) 2.311(2), Ru−C(2) 2.243(2), Ru−C(5) 2.226(2), Ru−C(6) 2.219(2), Ru−Cl 2.427(1), C(1)−C(2) 1.385(2), C(5)−C(6) 1.384(2), C(9)−C(10) 1.335(3); N(6)−Ru−Cl 159.9(1), N(4)−Ru−N(2) 87.3(1), N(4)−Ru−N(6) 86.2(1), N(2)−Ru−N(6) 79.7(1)

It is interesting to note that only the (*Z*) isomer is formed in which the −CH=CHPh substituent points towards the chloride ligand. Complex **3** did not undergo a further coupling reaction with HC≡CPh (to give a COD ligand containing two −CH=CHPh substituents). It is interesting that under the same reaction conditions (and even after prolonged heating and extended reaction times) internal acetylenes such as PhC≡CPh and MeOOCC≡CCOOMe did not undergo an oxidative coupling. Instead, unchanged **1** was largely recovered together with about 15% of the known hydride complex [Ru(tp)(COD)H].[11]

In order to establish whether [Ru(tp)(COD)H] is an intermediate on the pathway to **3**, [Ru(tp)(COD)H] (in place of **1**) was treated with HC≡CPh under otherwise the same conditions. However, no **3** but small amounts (< 20%) of the new compound η^3-butadienyl complex [Ru(tp){(5,6-η;η^3)-2-[(*E*)-2-phenyl-1-ethenylidene]-5-cyclooctenyl}] (**5a**) (vide infra) were obtained, in addition to polyacetylenes as the main products. Likewise, internal alkynes, such as PhC≡CPh do not react with **1** and [Ru(tp)(COD)H] is apparently not a precursor to **3**. Accordingly, the formation of **5a** can be interpretated that under basic conditions ([Ru(tp)(COD)H] may act as a base) a different course of reaction is followed. Treatment of Ru(tp)(COD)Cl (**1**)[10] with terminal acetylenes HC≡CR (R = Ph, C_6H_9, ferrocenyl, CH_2Ph, *n*Bu) in MeOH in the presence of NaOEt (1 equiv., 65°C, 24 h) afforded the η^3-butadienyl complexes **4a**−**e** and **5a**−**e** in high yields (Table 1). Characterization of **4** and **5** was again by elemental analysis, and ^{1}H- and $^{13}C\{^1H\}$-NMR spectroscopy. The solution ^{1}H-NMR spectra for **4** include a singlet between δ = 5.9 and 6.9 assigned to the terminal (*E*)-butadienyl proton, while in the corresponding (*Z*)-butadienyl fragment there is a slight upfield shift of the terminal proton giving rise to a signal between δ = 4.7 and 5.9. In the $^{13}C\{^1H\}$-NMR spectrum, the enynyl carbon atoms exhibit a characteristic resonance at δ = 171−181. All other resonances are unremarkable.

Table 1. Conversion and product distribution of the reaction of **1** with terminal acetylenes



			products[a]	
entry	R	% conversion[a]	% Z	% E
1	Ph	100	**4a** 98	
2	C_6H_9	100	**4b** 24	**5b** 76
3	ferrocenyl	100		**5c** 97
4	CH_2Ph	97	**4d** 94	**5d** 6
5	*n*-Bu	93	**4e** 66	**5e** 33

[a] Conversions and product distributions have been determined by ^{1}H NMR spectroscopy

It may be emphasized that **4a** appears to be the first (η^3-butadienyl)ruthenium complex with tp as a co-ligand. The molecular structure determined by X-ray crystallography is shown in Figure 2, with selected bond lengths and angles given in the caption. The most notable feature is the distorted *s-trans* structure of the butadienyl moiety. Since the two allyl carbon atoms, C(1), C(2), are noticeably further from the Ru center [Ru−C(1) = 2.153(3) Å, Ru−C(2) = 2.154(3) Å] than the enynyl carbon atom C(9) [Ru−C(9) = 2.038(3) Å], a major resonance contribution from the vinyl alkene structure is indicated. Furthermore, the relatively uniform bond lengths for the three allyl carbon atoms point to a substantial π-electron delocalization [C(1)−C(2) =

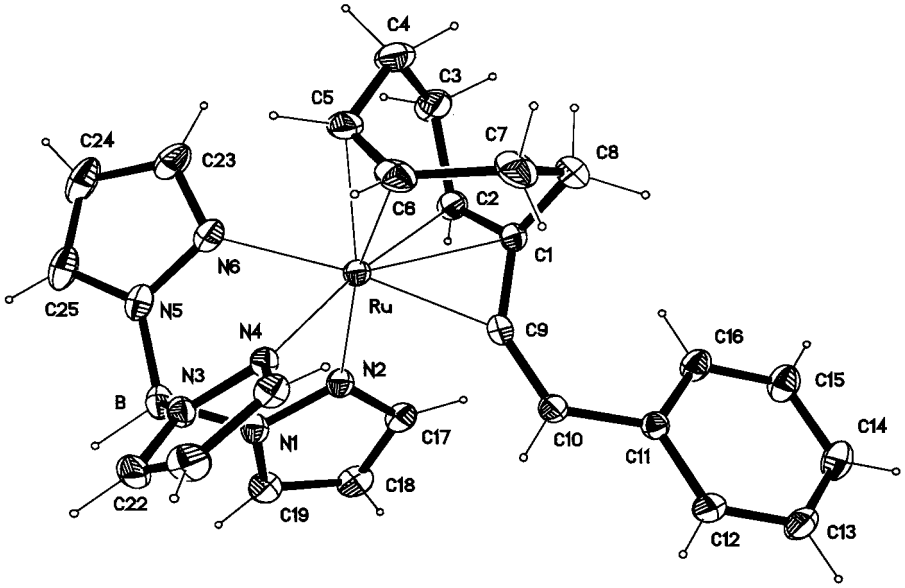
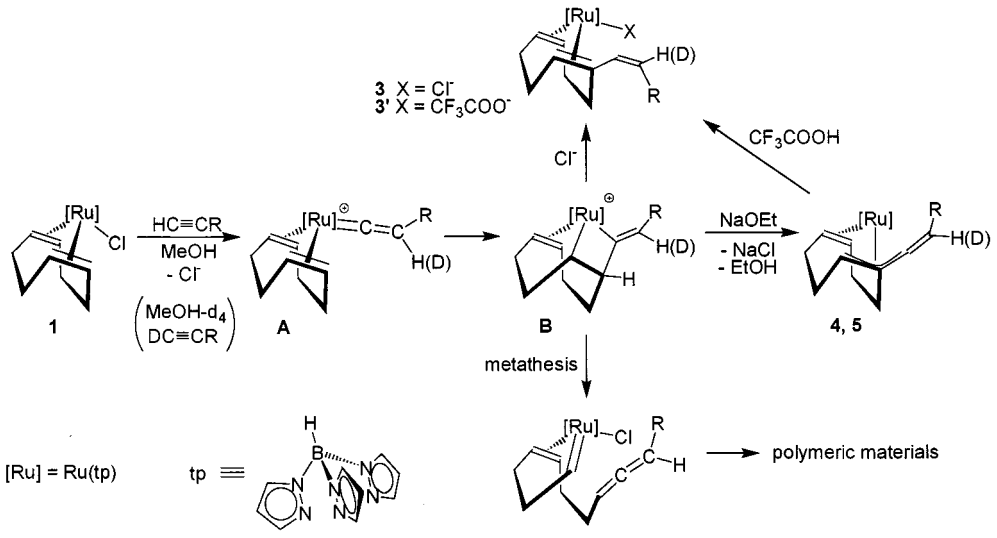


Figure 2. Structural view of **4a**; selected bond lengths [Å] and angles [°]: Ru−N(2) 2.149(2), Ru−N(4) 2.158(2), Ru−N(6) 2.223(2), Ru−C(1) 2.153(3), Ru−C(2) 2.154(3), Ru−C(9) 2.038(3), Ru−C(5) 2.184(3), Ru−C(6) 2.218(3), C(1)−C(9) 1.418(4), C(1)−C(2) 1.425(4), C(9)−C(10) 1.328(4), C(5)−C(6) 1.386(5); C(9)−Ru−N(2) 80.4(1), C(9)−Ru−C(1) 39.4(1), N(2)−Ru−C(1) 101.1(1), C(9)−Ru−C(2) 71.6(1), N(2)−Ru−C(2) 90.5(1), C(1)−Ru−C(2) 38.7(1), C(9)−Ru−N(4) 103.0(1), C(9)−Ru−N(6) 160.1(1)

1.425(4) Å, C(2)−C(9) = 1.418(4) Å].[2c,5] The Ru−N(tp) bond lengths are within the usual range.[10][12]

