Facile γ-C–H Bond Activation in Phosphinoamine Ligands Resulting in Regio- and Stereoselective C–C Coupling with Terminal Acetylenes**

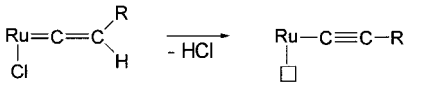
Christian Slugovc, Klaus Mauthner, Martin Kacetl, Kurt Mereiter, Roland Schmid, and Karl Kirchner*

Abstract: Tris(pyrazolyl)borate ruthenium complexes that contain the phosphinoamine ligands $Ph_2PCH_2CH_2NMe_2$, $Ph_2PCH_2CH_2NEt_2$, and $Ph_2PCH_2CH_2N$*i*Pr_2 react with terminal acetylenes HC≡CR (R = Ph, COOEt, CH_2Ph, ferrocenyl, C_6H_9, *n*Bu) to yield the novel coupling products [Ru(tp)(Cl)(κ^3(*P*,*C*,*C*)-$Ph_2PCH{=}CHC(R){=}CH_2$)], [Ru(tp)(Cl)(κ^3(*P*,*C*,*C*)-$Ph_2PCH_2CH(NEt_2)CH{=}CHR$)], [Ru(tp)(Cl)($\kappa^3$(*P*,*C*,*C*)-$Ph_2PCH_2CH(N$*i*$Pr_2)CH{=}CHR$)], [Ru(tp)(Cl)($\kappa^3$(*P*,*C*,*C*)-$Ph_2PCH_2CH(NEt_2)C(R){=}CH_2$)], and [Ru(tp)(Cl)($\kappa^3$(*P*,*C*,*C*)-$Ph_2PCH_2CH(N$*i*$Pr_2)C(R){=}CH_2$)]. The C–C couplings involved take place regioselectively at the γ-carbon atom of the phosphinoamine ligand and, depending on the steric requirements of R, either at the internal or terminal carbon atom of the acetylene molecule. All these reactions proceed in a highly diastereoselective fashion. With $Ph_2PCH_2CH_2NMe_2$ as the ligand, the C–C coupling involves C–N bond cleavage and elimination of $HNMe_2$ leading to dehydrogenation of the $-CH_2CH_2-$ chain.

Keywords: C–H activation · C–C coupling · ruthenium · tripodal ligands · vinylidene complexes

Introduction

In recent years there has been growing interest in vinylidene complexes as attractive candidates for stoichiometric as well as catalytic applications in organic synthesis. Several new stoichiometric reactions involving vinylidene complexes have been discovered. These include C–C coupling reactions, such as the migratory insertion of alkyl, aryl, vinyl, and alkynyl ligands onto the electrophilic α-carbon of the vinylidene moiety,[1] and cycloaddition of alkynes and olefins to the M=C bond to give metallacyclobutene and metallacyclobutane intermediates, respectively.[2] The latter is observed if the α-carbon atom of the vinylidene moiety is nucleophilic. Examples of catalytic reactions involving vinylidene complexes have been reported for the cyclization of dienylalkynes,[3] the tandem cyclization–reconstructive addition of propargyl alcohols with allyl alcohols,[4] the reconstitutive condensation of acetylenes and allyl alcohols,[5] and the dimerization of terminal alkynes.[6] We[6b, c] and others[6d, 7] have shown that C–C coupling processes can be initiated by neutral vinylidene complexes via HCl elimination to afford highly reactive, coordinatively unsaturated alkynyl complexes (Scheme 1). This reaction takes place at elevated temperatures and/or in the presence of a base.



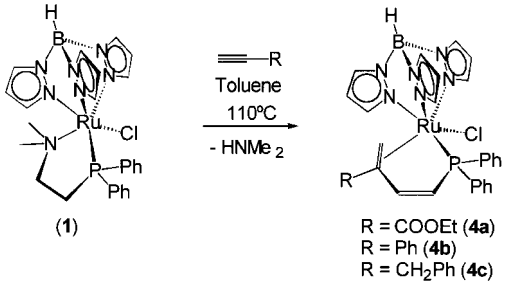
□ ... vacant coordination site

Scheme 1. The formation of highly reactive, coordinatively unsaturated alkynyl complexes for subsequent C–C coupling processes.

In a recent communication[8] we have attempted to catalytically dimerize terminal alkynes HC≡CR (R = Ph, CH_2Ph, COOEt) with [Ru(tp)(κ^2(*P*,*N*)-$Ph_2PCH_2CH_2NMe_2$)Cl] (tp = tris(pyrazolyl)borate) (**1**) as the catalyst precursor. What we expected was a one-end cleavage of the $Ph_2PCH_2CH_2NMe_2$ ligand with formation of the vinylidene complex [Ru(tp)(κ^1(*P*)-$PPh_2CH_2CH_2NMe_2$)(Cl)(=C=CHR)] followed by deprotonation by the pendant basic $CH_2CH_2NMe_2$ moiety to afford the 16 electron alkynyl complex [Ru(tp)(κ^1(*P*)-$PPh_2CH_2CH_2NHMe_2$)(−C≡CR)]Cl. Phosphinoamine ligands are in fact hemilabile and promote the formation of vinylidene complexes.[9] However, **1** was catalytically inactive; instead of the expected reaction, it initiated the unusual C–C coupling process shown in Scheme 2. The formation of the

[*] Prof. Dr. K. Kirchner, Dr. C. Slugovc, Dr. K. Mauthner, Prof. Dr. R. Schmid, M. Kacetl
Institute of Inorganic Chemistry, Vienna University of Technology
Getreidemarkt 9, A-1060 Vienna (Austria)
Fax: (+43) 1-5816668
E-mail: kkirch@fbch.tuwien.ac.at
Prof. Dr. K. Mereiter
Institute of Mineralogy, Crystallography, and Structural Chemistry
Vienna University of Technology
Getreidemarkt 9, A-1060 Vienna (Austria)

[**] Ruthenium Tris(pyrazolyl)borate Complexes, Part 11. Part 10: C. Slugovc, K. Mereiter, R. Schmid, K. Kirchner, *J. Am. Chem. Soc.* **1998**, *120*, 6175.