The reaction mechanism shown in Scheme 3 represents our final working hypothesis providing the formation of the η^2-butadiene complexes **3**, the η^3-butadienyl products **4** and **5**, and polymeric materials. For the first step, the formation of the cationic vinylidene complex **A** by a 1,2-hydrogen shift is a now well-established process.[13] Prerequisite for this process is the availiability of a vacant coordination site. In this context, it has to be noted that the chloride ligand in **1** is easily replacable by Br^- and CN^- on treatment with KBr and KCN in MeOH at elevated temperatures indicating that the Cl^- ligand is substitutionally labile under these conditions.[14] Attempts to prepare **A** by treating **1** with 1 equiv. of $AgCF_3SO_3$ and HC≡CPh in CH_2Cl_2 failed.[10] The metallacyclobutane complex **B** is subsequently formed by a [2+2] cycloaddition, followed by deprotonation of one of the β-hydrogen atoms of **B**, yielding the stable η^3-butadienyl complex. The following observations may be taken to support this mechanism. (i) The occurrence of a vinylidene intermediate could be verified by a labeling experiment. Thus, the η^3-butadienyl product **[D$_1$]4a** of the reaction of deuterium-labeled phenylacetylene DC≡CPh and **1** contain deuterium bound exclusively at the olefinic carbon atom of the butadienyl moiety (Scheme 3). On the other hand, the η^3-butadienyl complex **4a** did not incorporate deuterium to give **[D$_1$]4a** under reflux in [D$_4$]MeOH in the presence of NaOEt.



Scheme 3. Vinylidene mechanism

(ii) In the absence of base only polyacetylenes[9] were obtained with decomposition of the Ru complex to intractable materials. (iii) When in place of NaOEt an excess of KCl is added, **B** rearranges presumably by a β-hydrogen elimination/reductive elimination sequence (equivalent to a 1,2-hydrogen shift) to the neutral η^2-butadiene complex **3**. The vacant coordination site of the resulting 16-electron intermediate is occupied by the incoming chloride.

The stereochemistry of **4** and **5**, difficult to determine by NMR methods, is established on the basis of the products formed from the reaction with CF_3COOH at room temperature included in Scheme 3. In this way the corresponding olefin complexes **3′** [(*Z*) and (*E*) isomers] with the vinyl side chain are formed. Under this experimental condition no isomerization takes place and the stereochemistry of the butadienyl fragment is readily apparent from the vicinal coupling constant $^3J_{HH}$ of the vinyl moiety (about 11 and 16 Hz in case of a *cis* and *trans* arrangement, respectively). From this it is concluded that the enynyl carbon atom of η^3-butadienyl complexes is nucleophilic, which offers the possibility of further kinds of functionalization by treating them with electrophiles. In fact, **4a** reacts with I_2 to yield complex **6** in essentially quantitative yield (Scheme 4). The NMR spectra of **6** are similar to those of **3** and are not discussed here. The solid-state structure of **6** is depicted in Figure 3 with selected bond lengths and angles given in the caption. The overall structures of **6** and **3** are very similar. The three Ru−N(Tp) bond lengths show only minor variations [on average the Ru−N(tp) distance is 2.141(1) Å] and are within the range of other ruthenium(tp) complexes. The Ru−I(1) and C(9)−I(2) distances are 2.780(1) and 2.126(2) Å, respectively. Additionally, a weak intermolecular interaction between the two I(2) atoms of pairs of neighboring molecules is observed, where the I(2)···I(2) distance is found to be 3.67 Å. Despite this interaction molecular packing is not very efficient in crystalline **6** and the structure contains voids of about 40 $Å^3$ per unit cell. If an excess of I_2 is present during crystallization of **6**, a new kind of crystal, **6**·0.5 I_2, is readily formed which will be reported elsewhere.

It may be mentioned that the above reactions are not restricted to COD complexes. In similar fashion to **1**, [Ru(tp){η^3-(*P*,*C*,*C*)-$Ph_2PCH{=}CHC(Ph){=}CH_2$}Cl] (**2**) was found to react with HC≡CR (R = Ph, C_6H_9) to give the η^3-butadienyl complexes **7a**,**b** (Scheme 5). In addition to full spectroscopic and analytical characterizations of the products, the solid-state structure of **7b** was determined by X-ray crystallography. As shown in Figure 4 the coordination geometry around the ruthenium center is a distorted octahedron in which three coordination positions are occupied by the tp ligand, and the remaining three are taken by the phosphorus atom and the butadienyl fragment of the $Ph_2PCH{=}CHC(Ph)CHCCHC_6H_9$ ligand. The Ru−C(24), Ru−C(25), and Ru−C(26) bond lengths are 2.255(3), 2.110(3), and 2.077(3) Å, respectively. Similar to the other η^3-butadienyl complexes,[5] the two allyl carbon atoms, C(24), C(25), are significantly further from the Ru center than is the enynyl carbon atom C(26). The bond lengths between the two allyl and the enynyl carbon atoms are 1.419(4) and 1.445(4) Å. The C(26)−C(27) bond length is 1.341(4) Å. The Ru−N(tp) and Ru−P bond lengths are within the usual ranges.[10][12] The cyclohexene ring consisting of C(34) through C(39) has an envelope conformation with an up/down disorder of C(37a)/C(37b) and C(38a)/C(38b). Only the b-orientation [C(37b/(C(38b)] is shown in Figure 4.

Conclusion

It is shown that selective coupling of olefins and terminal acetylenes is feasible in the coordination sphere of Ru^{II}. Although in the present case there is particular assistance by

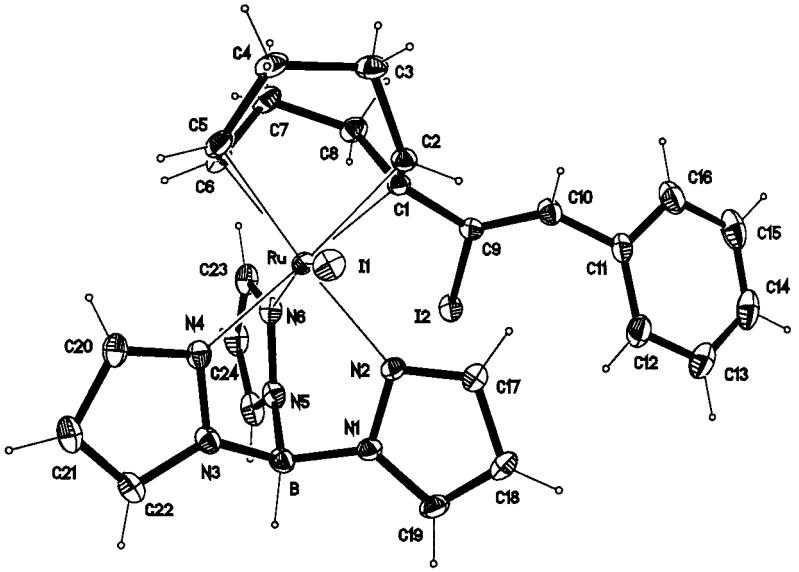


Figure 3. Structural view of **6**; selected bond lengths [Å]: Ru−N(2) 2.114(2), Ru−N(4) 2.133(2), Ru−N(6) 2.177(2), Ru−C(2) 2.206(2), Ru−C(6) 2.227(2), Ru−C(5) 2.249(2), Ru−C(1) 2.267(2), Ru−I(1) 2.780(1), I(2)−C(9) 2.126(2), C(1)−C(9) 1.498(3), C(9)−C(10) 1.329(3)

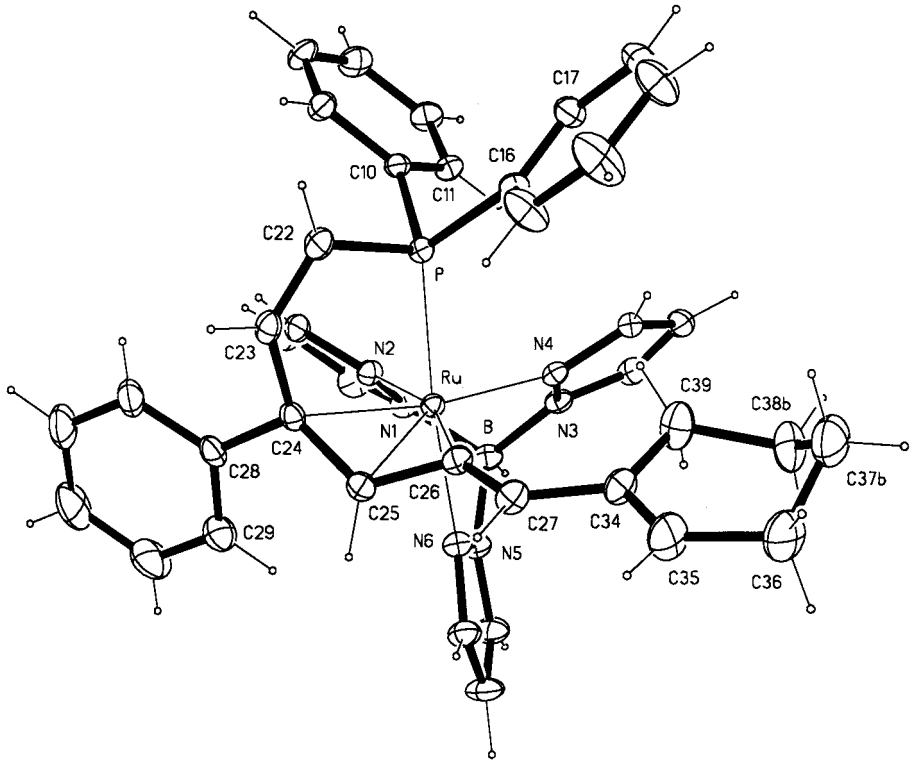
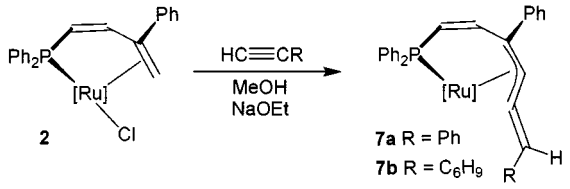


Figure 4. Structural view of **7b**; selected bond lengths [Å] and angles [°]: Ru−C(24) 2.255(3), Ru−C(25) 2.110(3), Ru−C(26) 2.077(3), Ru−N(2) 2.164(2), Ru−N(4) 2.151(2), Ru−N(6) 2.183(2), Ru−P 2.280(1), C(22)−C(23) 1.312(4), C(23)−C(24) 1.490(4), C(24)−C(25) 1.419(4), C(24)−C(28) 1.501(4), C(25)−C(26) 1.445(4), C(26)−C(27) 1.341(4), C(27)−C(34) 1.468(4), C(34)−C(35) 1.344(4); N(4)−Ru−N(2) 84.6(1), N(4)−Ru−C(24) 171.5(1), C(24)−Ru−P 80.5(1)



Scheme 5. Reaction of **2** with HC≡CR (R = Ph, C_6H_9)

the intramolecular mode with favorable stereochemical conditions imposed by an anchoring group, an extension to the intermolecular mode should be conceivable. The deprotonation pathway for the onward reaction of the metallacyclobutane complex has not yet been considered. The butadienyl fragment is nucleophilic at the enynyl carbon atom and is capable of reacting with electrophiles such as H^+ and I_2 to give the 1,3-diene unit. We believe this work may initiate a systematic search of coupling olefins with acetylenes into functionalized 1,3-dienes in a synthetically useful fashion

Experimental Section

General Techniques: All compounds were manipulated with standard Schlenk techniques and/or a glove box under purified argon. All chemicals were of standard reagent grade and used without further purification. The solvents were purified according to standard procedures.[15] The deuterated solvents were purchased from Aldrich and dried with 4-Å molecular sieves. For column chromatography silica gel purchased from Merck, grade 60, 70−230 mesh, 60 Å, or neutral MN aluminum oxide, purchased from Macherey−Nagel, was used. [Ru(tp)(COD)Cl] (**1**) and [Ru(tp){η^3-(*P*,*C*,*C*)-$Ph_2PCH{=}CH(Ph){=}CH_2$}Cl] (**2**) were prepared according to the literature.[7][10] − ^{1}H-, ^{13}C{^{1}H}-, and ^{31}P{^{1}H}-NMR spectra were recorded with a Bruker AC-250 spectrometer operating at 250.13, 62.86, and 101.26 MHz, respectively, and were referenced to $SiMe_4$ and to H_3PO_4 (85%). − Microanalysis were done by Microanalytical Laboratories, University of Vienna.

Synthetic Studies

Ru(tp)(η^4-1,5-cyclooctadiene)H: A suspension of **1** (100 mg, 0.22 mmol) and NaOEt (14.9 mg, 0.22 mmol) in MeOH (5 mL) was heated under reflux for 2.5 h. The reaction mixture was cooled to room temperature and the resulting yellow precipitate was collected on a glass frit, washed with MeOH (5 × 1.5 mL) and Et_2O (2 × 1 mL), and dried under vacuum. Yield: 65 mg (70%). In the absence of base the conversion is completed after about 20 h with 64% yield of isolated [Ru(tp)(η^4-1,5-cyclooctadiene)H]. The NMR spectra are in agreement with the published values.[11]

Ru(tp){(1,2-η;5,6-η)-1-[(*Z*)-2-phenylethenyl]cyclooctadiene}Cl (3): To a suspension of **1** (200 mg, 0.44 mmol) in MeOH (4 mL), KCl (200 mg, 2.68 mmol) and HC≡CPh (144 μL, 1.32 mmol) were added and heated at reflux for 20 h. The reaction mixture was then cooled to 0 °C and the resulting orange precipitate was collected on a glass frit and washed twice with methanol (1.5 mL). The crude product was redissolved in CH_2Cl_2 and insoluble materials were removed by filtration. After removal of the solvent, analytically pure product was obtained. Yield 180 mg (74%). − $C_{25}H_{28}BClN_6Ru$ (559.86): calcd. C 53.63, H 5.04, N 15.01; found C 53.64, H 5.12, N 14.88. − ^{1}H NMR ($CDCl_3$, 20 °C): δ = 8.24

(d, J = 2.2 Hz, 1 H, tp), 7.88 (d, J = 2.2 Hz, 1 H, tp), 7.80 (d, J = 2.2 Hz, 1 H, tp), 7.67 (d, J = 2.2 Hz, 1 H, tp), 7.59 (d, J = 2.2 Hz, 2 H, tp), 7.29−7.18 (m, 5 H, Ph), 6.82 (d, $^3J_{HHcis}$ = 11.7 Hz, CH=CH), 6.58 (d, $^3J_{HHcis}$ = 11.7 Hz, CH=CH), 6.25 (t, J = 2.2 Hz, 2 H, tp), 6.19 (t, J = 2.2 Hz, 1 H, tp), 4.91 (m, 1 H, olefinic H of COD), 3.90 (m, 2 H, olefinic H of COD), 3.31 (m, 1 H, aliphatic H), 2.74−1.91 (m, 7 H, aliphatic H). − $^{13}C\{^1H\}$NMR ($CDCl_3$, 20°C): δ = 145.8 (tp), 143.2 (tp), 142.2 tp), 138.8 (tp), 138.4 (C_{COD}-CH=CHPh), 138.2 (Ph^1), 136.0 tp), 135.2 (tp), 130.0 (C_{COD}-CH=CHPh), 129.1 (2 C, $Ph^{3,5}$), 128.6 (2 C, $Ph^{2,6}$), 127.3 (Ph^4), 107.4 (C_{COD}-CH=CHPh), 106.9 (tp), 106.8 (tp), 105.8 (tp), 91.5 (olefinic C of COD), 88.5 (olefinic C of COD), 85.8 (olefinic C of COD), 38.4 (aliphatic C of COD), 32.5 (aliphatic C of COD), 30.1 (aliphatic C of COD), 27.8 (aliphatic C of COD).

Ru(tp){(5,6-η;η^3)-1-[(*Z*)-2-phenylethenylidene]-5-cyclooctenyl} (4a): To a suspension of **1** (370 mg, 0.81 mmol) in MeOH (5 mL), NaOEt (55 mg, 0.81 mmol) and HC≡CPh (266 μL, 2.42 mmol) were added and heated under reflux for 20 h. The reaction mixture was cooled to 0 °C and the resulting yellow precipitate was collected on a glass frit, washed twice with 1.5 mL of MeOH, and dried under vacuum. Yield: 340 mg (80%). − $C_{25}H_{27}BN_6Ru$ (523.41): calcd. C 57.37, H 5.20, N 16.06; found C 57.40, H 5.21, N 15.97. − ^1H NMR ($CDCl_3$, 20°C): δ = 8.33 (d, J = 1.9 Hz, 1 H, tp), 8.08 (d, 1 H, J = 1.9 Hz, tp), 7.78 (d, J = 2.3 Hz, 1 H, tp), 7.76 (d, J = 2.3 Hz, 1 H, tp), 7.48 (d, J = 2.6 Hz, 1 H, tp), 7.34−7.27 (m, 4 H, Ph), 7.09 (m, 1 H, Ph), 6.47 (d, 1 H, J = 2.3 Hz, tp), 6.40 (vt, J = 2.3 Hz, 1 H, tp), 6.36 (dd, J = 2.3 Hz, J = 1.9 Hz, 1 H, tp), 5.90 (s, 1 H, C=C*H*Ph), 5.86 (dd, J = 2.3 Hz, J = 1.9 Hz, 1 H, tp), 3.81 (m, 1 H, olefinic H of COD), 3.45 (m, 1 H, olefinic H of COD), 3.03 (d, J = 5.0 Hz, 1 H, olefinic H of COD), 2.91−2.11 (m, 7 H), 1.70 (m, 1 H). − $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20°C): δ = 181.2 (C_{COD}=*C*=CHPh), 143.9 (tp), 143.0 (tp), 141.3 tp), 137.6 (Ph^1), 135.8 (tp), 135.4 (tp), 134.1 (tp), 129.0 (2 C, $Ph^{3,5}$), 126.3 (2 C, $Ph^{2,6}$), 124.9 (Ph^4), 114.4 (C_{COD}=C=*C*HPh), 106.3 (tp), 106.2 (tp), 104.8 (tp), 90.8 (C_{COD}=C=CHPh), 82.8 (olefinic C of COD), 80.7 (olefinic C of COD), 63.2 (olefinic C of COD), 33.3 (aliphatic C of COD), 33.0 (aliphatic C of COD), 30.4 (aliphatic C of COD), 26.8 (aliphatic C of COD).