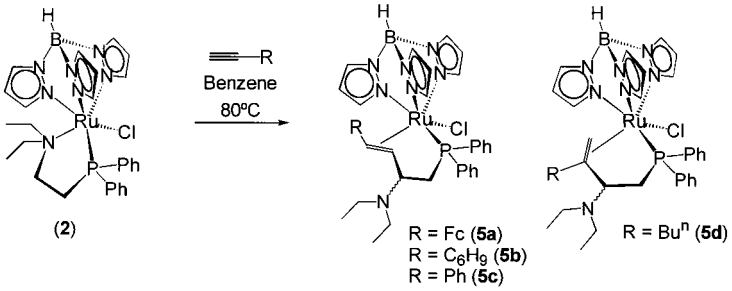
Scheme 2. The unusual C–C coupling process between **1** and terminal acetylenes.

products [Ru(tp)(Cl)(κ^3(*P*,*C*,*C*)-$Ph_2PCH{=}CHC(R){=}CH_2$)] (**4a–c**) requires drastic conditions (prolonged refluxing in toluene) for the Ru–N bond to be cleaved, which creates a vacant coordination site for an incoming acetylene molecule. In continuation our studies on Ru(tp) complexes containing phosphinoamine ligands, we report herein on new C–C coupling reactions between $Ph_2PCH_2CH_2NEt_2$ and $Ph_2PCH_2CH_2NiPr_2$ coordinated to ruthenium and terminal acetylenes HC≡CR with the regio- and diastereoselective formation of complexes of the types [Ru(tp)(Cl)(κ^3(*P*,*C*,*C*)-$Ph_2PCH_2CH(NEt_2)C(R){=}CH_2$)], [Ru(tp)(Cl)($\kappa^3$(*P*,*C*,*C*)-$Ph_2PCH_2CH(NEt_2)CH{=}CHR$)], [Ru(tp)(Cl)($\kappa^3$(*P*,*C*,*C*)-$Ph_2PCH_2CH(NiPr_2)C(R){=}CH_2$)], and [Ru(tp)(Cl)($\kappa^3$(*P*,*C*,*C*)-$Ph_2PCH_2CH(NiPr_2)CH{=}CHR$)]. This study aims at the mechanistic details and structural aspects of these interesting and extremely facile processes.

Results and Discussion

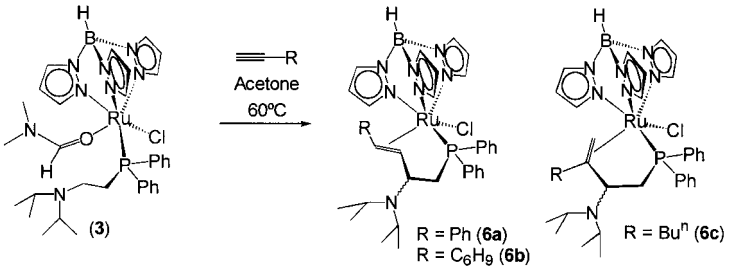
The crucial step in Scheme 2 appears to be the opening of the chelate κ^2(*P*,*N*), which requires relatively high temperatures. Since this process might be facilitated by an increase in the steric demand of the N-donor site of the phosphinoamine ligand, we replaced NMe_2 by NEt_2 and $NiPr_2$. Thus, in a synthesis analogous to that for **1**,[10] $Ph_2PCH_2CH_2NEt_2$ and $Ph_2PCH_2CH_2NiPr_2$ were treated with [Ru(tp)(COD)Cl] in boiling DMF to produce both [Ru(tp)(κ^2(P,N)-$Ph_2PCH_2CH_2NEt_2$)Cl] (**2**) and [Ru(tp)(κ^1(*P*)-$Ph_2PCH_2CH_2NiPr_2$)(dmf)Cl] (**3**), respectively, in high yields. Apparently for steric reasons, the $Ph_2PCH_2CH_2NiPr_2$ ligand is coordinated in a κ^1(*P*) fashion only, and the sixth coordination site is occupied by a DMF molecule.

As expected, complexes **2** and **3** are more reactive than **1**. Thus, the reaction of **2** with HC≡CR (R = Fc (ferrocenyl), C_6H_9 (cyclohexenyl), Ph, *n*Bu) takes place at only 80 °C in benzene to give [Ru(tp)(Cl)(κ^3(*P*,*C*,*C*)-$Ph_2PCH_2CH(NEt_2)$-CH=CHR)] (R = Fc, C_6H_9, Ph; **5a–c**) and [Ru(tp)(Cl)-(κ^3(*P*,*C*,*C*)-$Ph_2PCH_2CH(NEt_2)C(n$Bu$){=}CH_2$)] (**5d**) in high yields (Scheme 3).