Ru(tp){(5,6-η;η^3)-2-[(*Z*)-2-deuterio-2-phenylethenylidene]-5-cyclooctenyl} ([D_1]4a): This complex was prepared analogously to **4a** (77 mg, 0.168 mmol) in [D_4]MeOH (1 mL) as the solvent, with **1**, NaOEt (11.4 mg, 0.168 mmol), and DC≡CPh (55 μL, 0.504 mmol) as the starting materials. Yield: 61 mg (69%). − $C_{25}H_{26}BDN_6Ru$ (524.42): calcd. C 57.37, H 5.20, N 16.06; found C 57.43, H 5.26, N 15.92. − ^1H NMR ($CDCl_3$, 20°C): δ = 8.35 (d, J = 1.9 Hz, 1 H, tp), 8.11 (d, 1 H, J = 1.9 Hz, tp), 7.78 (d, J = 2.3 Hz, 1 H, tp), 7.76 (d, J = 2.3 Hz, 1 H, tp), 7.51 (d, J = 2.6 Hz, 1 H, tp), 7.34−7.27 (m, 4 H, Ph), 7.09 (m, 1 H, Ph), 6.47 (d, 1 H, J = 2.3 Hz, tp), 6.40 (vt, J = 2.3 Hz, 1 H, tp), 6.36 (dd, J = 2.3 Hz, J = 1.9 Hz, 1 H, tp), 5.86 (dd, J = 2.3 Hz, J = 1.9 Hz, 1 H, tp), 3.81 (m, 1 H, olefinic H of COD), 3.45 (m, 1 H, olefinic H of COD), 3.03 (d, J = 5.0 Hz, 1 H, olefinic H of COD), 2.91−2.11 (m, 7 H), 1.70 (m, 1 H). − $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20°C): δ = 181.1 (C_{COD}=*C*=CDPh), 144.0 (tp), 143.0 (tp), 141.3 (tp), 137.6 (Ph^1), 135.8 (tp), 135.4 (tp), 134.1 (tp), 129.0 (2 C, $Ph^{3,5}$), 126.3 (2 C, $Ph^{2,6}$), 124.9 (Ph^4), 114.1 (t, $^1J_{DC}$ = 22.7 Hz, C_{COD}=C=*C*DPh), 106.3 (tp), 106.2 (tp), 104.8 (tp), 90.1 (C_{COD}=C=CDPh), 82.9 (olefinic C of COD), 80.8 (olefinic C of COD), 63.2 (olefinic C of COD), 33.3 (aliphatic C of COD), 33.1 (aliphatic C of COD), 30.5 (aliphatic C of COD), 26.8 (aliphatic C of COD).

Ru(tp){(5,6-η;η^3)-1-[(*E*)-2-phenylethenylidene]-5-cyclooctenyl} (5a): To a suspension of Ru(tp)(η^4-1,5-cyclooctadiene)H (62 mg, 0.146 mg) in methanol (4 mL), NaOEt (9.5 mg, 0.146 mmol) and HC≡CPh (48 μL, 0.439 mmol) were added and heated at reflux for 20 h. The solvent was evaporated and the crude reaction mixture was purified by column chromatography (neutral Al_2O_3). The first yellow band was eluted with CH_2Cl_2. Yield: 27 mg (35%). − $C_{25}H_{27}BN_6Ru$ (523.41): calcd. C 57.37, H 5.20, N 16.06; found C 57.48, H 5.29, N 16.22. − ^1H NMR ($CDCl_3$, 20°C): δ = 8.29 (d, J = 1.9 Hz, 1 H, tp), 7.89 (d, 1 H, J = 1.9 Hz, tp), 7.84 (d, J = 2.8 Hz, 1 H, tp), 7.56 (d, J = 2.4 Hz, 1 H, tp), 7.48 (d, J = 2.3 Hz, 1 H, tp), 6.91 (s, 1 H, C=C*H*Ph), 6.86 (d, 1 H, J = 2.4 Hz, tp), 6.87−6.71 (m, 3 H, $Ph^{3,4,5}$), 6.55 (d, 2 H, $Ph^{2,6}$), 6.39 (dd, J = 2.4 Hz, J = 1.9 Hz, 1 H, tp), 6.22 (dd, J = 2.4 Hz, J = 1.9 Hz, 1 H, tp), 5.86 (vt, J = 2.4 Hz, 1 H, tp), 3.73 (m, 1 H, olefinic H of COD), 3.48 (m, 1 H, olefinic H of COD), 3.01−2.02 (m, 7 H), 1.20 (m, 2 H), 0.94 (m, 1 H). − $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20°C): δ = 176.8 (C_{COD}=*C*=CHPh), 145.4 (tp), 142.6 (tp), 141.5 (tp), 139.7 (Ph^1), 135.78 (tp), 135.5 (tp), 134.5 (tp), 128.0 (2 C, $Ph^{3,5}$), 126.7 (2 C, $Ph^{2,6}$), 125.0 (Ph^4), 117.3 (C_{COD}=C=*C*HPh), 106.3 (tp), 106.2 (tp), 105.5 (tp), 91.1 (C_{COD}=C=CHPh), 83.3 (olefinic C of COD), 82.8 (olefinic C of COD), 63.2 (olefinic C of COD), 33.5 (aliphatic C of COD), 32.4 (aliphatic C of COD), 31.5 (aliphatic C of COD), 30.1 (aliphatic C of COD).

Ru(tp){(5,6-η;η^3)-1-[(*Z*)-2-(1-cyclohexenyl)ethenylidene]-5-cyclooctenyl} (4b): The (*Z*) isomer **4b** was obtained by adding *n*-hexane to the methanolic filtrate of **5b**. The resulting solid was collected on a glass frit, and dried under vacuum. Yield: 32 mg (14%). − $C_{25}H_{31}BN_6Ru$ (527.44): calcd. C 56.93, H 5.92, N 15.93; found C 57.12, H 6.12, N 15.73. − ^1H NMR ($CDCl_3$, 20°C): δ = 8.30 (d, J = 2.0 Hz, 1 H, tp), 8.02 (d, 1 H, J = 2.0 Hz, tp), 7.74 (d, J = 2.0 Hz, 1 H, tp), 7.70 (d, J = 2.3 Hz, 1 H, tp), 7.47 (d, J = 2.0 Hz, 1 H, tp), 6.42 (d, 1 H, J = 2.0 Hz, tp), 6.36 (dd, J = 2.3 Hz, J = 2.0 Hz, 1 H, tp), 6.31 (vt, J = 2.0 Hz, 1 H, tp), 5.94 (dd, J = 2.3 Hz, J = 2.0 Hz, 1 H, tp), 5.48 (s, 1 H, C=C*H*C_6H_9), 5.26 (m, 1 H, olefinic H of C_6H_9), 3.79−3.56 (m, 2 H, olefinic H of COD), 2.81−0.84 (m, 17 H). − $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20°C): δ = 176. (C_{COD}=*C*=CHC_6H_9), 143.8 (tp), 143.0 (tp), 141.8 (tp), 135.8 (C_6H_9), 135.6 (tp), 135.1 (tp), 134.0 (tp), 121.9 (C_6H_9), 118.2 (C_{COD}=C=*C*HC_6H_9), 106.2 (tp), 106.1 (tp), 104.6 (tp), 90.4 7 (C_{COD}=C=CHC_6H_9), 82.0 (olefinic C of COD), 80.3 (olefinic C of COD), 62.1 (olefinic C of COD), 33.3 (aliphatic C of COD), 33.1 (aliphatic C of COD), 30.5, 29.4 (aliphatic C of COD and aliphatic C of C_6H_9), 27.0, 26.2, 23.7, 23.5 (aliphatic C of COD and aliphatic C of C_6H_9).