Scheme 3. Reaction of complex **2** with terminal acetylenes.

On account of the different coordination mode of the phosphinoamine in **3**, even lower temperatures are required for complete conversion (24 h at −5°C and 2 h at 60 °C, as monitored by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy), according to Scheme 4.



Scheme 4. Reaction of complex **3** with terminal acetylenes.

All final products are stable in air, both in solution and in the solid state, and were characterized by elemental analysis and NMR (^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H}). Accordingly, the ^{1}H and ^{13}C{^{1}H} NMR spectra of **5a–c** and **6a**,**b** are consistent with the presence of κ^3*P*,*C*,*C*-coordinated $Ph_2PCH_2CH(NEt_2)$-CH=CHR and $Ph_2PCH_2CH(NiPr_2)CH{=}CHR$ ligands, respectively. The stereochemistry of the olefin fragment was unambiguously established as the *E* isomer by ^{1}H NMR spectroscopy from the vicinal coupling constant ^3J(H,H) = 11.2 to 12.7 Hz. All the other resonances are unremarkable and are not discussed here. The ^{1}H NMR spectra of **5d** and **6c**, on the other hand, exhibit two characteristic singlets at $\delta \approx 4.5$ and 4.8, which are assignable to the terminal $=CH_2$ group of

Abstract in German: *Rutheniumtris(pyrazolylborat) Komplexe mit den Phosphinoamin-Koliganden $Ph_2PCH_2CH_2NMe_2$, $Ph_2PCH_2CH_2NEt_2$ and $Ph_2PCH_2CH_2NiPr_2$ reagieren mit terminalen Alkinen HC≡CR (R = Ph, COOEt, CH_2Ph, Ferrocenyl, C_6H_9, nBu) zu Kupplungsprodukten des Typs [Ru(tp)(Cl)(κ^3(P,C,C)-$Ph_2PCH{=}CHC(R){=}CH_2$)], [Ru(tp)(Cl)(κ^3(P,C,C)-$Ph_2PCH_2CH(NEt_2)CH{=}CHR$)], [Ru(tp)(Cl)($\kappa^3$(P,C,C)-$Ph_2PCH_2CH(NiPr_2)CH{=}CHR$)], [Ru(tp)(Cl)($\kappa^3$(P,C,C)-$Ph_2PCH_2CH(NEt_2)C(R){=}CH_2$)] und [Ru(tp)(Cl)($\kappa^3$(P,C,C)-$Ph_2PCH_2CH(NiPr_2)C(R){=}CH_2$)]. Die C–C-Kupplungsreaktion findet regioselektiv am γ-Kohlenstoffatom des Phosphinoamin-Liganden statt. Die sterischen Gegebenheiten der Substituenten am Alkin und der Aminogruppe bestimmen, ob das interne oder das terminale Kohlenstoffatom des Alkins an der Kupplung teilnimmt. Alle Reaktionen verlaufen diastereoselektiv. Mit $Ph_2PCH_2CH_2NMe_2$ als Ligand findet zusätzlich Eliminierung von $HNMe_2$ statt.*

0947-6539/98/0410-2044 $ 17.50+.50/0 *Chem. Eur. J.* **1998**, *4*, No. 10

the $Ph_2PCH_2CH(NEt_2)C(n\text{Bu})=CH_2$ and $Ph_2PCH_2CH(N\text{i}Pr_2)C(n\text{Bu})=CH_2$ ligands, respectively.

Both **2** and **3,** each introduced as a racemic mixture of *R* and *S* isomers, coupled with the terminal acetylenes HC≡CR regioselectively at the γ-carbon atom of the phosphinoamine ligand and, depending on R, either at the internal or terminal carbon atom of the acetylene molecule. Although a second chiral center is developed, and thus several diastereomers can be formed, only one predominant diastereomeric pair of enantiomers is produced, according to the ^1H, ^{13}C, and ^{31}P NMR data (Table 1). The nature of the minor pair of enantiomers could not be established.

Table 1. Yields and diastereomeric excess (*de*) found in the reactions of **2** and **3** with terminal acetylenes

	configuration	yield	*de*[a]
5a	$R_{Ru}R_C/S_{Ru}S_C$	58%	88%
5b	$R_{Ru}R_C/S_{Ru}S_C$	72%	> 97%
5c	$R_{Ru}R_C/S_{Ru}S_C$	82%	91%
5d	$R_{Ru}S_C/S_{Ru}R_C$	69%	95%
6a	$R_{Ru}R_C/S_{Ru}S_C$	83%	75%
6b	$R_{Ru}R_C/S_{Ru}S_C$	80%	95%
6c	$R_{Ru}S_C/S_{Ru}R_C$	77%	91%

[a] Determined by ^{31}P NMR spectroscopy.

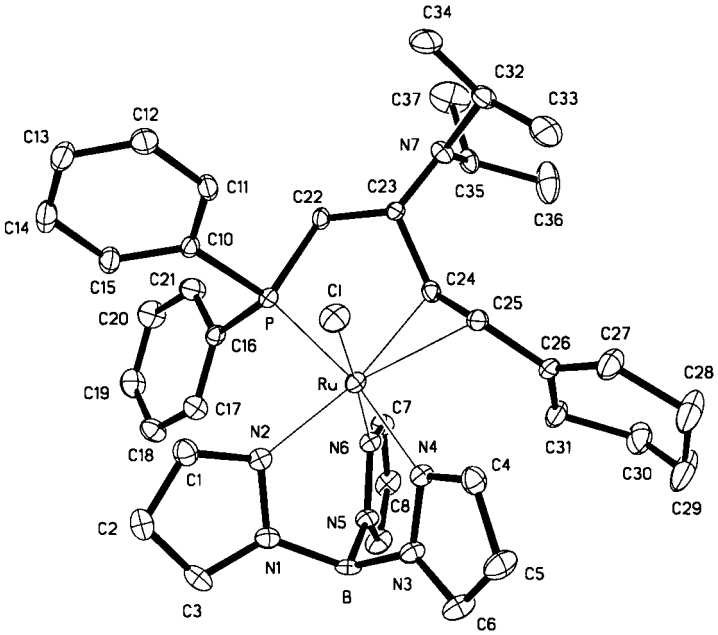


Figure 2. Crystal structure of [Ru(tp)(Cl)(κ^3(*P*,*C*,*C*)-$Ph_2PCH_2CH(N\text{i}Pr_2)CH{=}CH{-}C_6H_9$)] (**6b**). Only the ($S_{Ru}$,$S_C$)-enantiomer is shown. Priority for the assignment of the absolute configurations: a) for Ru: tp > Cl > P > C=C; b) for C23: $N\text{i}Pr_2$ > =CH > CH_2 > H.

The structural identity and the absolute configuration of **5a**, **6b**, and **6c** were unequivocally proven by X-ray crystallography. The results are depicted in Figures 1–3. Selected bond distances and angles are given in Table 2. The configuration of **5a** and **6b** is S_{Ru},S_C/R_{Ru},R_C whereas that of **6c** is S_{Ru},R_C/R_{Ru},S_C. Throughout, the coordination geometry around ruthenium is slightly distorted octahedral; four coordination sites are occupied by the tp ligand and chlorine, and the remaining two are used by the phosphorus atom and the C=C bond of $Ph_2PCH_2CH(NEt_2)CH{=}CH{-}C_{10}H_9Fe$, $Ph_2PCH_2CH(NEt_2)CH{=}CH{-}C_6H_9$, and $Ph_2PCH_2C(NEt_2)C(n\text{Bu})=CH_2$, respectively. All the Ru–N(tp), Ru–P, and Ru–Cl bond lengths are within the usual range.[8, 10, 11, 13] Both in **5a** and **6b**, the Ru–C24 bond of 2.258(3) and 2.253(6) Å is somewhat shorter than that of Ru–C25 (2.314(3) and 2.309(5) Å), while this pattern is reversed in **6c** (Ru–C24 = 2.345(6) and Ru–C25 = 2.196(7) Å). It is safe to assume that the diastereoselectivity of the formation of **5** and **6**, as proved by the crystallographic data, is sterically controlled, since the alternative diastereomeric pair of enantiomers would force the dialkylamino moiety to approach the chloride ligand very closely and, in the case of **5d** and **6c**, one of the pyrazolyl groups of tp.

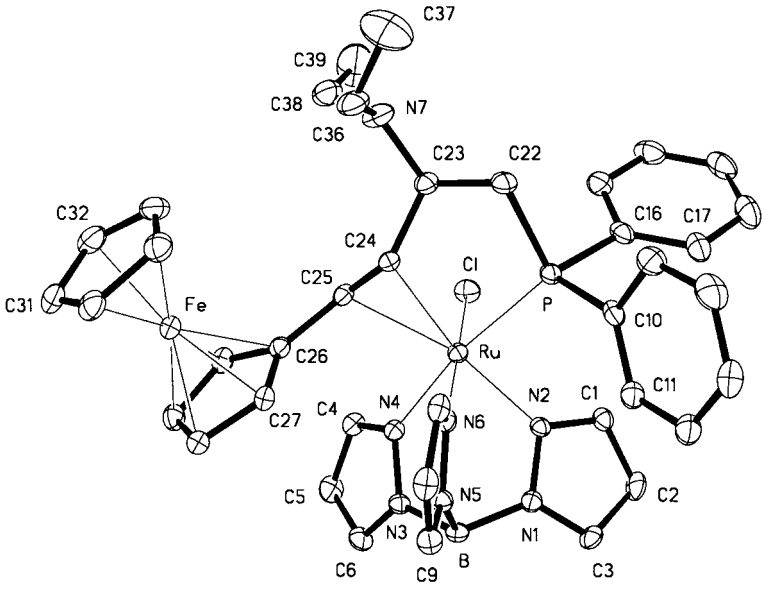


Figure 1. Crystal structure of [Ru(tp)(Cl)(κ^3(*P*,*C*,*C*)-$Ph_2PCH_2CH(NEt_2)CH{=}CH{-}C_{10}H_9Fe$)] (**5a**). Only the ($S_{Ru}$,$S_C$)-enantiomer is shown. Priority for the assignment of the absolute configurations: a) for Ru: tp > Cl > P > C=C; b) for C23: NEt_2 > =CH > CH_2 > H.