Ru(tp){(5,6-η;η^3)-1-[(*E*)-2-(1-cyclohexenyl)ethenylidene]-5-cyclooctenyl} (5b): This compound was prepared analogously to **4a** with **1** (203 mg, 0.443 mmol), NaOEt (30.2 mg, 0.443 mmol), and HC≡CC_6H_9 (156 μL, 1.33 mmol) as the starting materials. Yield: 145 mg (62%). − $C_{25}H_{31}BN_6Ru$ (527.44): calcd. C 56.93, H 5.92, N 15.93. found: C 56.99, H 6.05, N 15.88. − ^1H NMR ($CDCl_3$, 20°C): δ = 8.26 (d, J = 2.0 Hz, 1 H, tp), 7.97 (d, 1 H, J = 2.0 Hz, (tp), 7.73 (d, J = 2.0 Hz, 1 H, (tp), 7.70 (d, J = 2.3 Hz, 1 H, tp), 7.55 (d, J = 2.0 Hz, 1 H, tp), 6.80 (d, 1 H, J = 2.0 Hz, (tp), 6.47 (s, 1 H, C=C*H*C_6H_9), 6.35 (dd, J = 2.3 Hz, J = 2.0 Hz, 1 H, (tp), 6.25 (vt, J = 2.0 Hz, 1 H, (tp), 5.99 (dd, J = 2.3 Hz, J = 2.0 Hz, 1 H, (tp), 5.27 (m, 1 H, olefinic H of C_6H_9), 3.78−3.58 (m, 2 H, olefinic H of COD), 2.83−0.86 (m, 16 H), 0.53−0.41 (m, 1 H). − $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20°C): δ = 172.0 (C_{COD}=*C*=CHC_6H_9), 144.8 (tp), 142.6 (tp), 142.3 (tp), 138.4 (C_6H_9), 135.6 (tp), 135.3 (tp), 134.4 (tp), 123.7 (C_6H_9), 120.6 (C_{COD}=C=*C*HC_6H_9), 106.2 (tp), 105.7 (tp), 104.9 (tp), 91.7 (C_{COD}=C=CHC_6H_9), 82.6 (olefinic C of COD), 81.9 (olefinic C of COD), 63.0 (olefinic C of COD), 33.7 (aliphatic C of COD), 32.3 (aliphatic C of COD), 31.4, 30.2

(aliphatic C of COD and aliphatic C of C_6H_9), 26.4, 25.6, 23.5, 23.2 (aliphatic C of COD and aliphatic C of C_6H_9).

Ru(tp){(5,6-η;η^3)-1-[(*E*)-2-ferrocenylethenylidene]-5-cyclooctenyl} (5c): This compound was prepared analogously to **4a** with **1** (123 mg, 0.269 mmol), NaOEt (18.3 mg, 0.269 mmol) and ferrocenylacetylene (67.7 mg, 0.322 mmol) as the starting materials. Yield: 122 mg (72%). − $C_{29}H_{31}BFeN_6Ru$ (631.33): calcd. C 55.17, H 4.95, N 13.31; found C 55.06, H 5.04, N 13.19. − ^{1}H NMR ($CDCl_3$, 20°C): δ = 8.27 (d, *J* = 1.6 Hz, 1 H, tp), 7.78−7.70 (m, 4 H, tp), 6.91 (d, 1 H, *J* = 2.1 Hz, tp), 6.62 (s, 1 H, C=C*H*-Fc), 6.38 (vt, *J* = 2.1 Hz, 1 H, tp), 6.15−6.13 (m, 2 H, tp), 3.98−3.91 (m, 2 H, Fc), 3.90 (s, 5 H, Fc) 3.71 (m, 1 H, olefinic H of COD), 3.60−3.48 (m, 4 H, Fc, olefinic H of COD), 2.92 (m, 1 H, aliphatic H of COD), 2.80−2.62 (m, 2 H, aliphatic H of COD), 2.48−2.35 (m, 3 H, aliphatic H of COD), 2.19−2.11 (m, 1 H, aliphatic H of COD), 1.80−1.67 (m, 1 H, aliphatic H of COD). − ^{13}C{^{1}H} NMR ($CDCl_3$, 20°C): δ = 173.6 (C_{COD}=*C*=CHFc), 145.3 (tp), 142.6 (tp), 141.7 (tp), 135.5 (tp), 135.3 (tp), 134.5 (tp), 112.8 (C_{COD}=C=*C*HFc), 106.2 (tp), 106.1 (tp), 105.2 (tp), 90.1 (*C*$_{COD}$=C=CHFc), 87.1 (Fc^1), 82.2 (olefinic C of COD), 81.9 (olefinic C of COD), 69.1 (5 C, Fc), 67.9 (Fc), 67.7 (Fc), 67.1 (Fc), 66.7 (Fc), 64.1 (olefinic C of COD), 33.1, 32.6, 31.3, 30.3 (aliphatic C of COD).

Ru(tp){(5,6-η;η^3)-1-[(*Z*)-3-phenylpropenylidene]-5-cyclooctenyl} (4d): This compound was prepared analogously to **4a** with **1** (308 mg, 0.672 mmol), NaOEt (46 mg, 0.672 mmol), and HC≡CCH$_2$Ph (250 µL, 2.02 mmol) as the starting materials. Yield: 300 mg (83%). − $C_{26}H_{29}BN_6Ru$ (537.44): calcd. C 58.11, H 5.48, N 15.64; found C 58.22, H 5.58, N 15.61. − ^{1}H NMR ($CDCl_3$, 20°C): δ = 8.29 (d, *J* = 2.1 Hz, 1 H, tp), 8.04 (d, 1 H, *J* = 2.1 Hz, (tp), 7.76 (d, *J* = 2.5 Hz, 1 H, tp), 7.74 (d, *J* = 2.5 Hz, 1 H, tp), 7.55 (d, *J* = 2.5 Hz, 1 H, tp), 7.31−7.11 (m, 3 H, Ph), 6.98 (m, 2 H, Ph), 6.81 (d, 1 H, *J* = 2.1 Hz, tp), 6.37 (vt, *J* = 2.1 Hz, 1 H, tp), 6.21 (dd, *J* = 2.5 Hz, *J* = 2.1 Hz, 1 H, tp), 5.96 (t, *J* = 7.1 Hz, 1 H, C=C*H*-CH$_2$Ph), 5.96 (dd, *J* = 2.5 Hz, *J* = 2.1 Hz, 1 H, tp), 3.73 (m, 1 H, olefinic H of COD), 3.49 (m, 2 H, olefinic H of COD), 3.06−2.96 (m, 1 H, diastereotopic CH$_2$), 2.83−2.13 (m, 8 H), 1.71 (m, 1 H). − ^{13}C{^{1}H} NMR ($CDCl_3$, 20°C): δ = 175.2 (C_{COD}=*C*=CH-CH$_2$Ph), 144.8 (tp), 144.0 (Ph^1), 142.8 (tp), 141.6 (tp), 135.6 (tp), 135.8 (tp), 135.4 (tp), 134.2 (tp), 129.0 (2 C, Ph^{3,5}), 128.6 (2 C, Ph^{2,6}), 125.7 (Ph^4), 112.6 (C_{COD}=C=*C*H-CH$_2$Ph), 106.2 (tp), 105.6 (tp), 104.8 (tp), 89.2 (*C*$_{COD}$=C=CH-CH$_2$Ph), 81.4 (olefinic C of COD), 81.2 (olefinic C of COD), 63.0 (olefinic C of COD), 37.7 (*C*H$_2$-Ph), 33.7 (aliphatic C of COD), 32.8 (aliphatic C of COD), 30.7 (aliphatic C of COD), 30.4 (aliphatic C of COD).

Ru(tp){(5,6-η;η^3)-1-[(*E*)-3-phenylpropenylidene]-5-cyclooctenyl} (5d): This isomer could not be obtained in pure form. The ratio of (*Z*)/(*E*) diastereomers of 94:6 was determined by ^{1}H-NMR spectroscopy.

Ru(tp){(5,6-η;η^3)-1-[(*E*/*Z*)-1-hexenylidene]-5-cyclooctenyl} (4e, 5e): To a suspension of **1** (200 mg, 0.437 mmol) in MeOH (5 L), NaOEt (29.7 mg, 0.437 mmol) and HC≡C*n*Bu (150 µL, 1.311 mmol) were added and the solution was kept at reflux for 20 h. The reaction mixture was allowed to cool to room temperature and the solvent was removed under reduced pressure. The crude product (orange oil) was purified by column chromatography (neutral Al_2O_3). The first yellow band was eluted with CH_2Cl_2. Yield: 300 mg (83%) of a mixture of (*Z*) and (*E*) diastereomeres in a 2:1 ratio. The diastereomers could not be seperated. − $C_{23}H_{31}BN_6Ru$ (503.42): calcd. C 54.88, H 6.21, N 16.69; found C 54.62, H 6.28, N 16.61. − ^{1}H NMR for the (*Z*) diastereomer **4e** ($CDCl_3$, 20°C): δ = 8.32 (d, *J* = 1.7 Hz, 1 H, tp), 8.08 (d, 1 H, *J* = 2.1 Hz, tp), 7.77 (d, *J* = 2.5 Hz, 1 H, tp), 7.76 (d, *J* = 2.1 Hz, 1 H, tp), 7.56 (d, *J* = 2.1 Hz, 1 H, tp), 6.84 (d, 1 H, *J* = 2.5 Hz, tp), 6.39 (vt, *J* = 2.1 Hz, 1 H, tp), 6.29 (vt, *J* = 2.8 Hz, 1 H, tp), 5.99 (vt, *J* = 2.1 Hz, 1 H, tp), 5.96 (t, *J* = 7.2 Hz, 1 H, C=C*H*-*n*Bu), 3.73 (m, 1 H, olefinic H of COD), 3.49 (m, olefinic H of COD), 2.86−2.01 (m, 5 H), 1.75−0.99 (m, 10 H), 0.96 (t, *J* = 7.2 Hz, 3 H). − ^{13}C{^{1}H} NMR ($CDCl_3$, 20°C): δ = 174.0 (C_{COD}=*C*=CH-*n*Bu), 144.6 (tp), 142.7 (tp), 141.6 (tp), 135.5 (tp), 135.1 (tp), 134.0 (tp), 113.5 (C_{COD}=C=*C*H-*n*Bu), 106.1 (tp), 105.4 (tp), 104.4 (tp), 88.7 (*C*$_{COD}$=C=CH-*n*Bu), 80.9 (olefinic C of COD), 80.7 (olefinic C of COD), 62.7 (olefinic C of COD), 33.7, 33.5, 32.9, 31.0, 30.4, 28.8, 28.5, 23.2 (aliphatic C of COD and *n*Bu). − ^{1}H NMR for the (*E*) diastereomer **5e** ($CDCl_3$, 20°C): δ = 8.34 (d, *J* = 2.1 Hz, 1 H, tp), 8.06 (d, 1 H, *J* = 1.7 Hz, tp), 7.74 (d, *J* = 2.1 Hz, 1 H, tp), 7.61 (d, *J* = 2.5 Hz, 1 H, tp), 7.52 (d, *J* = 2.5 Hz, 1 H, tp), 6.67 (d, 1 H, *J* = 2.1 Hz, tp), 6.39 (vt, *J* = 2.1 Hz, 1 H, tp), 6.29 (dd, *J* = 2.5 Hz, *J* = 2.1 Hz, 1 H, tp), 6.22 (vt, *J* = 2.1 Hz, 1 H, tp), 4.79 (t, *J* = 6.8 Hz, 1 H, C=C*H*-*n*Bu), 3.73 (m, 1 H, olefinic H of COD), 3.46 (m, 1 H, olefinic H of COD), 2.86−2.01 (m, 5 H), 1.75−0.99 (m, 10 H), 0.78 (t, *J* = 7.2 Hz, 3 H). − ^{13}C{^{1}H} NMR ($CDCl_3$, 20°C): δ = 173.8 (C_{COD}=*C*=CH-*n*Bu), 143.8 (tp), 143.0 (tp), 141.2 (tp), 135.5 (tp), 135.1 (tp), 133.7 (tp), 113.4 (C_{COD}=C=*C*H-*n*Bu), 105.9 (tp), 105.6 (tp), 104.3 (tp), 87.9 (*C*$_{COD}$=C=CH-*n*Bu), 81.5 (olefinic C of COD), 79.5 (olefinic C of COD), 63.1 (olefinic C of COD), 33.8, 33.5, 33.0, 31.0, 30.4, 28.6, 28.5, 23.2 (aliphatic C of COD and *n*Bu).

Reaction of 4 and 5 with CF_3COOH. − Formation of Ru(tp){(1,2-η;5,6-η)-1-[(*E*/*Z*)-2-R-ethenyl]cyclooctadiene}(OCOCF$_3$) (R = Ph, C_6H_9, ferrocenyl, CH_2Ph, *n*Bu) (3′): Typically, a 5-mm NMR tube was charged with either **4** or **5** (30 mg) and was capped with a septum. A solution of CF_3COOH (ca. 2 equiv.) in $CDCl_3$ (0.5 mL) was added by syringe and the sample was transferred into a NMR probe. ^{1}H-NMR spectra were immediately recorded. The following coupling constants were observed for the reactions with **4a**: δ = 6.82 (d, $^3J_{HHcis}$ = 11.7 Hz, CH=CH), 6.58 (d, $^3J_{HHcis}$ = 11.7 Hz, CH=CH); with **5a**: δ = 6.92 (d, $^3J_{HHtrans}$ = 16.3 Hz, CH=CH), 5.95 (d, $^3J_{HHtrans}$ = 16.3 Hz, CH=CH); with **4b**: δ = 6.48 (d, $^3J_{HHcis}$ = 11.6 Hz, CH=CH), 6.01 (d, $^3J_{HHcis}$ = 11.6 Hz, CH=CH); with **5b**: δ = 6.51 (d, $^3J_{HHtrans}$ = 16.3 Hz, CH=CH), 5.45 (d, $^3J_{HHtrans}$ = 16.3 Hz, CH=CH); with **5c**: δ = 6.50 (d, $^3J_{HHtrans}$ = 15.9 Hz, CH=CH), 5.58 (d, $^3J_{HHtrans}$ = 15.9 Hz, CH=CH); with **4d**: δ = 6.18 (d, $^3J_{HHcis}$ = 11.1 Hz, CH=CH), 5.90 (ddd, $^3J_{HHcis}$ = 11.1 Hz, CH=CH); with **5d**: could not be observed; with **4e**: δ = 6.03 (d, $^3J_{HHcis}$ = 11.8 Hz, CH=CH), 5.68 (ddd, $^3J_{HHcis}$ = 11.7 Hz, CH=CH); with **5e**: δ = 6.80 (d, $^3J_{HHtrans}$ = 15.7 Hz, CH=CH), 5.40 (ddd, $^3J_{HHtrans}$ = 15.7 Hz, CH=CH).

Ru(tp){(1,2-η;5,6-η)-1-[(*Z*)-1-iodo-2-phenylethenyl]cyclooctadiene}I (6): To a solution of **4a** (70 mg, 0.134 mmol) in CH_2Cl_2 (2 mL), I_2 (37 mg, 0.150 mmol) was added and stirred for 2 h at room temperature. The volume of the solution was reduced to about 0.5 mL and the product was precipitated upon addition of Et_2O. The residue was collected on a glass frit, washed twice with 1.5 mL of Et_2O, and dried under vacuum. Yield: 85 mg (82%). − $C_{25}H_{27}BI_2N_6Ru$ (777.21): calcd. C 38.63, H 3.05, N 10.81; found C 38.55, H 3.02, N 10.62. − ^{1}H NMR ($CDCl_3$, 20°C): δ = 8.28 (d, *J* = 2.2 Hz, 1 H, tp), 7.87 (d, 1 H, *J* = 2.6 Hz, tp), 7.86 (d, *J* = 2.2 Hz, 1 H, tp), 7.75 (d, *J* = 2.2 Hz, 1 H, tp), 7.71 (d, *J* = 2.2 Hz, 1 H, tp), 7.67 (d, 1 H, *J* = 2.2 Hz, tp), 7.23−7.20 (m, 4 H, Ph), 6.96 (m, 1 H, Ph), 6.42 (dd, *J* = 2.2 Hz, *J* = 2.6 Hz, 1 H, tp), 6.26 (dd, *J* = 2.2 Hz, *J* = 1.8 Hz, 1 H, (tp), 6.20 (dd, *J* = 2.2 Hz, *J* = 1.8 Hz, 1 H, tp), 5.74−5.69 (m, 2 H, CI=C*H*-Ph and olefinic H of COD), 5.14 (m, 1 H, olefinic H of COD), 4.03 (m, 1 H, olefinic H of COD), 3.80−3.59 (m, 1 H, COD), 3.31−2.85 (m, 4 H), 2.78−2.46 (m, 1 H), 2.30−2.02 (m, 2 H). − ^{13}C{^{1}H} NMR ($CDCl_3$, 20°C):