A reasonable suggestion for the reaction mechanism for **2** and **3** is summarized in Scheme 5. After the initial Ru–N bond cleavage the vinylidene intermediate **A** is formed from a 1,2-hydrogen shift.[12] It is noteworthy that neutral vinylidene complexes of the type [Ru(tp)(PR_3)(Cl)(=C=CHR′)] (R = Ph, Cy; R′ = Ph, *n*Bu, *t*Bu, $SiMe_3$, C_6H_9, COOEt) have been reported.[6b, 12a] The subsequent elimination of HCl, promoted by the presence of the dialkylamino group, yields the coordinatively unsaturated alkynyl complex **B**. We[6c, 13] and others[6d, 7, 14] have shown that such species can be trapped by CO, which occupies the vacant coordination site. It is conceivable that the γ-C–H bond of the phosphinoamine ligand is weakened by an agostic interaction that eventually leads to hydrogen migration by means of a σ-bond metathesis pathway to give the four-membered phospharuthenacycle **C**. Such species have already

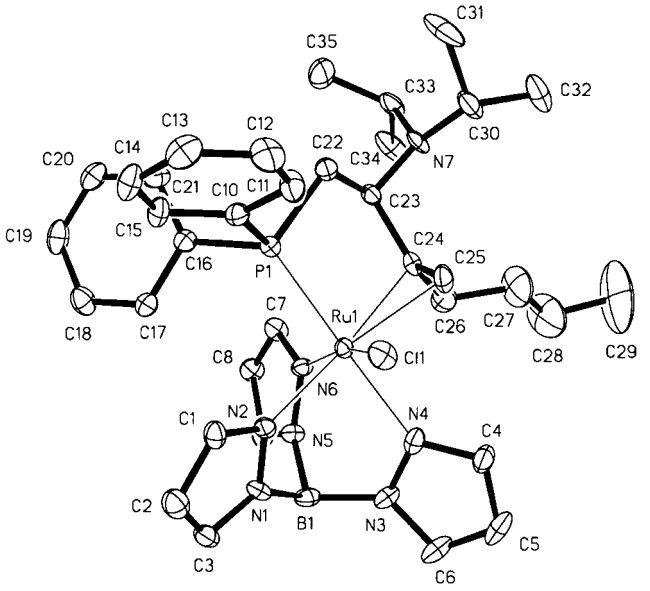
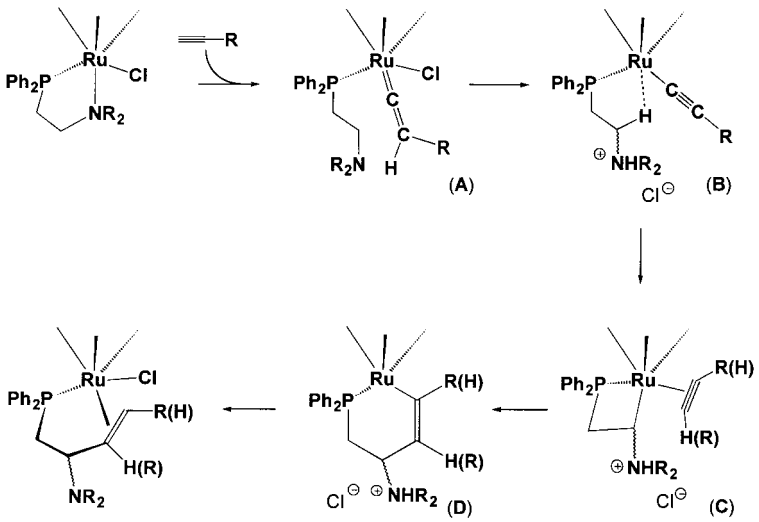


Figure 3. Crystal structure of [Ru(tp)(Cl)(κ^3(*P*,*C*,*C*)-$Ph_2PCH_2CH(NiPr_2)$-C(*n*Bu)=CH_2)] (**6c**). Only the (S_{Ru},R_C)-enantiomer and one of the two crystallographically independent complexes is shown. Priority for the assignment of the absolute configurations: a) for Ru: tp > Cl > P > C=C; b) for C23: $NiPr_2$ > =CH > CH_2 > H.

Table 2. Selected bond distances [Å] and angles [°] for complexes **5a**, **6b**, and **6c**.

	5a	**6b**	**6c**[a]
Ru–N2	2.120(3)	2.089(5)	2.098(5)
Ru–N4	2.153(3)	2.136(5)	2.164(6)
Ru–N6	2.101(3)	2.081(5)	2.124(5)
Ru–Cl	2.445(1)	2.416(2)	2.422(2)
Ru–P	2.344(1)	2.334(2)	2.271(2)
Ru–C24	2.258(3)	2.253(6)	2.345(6)
Ru–C25	2.314(3)	2.309(5)	2.196(7)
C24–C25	1.373(5)	1.378(7)	1.380(9)
N2-Ru-N4	80.3(1)	80.8(2)	84.2(2)
N2-Ru-N6	87.0(1)	87.8(2)	83.6(2)
P-Ru-Cl	91.69(4)	91.74(6)	92.23(9)
C24-Ru-N2	164.1(1)	164.3(2)	165.6(2)
C25-Ru-N2	160.7(1)	160.6(2)	159.0(2)

[a] Ru is Ru1.



Scheme 5. Proposed mechanism for the reaction between complexes **2** or **3** and terminal acetylenes.

been reported.[15, 16] An alternative oxidative-addition/reductive-elimination sequence cannot be ruled out in principle, but it would require either a seven-coordinate species (as yet unknown in Ru(tp) chemistry) or an intermediate with a κ^2coordinated tp ligand (a rare bonding mode for Ru(tp) complexes).[17]

The η^2-bound acetylene ligand in **C** is orientated so that the repulsive interactions between the dialkylamino group and R are minimized. In this way, the substituent on the alkyne contributes to the regioselectivity of the C–C coupling process. Subsequent migratory insertion of the acetylene molecule into the Ru–C bond of the phosphametallacyclobutane ring affords the vinyl complex **D**, which, on protonation, yields the final product. For steric reasons, **D** is only able to adopt the *E* conformation and this also has a decisive influence on the stereochemistry of the final C–C coupled products.