Table 2. Crystallographic data for **3**, **4a**, **6**, and **7b**

	3	**4a**	**6**	**7b**
Empirical formula	$C_{25}H_{28}BClN_6Ru$	$C_{25}H_{27}BN_6Ru$	$C_{25}H_{27}BI_2N_6Ru$	$C_{39}H_{38}BN_6PRu$
Molecular mass	559.86	523.41	777.21	733.60
Crystal size [mm]	0.45 × 0.25 × 0.15	0 30 × 0.10 × 0.03	057 × 0.20 × 0.10	0.20 × 0.05 × 0.03
Space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)
a [Å]	8.191(1)	8.180(2)	8.287(2)	9.647(2)
b [Å]	9.852(1)	11.252(3)	12.157(3)	15.155(3)
c [Å]	16.335(2)	25.335(6)	13.987(3)	24.373(6)
α [deg]	103.53(1)	90	76.350(1)	90
β [deg]	93.55(1)	98.85(1)	86.260(1)	95.19(1)
γ [deg]	109.04(1)	90	77.690(1)	90
V [Å^3]	1197.7(2)	2304(1)	1337.7(5)	3549(1)
Z	2	4	2	4
$\rho_{calcd.}$ [g cm^{-3}]	1.552	1.509	1.930	1.373
T [K]	295(2)	303(2)	299(2)	295(2)
μ [mm^{-1}] (Mo-K_α)	0.793	0.706	2.920	0.524
Absorption correction	multi scan	multi scan	multi scan	multi scan
F(000)	572	1072	748	1512
Transmission factor, min/max	0.86/0.73	0.93/0.74	0.69/0.45	0.96/0.84
θ_{max} [°]	30	27	30	25
Index ranges	$-11 \le h \le 11$ $-13 \le k \le 13$ $-23 \le l \le 22$	$-11 \le h \le 11$ $-15 \le k \le 15$ $-35 \le l \le 35$	$-11 \le h \le 11$ $-17 \le k \le 17$ $-19 \le l \le 19$	$-11 \le h \le 11$ $-18 \le k \le 18$ $-29 \le l \le 29$
Number of relections measured	13687	29227	21311	58041
Number of unique reflections	6815	5029	7765	6265
Number of reflections with $I > 2\sigma(I)$	6136	3760	6550	5112
Number of parameters	317	307	317	453
R_1 [$I > 2\sigma(I)$]	0.024	0.032	0.023	0.031
R_1 (all data)	0.029	0.057	0.031	0.046
wR_2 (all data)	0.056	0.066	0.056	0.070
Difference Fourier peaks, min/max. [eÅ^{-3}]	−0.46/0.36	−0.31/0.30	−1.01/1.17	−0.31/0.75

$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o||$; $wR_2 = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma\{w(F_o^2)^2\}]^{1/2}$.

δ = 147.9 (tp), 145.9 (tp), 145.4 (tp), 139.8 (C_{COD}-CI=*C*HPh), 138.7 (Ph[1]), 137.9 (tp), 136.5 (tp), 135.4 (tp), 129.1 (2 C, Ph[3,5]), 128.3 (2 C, Ph[2,6]), 128.0 (Ph[4]), 113.0 (C_{COD}=C=CHPh), 107.5 (tp), 106.8 (tp), 106.6 (tp), 97.1 (olefinic C of COD), 94.1 (olefinic C of COD), 87.2 (olefinic C of COD), 82.3 (C_{COD}-*C*I=CHPh), 37.9 (aliphatic C of COD), 37.3 (aliphatic C of COD), 32.8 (aliphatic C of COD), 27.6 (aliphatic C of COD).

Ru(tp){(κ^1(*P*);2,3,4-η)-1,4-diphenyl-6-diphenylphosphanyl-1,3,5-hexatrien-2-yl} (7a): A suspension of **2** (155 mg, 0.229 mmol) in MeOH (4 mL) was treated with HC≡CPh (75.6 μL, 0.688 mmol) and NaOEt (15.6 mg, 0.229 mmol) and heated at reflux for 20 h. The reaction mixture was then cooled to room temperature and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (neutral Al_2O_3). The first yellow band was eluted with CH_2Cl_2. Yield: 98 mg (59%). − $C_{39}H_{34}BN_6PRu$ (729.59): calcd. C 64.20, H 4.70, N 11.52; found C 64.26, H 4.79, N 11.48. − ^{1}H NMR ($CDCl_3$, 20°C): δ = 8.14 (d, J = 1.9 Hz, 1 H, tp), 7.85 (m, 1 H, tp), 7.81 (m, 2 H, tp), 7.70 (d, J = 2.3 Hz, 1 H, tp), 7.65−7.00 (m, 19 H), 6.86−6.79 (m, 2 H), 6.77−6.66 (m, 1 H), 6.28 (d, J = 2.3 Hz, 1 H, tp), 6.24 (m, 1 H), 6.10 (vt, J = 2.3 Hz, 1 H, tp), 5.98 (d, J = 1.9 Hz, 1 H, tp), 5.38 (vt, J = 2.3 Hz, 1 H, tp), 4.64 (m, 1 H, tp). − ^{13}C{^{1}H} NMR ($CDCl_3$, 20°C): δ = 164.8 [d, $^2J_{PC}$ = 13.8 Hz, P-CH=CH-C(Ph)=CH=*C*=CH-Ph], 155.4 [d, $^2J_{PC}$ = 23.6 Hz, P-CH=*C*H-C(Ph)=CH=C=CH-Ph], 147.2 [d, $^3J_{PC}$ = 1.9 Hz, (tp), 146.4 (quaternary C of a Ph], 144.1 (tp), 142.4 (quaternary C of a Ph), 141.9 (tp), 140.0 (d, $^5J_{PC}$ = 2.4 Hz, tp), 136.7 (d, $^1J_{PC}$ = 48.1 Hz, PPh[1]), 136.2 (d, $^5J_{PC}$ = 2.4 Hz, tp), 135.6 (tp), 133.9, 133.8, 133.2 (quaternary C), 133.1 (quaternary C), 132.7, 132.1, 129.6−128.0 (m, 11C), 126.4 (d, J_{PC} = 1.4 Hz), 126.0, 125.6, 125.5, 125.2, 105.8 (d, $^4J_{PC}$ = 2.4 Hz, 1 C, tp), 104.7 (tp), 104.6 (tp), 86.0 [d, J_{PC} = 4.8 Hz, P-CH=CH-*C*(Ph)=CH=C=CH-Ph], 74.9 [P-CH=CH-C(Ph)=*C*H=C=CH-Ph]. − ^{31}P{^{1}H} NMR ($CDCl_3$, 20°C): δ = 70.1.

Ru(tp){(κ^1(*P*);2,3,4-η)-1-(1-cyclohexenyl)-4-phenyl-6-(diphenylphosphanyl)-1,3,5-hexatriene-2-yl} (7b): This compound was prepared analogously to **7a** with **2** (68 mg, 0.101 mmol), NaOEt (6.8 mg, 0.229 mmol) and HC≡CC_6H_9 (35.5 μL, 0.303 mmol) as the starting materials. Upon cooling the reaction mixture to room temperature a precipitate was formed, which was collected on a glass frit, washed with methanol and *n*-hexane, and dried under vacuum. Yield: 32 mg (43%). − $C_{39}H_{38}BN_6PRu$ (733.60): calcd. C 63.85, H 5.22, N 11.46; found C 63.99, H 5.35, N 11.32. − ^{1}H NMR ($CDCl_3$, 20°C): δ = 8.00 (d, J = 2.1 Hz, 1 H, tp), 7.67 (d, J = 2.1 Hz, 1 H, tp), 7.59 (d, J = 2.1 Hz, 1 H, tp), 7.52−6.61 (m, 19 H), 6.20 (m, 2 H), 6.02 (vt, J = 2.1 Hz, 1 H, tp), 5.87 (d, J = 2.1 Hz, 1 H, tp), 5.62 (m, 1 H), 5.29 (vt, J = 2.1 Hz, 1 H, tp), 4.39 (m, 1 H, tp), 2.01−1.85 (m, 4 H), 1.45−1.23 (m, 4 H). − ^{13}C{^{1}H} NMR ($CDCl_3$, 20°C): δ = 159.2 [d, $^2J_{PC}$ = 14.3 Hz, P-CH=CH-C(Ph)=CH=*C*=CHC_6H_9], 155.7 [d, $^2J_{PC}$ = 23.4 Hz, P-CH=*C*H-C(Ph)=CH=C=CHC_6H_9], 146.7 (d, $^3J_{PC}$ = 2.3 Hz, tp), 144.4 (1 C, quaternary C of Ph), 140.2 (tp), 139.2 (tp), 138.4 (d, $^1J_{PC}$ = 48.2 Hz, PPh[1]), 135.8 [d, $^1J_{PC}$ = 38.6 Hz, P-*C*H=CH-C(Ph)=CH=C=CHC_6H_9], 134.2 (tp), 134.1 (tp), 131.2 (d, $^1J_{PC}$ = 45.3 Hz, PPh[1′]), 131.6, 129.6−128.3 (m, 13 C), 126.3, 126.1, 125.6 (d, J = 3.8 Hz), 125.0, 123.0, 105.8 (d, $^4J_{PC}$ = 1.9 Hz, 1 C, tp), 104.7 (tp), 104.5 (tp), 85.0 [d, J_{PC} = 4.7 Hz, P-CH=CH-*C*(Ph)=CH=C=CHC_6H_9], 75.8 [P-CH=CH-C(Ph)=*C*H=C=CHC_6H_9], 28.5, 26.4, 23.34, 23.27. − ^{31}P{^{1}H} NMR ($CDCl_3$, 20°C): δ = 69.9.