The reaction of **1** with acetylenes, due to the higher temperatures necessary to cleave the Ru–N bond, proceeds somewhat differently (Scheme 6). Accordingly, the intermediate **B** eliminates the quaternary ammonium salt (H_2NMe_2)Cl prior to C–C coupling to give the phospharuthenacyclobutene complex **C′,** which then reacts via the vinyl intermediate **D′** (not shown in Scheme 6) to give the final products and $HNMe_2$. In the case of R = COOEt, the secondary amine is trapped as the enamine Me_2NCH=CHCOOEt. The hypothesis that the elimination reaction occurs prior to C–C coupling is supported by the observation that neither **5** nor **6** tends to eliminate the secondary amine, even after prolonged refluxing in toluene. Note also that in **C′** no unfavorable steric interactions are involved. Therefore, the C–C coupling process can readily take place at the internal carbon atom of the alkyne, in agreement with the experimental findings (Scheme 2).

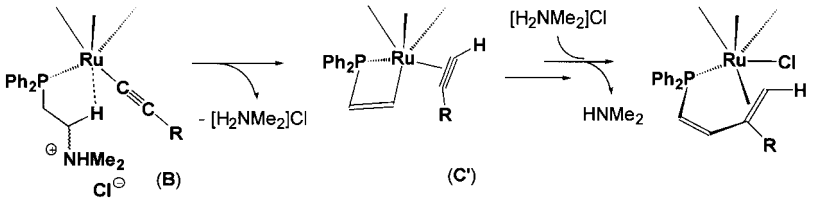
Conclusion

Coordinatively unsaturated alkynyl complexes, obtained through the elimination of HCl from vinylidene complexes, are capable of initiating selective coupling of alkanes and terminal acetylenes in the coordination sphere of Ru^{II}. Although the present C–H activation is particularly assisted by the intramolecular mode with favorable stereochemical conditions brought about by the anchoring phosphine group, an extension to the intermolecular mode is conceivable.

Experimental Section

General techniques: All compounds were manipulated with standard Schlenk techniques under an inert atmosphere of purified argon. All chemicals were standard reagent grade and used without further purification. The solvents were purified and dried according to standard procedures[18] and stored over molecular sieves (4 Å). [Ru(tp)(COD)Cl],[10] [Ru(tp)(κ^2(*P*,*N*)-$Ph_2PCH_2CH_2NMe_2$)Cl] (**1**),[10] and *N*,*N*-dialkyl-2-diphenylphosphino-ethanamines[19] were prepared according to reported

0947-6539/98/0410-2046 $ 17.50+.50/0 *Chem. Eur. J.* **1998**, *4*, No. 10



Scheme 6. Proposed mechanism for the reaction between complex **1** and terminal acetylenes.

procedures. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker AC250 spectrometer (vt = virtual triplet). Diffuse reflectance FT–IR spectra were recorded on a Mattson RS2 spectrometer. Microanalyses were performed by Microanalytical Laboratories, University of Vienna (Austria).

[Ru(tp)(κ^2(P,N)-*N,N*-diethyl-2-diphenylphosphinoethanamine)Cl] (**2**): A solution of [Ru(tp)(COD)Cl] (100 mg, 0.218 mmol) and $Ph_2PCH_2CH_2NEt_2$ (63 mg, 0.220 mmol) in DMF (4 mL) was refluxed for 2 h. After removal of the solvent, a yellow solid was obtained, which was collected on a glass frit, washed with *n*-hexane, and dried under vacuum. Yield: 123 mg (89%); ^{1}H NMR (250.13 MHz, $CDCl_3$, 25°C, TMS): $\delta = 8.35$ (d, $J = 2.3$ Hz, 1H; tp), 7.85 (d, $J = 2.3$ Hz, 1H; tp), 7.74 (d, $J = 2.3$ Hz, 1H; tp), 7.62 (m, 1H; tp), 7.45–7.22 (m, 7H; Ph), 7.11 (d, $J = 1.9$ Hz, 1H; tp), 7.06 (m, 2H; Ph), 6.68 (br m, 1H; Ph), 6.56 (d, $J = 2.3$ Hz, 1H; tp), 6.37 (m, 1H; tp), 5.93 (vt, $J = 2.3$ Hz, 1H; tp), 5.73 (vt, $J = 2.3$ Hz, 1H; tp), 4.24 (m, 1H; $N(CH_2CH_3)_2$), 3.64 (m, 1H; PCH_2CH_2N), 3.47 (m, 1H; $N(CH_2CH_3)_2$), 3.22–3.02 (m, 1H; PCH_2CH_2N), 2.89–2.76 (m, 2H; PCH_2CH_2N, $N(CH_2CH_3)_2$), 2.20 (m, 1H; $N(CH_2CH_3)_2$), 1.07 (t, 3H; $N(CH_2CH_3)_2$), 0.16 (t, 3H; $N(CH_2CH_3)_2$); ^{13}C{^{1}H} NMR (62.86 MHz, $CDCl_3$, 25°C, TMS): $\delta = 147.6$ (d, $J = 1.4$ Hz; tp), 147.1 (d, $J = 1.9$ Hz; tp), 144.4 (d, $J = 2.9$ Hz; tp), 138.8 (d, $^1J(C,P) = 39.1$ Hz; Ph^{1}), 136.9 (tp), 135.9 (tp), 135.8 (tp), 134.5 (d, $^1J(C,P) = 40.5$ Hz; Ph$^{1'}$), 133.4 (d, $^2J(C,P) = 8.6$ Hz, 4C; Ph^{2,6}), 129.9 (d, $^4J(C,P) = 2.4$ Hz; Ph^{4}), 129.1 (d, $^4J(C,P) = 2.4$ Hz; Ph$^{4'}$), 128.6 (d, $^3J(C,P) = 9.1$ Hz, 2C; Ph^{3,5}), 128.0 (d, $^3J(C,P) = 8.6$ Hz, 2C; Ph$^{3',5'}$), 106.1 (d, $J = 2.9$ Hz; tp), 106.0 (tp), 105.4 (tp), 59.3 (d, $^2J(C,P) = 5.3$ Hz; NCH_2CH_2P), 50.7 (NCH_2CH_3), 49.0 (NCH_2CH_3), 30.5 (d, $^1J(C,P) = 23.4$ Hz; NCH_2CH_2P), 11.0 (NCH_2CH_3), 6.8 (NCH_2CH_3); ^{31}P{^{1}H} NMR (101.26 MHz, $CDCl_3$, 25°C, H_3PO_4 (85%)): $\delta = 64.5$; $C_{27}H_{34}BClN_7PRu$ (634.9): calcd C 51.08, H 5.40, N 15.44; found C 51.17, H 5.45, N 15.24.

[Ru(tp)(κ^1(*P*)-*N,N*-di(methylethyl)-2-diphenylphosphinoethanamine)-(dmf)Cl] (**3**): This complex was synthesized analogously to **2** from [Ru(tp)(COD)Cl] (100 mg, 0.218 mmol) and $Ph_2PCH_2CH_2NiPr_2$ (69 mg, 0.218 mmol). Yield: 98 mg (61%); ^{1}H NMR (250.13 MHz, $CDCl_3$, 25°C, TMS): $\delta = 8.00$ (s, 1H; $OHCN(CH_3)_2$), 7.89 (d, $J = 2.3$ Hz, 1H; tp), 7.83 (d, $J = 2.3$ Hz, 1H; tp), 7.80–7.62 (m, 5H; tp, Ph), 7.42–7.32 (m, 5H; Ph), 7.18 (m, 1H; Ph), 7.06 (m, 2H; Ph), 6.96 (d, $J = 2.3$ Hz, 1H; tp), 6.21 (m, 1H; tp), 6.03 (vt, $J = 2.3$ Hz, 1H; tp), 5.92 (vt, $J = 2.3$ Hz, 1H; tp), 3.32 (m, 2H; $NCH(CH_3)_2$), 2.99–2.60 (m, 2H; PCH_2CH_2N), 2.67 (s, 3H; $OHCN(CH_3)_2$), 2.32 (s, 3H; $OHCN(CH_3)_2$), 2.29–2.22 (m, 2H; PCH_2CH_2N), 0.87 (d, 12H; CH_3); ^{13}C{^{1}H} NMR (62.86 MHz, $CDCl_3$, 25°C, TMS): $\delta = 168.3$ ($OHCN(CH_3)_2$), 148.0 (tp), 145.0 (tp), 141.2 (tp), 136.8–132.8 (m, 9C; tp, Ph), 129.0–127.8 (m, 6C; Ph), 106.3 (tp), 106.0 (tp), 105.7 (tp), 49.0 (2C, $NCH(CH_3)_2$), 43.7 (d, $^2J(C,P) = 27.1$ Hz; PCH_2CH_2N), 38.4 ($OHCN(CH_3)_2$), 32.4 ($OHCN(CH_3)_2$), 28.7 (d, $^1J(C,P) = 22.2$ Hz; PCH_2CH_2N), 21.4 (2C; $NCH(CH_3)_2$), 21.1 (2C; $NCH(CH_3)_2$); ^{31}P{^{1}H} NMR (101.26 MHz, $CDCl_3$, 25°C, H_3PO_4 (85%)): $\delta = 51.0$; $C_{32}H_{45}BClN_8OPRu$ (736.1): calcd C 52.22, H 6.16, N 15.22; found C 51.90, H 6.40, N 15.54.