Crystallographic Structure Determinations: Crystal, data collection, and refinement parameters for complexes **3**, **4a**, **6**, and **7b** are given

in Table 2. Crystals were obtained by diffusion of diethyl ether into CH_2Cl_2 solutions, except for **7b**, where crystals were grown by layering of *n*-hexane over a CH_2Cl_2 solution. All X-ray data were collected with a Siemens Smart CCD area detector diffractometer (graphite-monochromated Mo-K_α radiation, $\lambda = 0.71073$ Å, 0.3° ω-scan frames). Corrections for Lorentz and polarization effects, for crystal decay, and for absorption were applied. The structures were solved by direct or Patterson methods.[16] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were inserted in idealized positions and were refined riding with the atoms to which they were bonded. The structures were refined against F^2.[17] 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-105597/105598/105599/105600. Copies of data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

Financial support by the Jubliäumsfond der Österreichischen Nationalbank is greatfully acknowledged (Project No. 6474).

[1] P. J. Stang, F. Diederich, *Modern Acetylene Chemistry*, VCH, Weinheim, FRG, **1995**.

[2] [2a] H. E. Selnau, J. S. Merola, *J. Am. Chem. Soc.* **1991**, *113*, 4008. – [2b] R. Wiedmann, P. Steinert, M. Schäfer, H. Werner, *J. Am. Chem. Soc.* **1993**, *115*, 9864. – [2c] H. Werner, R. Wiedmann, P. Steinert, J. Wolf, *Chem. Eur. J.* **1997**, *3*, 127. – [2d] P.-C. Ting, Y.-C. Lin, G.-H. Lee, M.-C. Cheng, Y. Wang, *J. Am. Chem. Soc.* **1996**, *118*, 6433. – [2e] C. Bianchini, P. Innocenti, M. Peruzzini, A. Romerosa, F. Zanobini, *Organometallics* **1996**, *15*, 272. – [2f] S.-M. Yang, M. C.-W. Chan, K.-K. Cheung, C.-M. Che, S.-M. Peng, *Organometallics* **1997**, *16*, 2819. – [2g] Y. Wang, M. G. Finn, *J. Am. Chem. Soc.* **1995**, *117*, 8045. – [2h] C. A. Merlic, M. E. Pauly, *J. Am. Chem. Soc.* **1996**, *118*, 11319. – [2i] H. M. Lee, J. Yao, G. Jia, *Organometallics* **1997**, *16*, 3927. – [2j] D. Huang, M. Olivan, J. C. Huffman, O. Eisenstein, K. J. Caulton, *Organometallics* **1998**, *17*, 4700. – [2k] M. A. Esteruelas, L. A. Oro, C. Valero, *Organometallics* **1995**, *14*, 3596.

[3] [3a] R. Beckhaus, *Angew. Chem.* **1997**, *109*, 695. – [3b] R. Beckhaus, J. Sang, T. Wagner, B. Ganter, *Organometallics* **1996**, *15*, 1176. – [3c] H. G. Alt, H. E. Engelhardt, M. D. Rausch, L. B. Kool, *J. Organomet. Chem.* **1987**, *329*, 61. – (Vinylidene)-ruthenium complexes in ROMP: [3d] H. Katayama, F. Ozawa, *Chem. Lett.* **1998**, 67. – (Allenylidene)ruthenium in RCM: [3e] A. Fürstner, M. Picquet, C. Bruneau, P. H. Dixneuf, *J. Chem. Soc., Chem. Commun.* **1998**, 1415.

[4] [4a] K. McNeill, R. A. Anderson, R. G. Bergman, *J. Am. Chem. Soc.* **1997**, *119*, 11244. – [4b] A. Kinoshita, N. Sakakibara, M. Mori, *J. Am. Chem. Soc.* **1997**, *119*, 12388. – [4c] J. M. O′Connor, K. Hiibner, R. Merwin, P. K. Gantzel, B. S. Fong, M. Adams, A. L. Rheingold, *J. Am. Chem. Soc.* **1997**, *119*, 3631.

[5] For related η^3-butadienyl complexes see: [5a] C. S. Yi, N. Liu, A. L. Rheingold, L. M. Liable-Sands, *Organometallics* **1997**, *16*, 3910. – [5b] M. I. Bruce, D. N. Duffy, M. J. Liddell, E. R. T. Tiekink, B. K. Nicholson, *Organometallics* **1992**, *11*, 1527. – [5c] M. I. Bruce, T. W. Hambly, M. J. Liddell, M. R. Snow, A. G. Swincer, E. R. T. Tiekink, *Organometallics* **1990**, *9*, 96. – [5d] M. I. Bruce, T. W. Hambly, M. R.; Snow, A. G. Swincer, *Organometallics* **1985**, *4*, 501. – [5e] M. I. Bruce, J. R. Rodgers, M.R. Snow, A. G. Swincer, *J. Chem. Soc., Chem. Commun.* **1981**, 271.

[6] C. Slugovc, K. Mereiter, R. Schmid, K. Kirchner, *J. Am. Chem. Soc.* **1998**, *120*, 6175.

[7] C. Slugovc, P. Wiede, K. Mereiter, R. Schmid, K. Kirchner, *Organometallics* **1997**, *16*, 2768.

[8] [8a] B. M. Trost, G. Dyker, R. Kulawiec, *J. Am. Chem. Soc.* **1990**, *112*, 7809. – [8b] M. I. Bruce, B. C. Hall, N. N. Zaitseva, B. W. Skelton, A. H. White, *J. Organomet. Chem.* **1996**, *522*, 307.

[9] C. Slugovc, D. Doberer, C. Gemel, R. Schmid, K. Kirchner, B. Winkler, F. Stelzer, *Monatsh. Chem.* **1998**, *129*, 221.

[10] C. Gemel, G. Trimmel, C. Slugovc, S. Kremel, K. Mereiter, R. Schmid, K. Kirchner, *Organometallics* **1996**, *15*, 3998.

[11] [11a] T. V. Ashworth, E. Singleton, J. J. Hough, *J. Chem. Soc., Dalton Trans.* **1977**, 1809. – [11b] B. Moreno, S. Sabo-Etienne, B. Chaudret, A. Rodriguez, F. Jalon, S. Trofimenko, *J. Am. Chem. Soc.* **1995**, *117*, 7441.

[12] [12a] N.-Y. Sun, S. J. Simpson, *J. Organomet. Chem.* **1992**, *434*, 341. – [12b] N. W. Alcock, I. D. Burns, K. S. Claire, A. F. Hill, *Inorg. Chem.* **1992**, *31*, 2906. – [12c] N. W. Alcock, A. F. Hill, R. B. Melling, *Organometallics* **1991**, *10*, 3898. – [12d] A. F. Hill, *J. Organomet. Chem.* **1990**, *395*, C35. – [12e] M. M. deV. Steyn, E. Singleton, S. Hietkamp, D. C. Liles, *J. Chem. Soc., Dalton Trans.* **1990**, 2991. – [12f] A. M. McNair, D. C. Boyd, K. R. Mann, *Organometallics* **1986**, *5*, 303. – [12g] G. Trimmel, C. Slugovc, P. Wiede, K. Mereiter, V. N. Sapunov, R. Schmid, K. Kirchner, *Inorg. Chem.* **1997**, *36*, 1076.

[13] [13a] M. I. Bruce, *Chem. Rev.* **1991**, *91*, 197. – [13b] C. Slugovc, V. N. Sapunov, P. Wiede, K. Mereiter, R. Schmid, K. Kirchner, *J. Chem. Soc., Dalton Trans.* **1997**, 4209. – [13c] I. de los Rios, M. J. Tenorio, M. C. Puerta, P. Valerga, *J. Am. Chem. Soc.* **1997**, *119*, 6529.

[14] Unpublished results.

[15] D. D. Perrin, W. L. F. Armarego, *Purification of Laboratory Chemicals*, 3rd ed., Pergamon, New York, **1988**.

[16] G. M. Sheldrick, *SHELXS97*, *Program for the Solution of Crystal Structures*, University of Göttingen, Germany, **1997**.

[17] G. M. Sheldrick, *SHELXL97*, *Program for Crystal Structure Refinement*, University of Göttingen, Germany, **1997**.

Received December 4, 1998
[I98417]