[Ru(tp)(κ^3(*P,C,C*)-η-(1,2)-4-(diphenylphosphino)-buta-1,3-diene-2-carboxylic acid, ethylester)Cl] (**4a**): A suspension of **1** (210 mg, 0.35 mmol) in toluene (4 mL) was treated with HC≡CCOOEt (200 μL) and refluxed for 7 h. After removal of the solvent, the residue was dissolved in diethyl ether (2 mL). The addition of *n*-hexane afforded analytically pure **4a**. Yield: 216 mg (94%); ^{1}H NMR (250.13 MHz, $CDCl_3$, 25°C, TMS): $\delta = 8.04$ (d, $J = 2.5$ Hz, 1H; tp), 7.90 (dd, $^3J(H,H_{cis}) = 8.6$ Hz, $^2J(P,H) = 46.2$ Hz, 1H; PCH=CH−CR=CH_2), 7.84 (d, $J = 2.5$ Hz, 1H; tp), 7.68 (d, $J = 2.6$ Hz, 1H; tp), 7.63 (d, $J = 2.6$ Hz, 1H; tp), 7.55 (d, $J = 2.6$ Hz, 1H; tp), 7.42–7.19 (m, 5H), 7.10–6.96 (m, 4H), 6.59–6.51 (m, 2H), 6.47 (dd, $^3J(H,H) = 8.6$ Hz, $^3J(P,H) = 5.6$ Hz, 1H; PCH=CH−CR=CH_2), 6.26 (vt, $J = 2.5$ Hz, 1H; tp), 6.19 (vt, $J = 2.5$ Hz, 1H; tp), 5.98 (s, 1H; PCH=CH−CR=CH_2), 5.82 (m, 1H; tp), 4.92 (s, 1H; PCH=CH−CR=CH_2), 3.34 (m, 2H; diastereotopic CH_2CH_3), 0.30 (t, 3H; CH_2CH_3); ^{13}C{^{1}H} NMR (62.86 MHz, $CDCl_3$, 25°C, TMS): $\delta = 173.3$ (*C*OOEt), 157.4 (d, $^2J(C,P) = 18.6$ Hz; PCH=*C*H−CR=CH_2), 147.7 (tp), 146.2 (tp), 142.2 (tp), 137.0 (tp), 135.22 (tp), 135.17 (tp), 135.1 (d, $^1J(C,P) = 50.7$ Hz; Ph^{1}), 134.3 (d, $^2J(C,P) = 9.7$ Hz, 2C; Ph^{2,6}), 132.9 (d, $^2J(C,P) = 9.2$ Hz, 2C; Ph$^{2',6'}$), 130.7 (d, $^4J(C,P) = 2.2$ Hz; Ph^{4}), 130.5 (d, $^1J(C,P) = 46.9$ Hz; Ph$^{1'}$), 130.3 (d, $^4J(C,P) = 2.7$ Hz; Ph$^{4'}$), 128.6 (d, $^3J(C,P) = 10.4$ Hz, 2C; Ph^{3,5}), 128.4 (d, $^3J(C,P) = 9.8$ Hz, 2C; Ph$^{3',5'}$), 126.4 (d, $^1J(C,P) = 39.8$ Hz; P*C*H=CH−CR=CH_2), 106.5 (tp), 106.2 (d, $^4J(C,P) = 3.3$ Hz; tp), 106.0 (tp), 91.8 (d, $^3J(C,P) = 6.9$ Hz; PCH=CH−*C*R=CH_2), 87.5 (d, $^4J(C,P) = 2.2$ Hz; PCH=CH−CR=*C*H_2), 60.5 (CH_2CH_3), 13.5 (CH_2CH_3); ^{31}P{^{1}H} NMR (101.26 MHz, $CDCl_3$, 25°C, H_3PO_4 (85%)): $\delta = 64.9$; IR (diffuse reflection): $\tilde{\nu} = 2489$ (m, B–H), 1702 cm^{-1} (s, C=O); $C_{28}H_{29}BClN_6O_2PRu$ (659.9): calcd C 50.96, H 4.43, N 12.74; found C 51.18, H 4.63, N 12.51.

[Ru(tp)(κ^3(*P,C,C*)-η-(3,4)-diphenyl-(3-phenyl-1,3-butadienyl)phosphine)Cl] (**4b**): A suspension of **1** (300 mg, 0.49 mmol) in toluene (4 mL) was treated with HC≡CPh (300 μL) and refluxed for 20 h. After removal of the solvent, the crude product was purified by flash silica-gel chromatography. The column was eluted with CH_2Cl_2 until the solution was colorless and then with CH_3CN, and the first brown band was collected. The solvent was removed to produce a yellow oil, which was treated with methanol to give a solid material. Yield: 210 mg (63%); ^{1}H NMR (250.13 MHz, $CDCl_3$, 25°C, TMS): $\delta = 8.34$ (d, $J = 2.0$ Hz, 1H; tp), 7.90 (dd, $^3J(H,H) = 8.6$ Hz, $^1J(P,H) = 45.2$ Hz, 1H; P*C*H=CH−CR=CH_2), 7.80 (m, 1H; tp), 7.66 (m, 2H; Ph), 7.40–6.97 (m, 13H; Ph, tp), 6.80–6.64 (m, 2H; Ph), 6.64 (dd, $^3J(H,H) = 8.6$ Hz, $^2J(P,H) = 4.5$ Hz, 1H; PCH=CH−CR=CH_2), 6.37 (m, 1H; tp), 6.15 (m, 1H; tp), 5.44 (m, 1H; tp), 5.20 (d, $^3J(P,H) = 1.9$ Hz, 1H; PCH=CH−CR=CH_2), 4.91 (d, $^4J(P,H) = 1.8$ Hz, 1H; PCH=CH−CR=CH_2); ^{13}C{^{1}H} NMR (62.86 MHz, $CDCl_3$, 25°C, TMS): $\delta = 158.7$ (d, $^2J(P,C) = 18.6$ Hz; PCH=*C*H−CR=CH_2), 147.8 (d, $J(P,C) = 2.4$ Hz; tp), 146.1 (d, $J(P,C) = 1.4$ Hz; tp), 142.6 (d, $J(P,C) = 2.4$ Hz; tp), 141.6 (Ph^{R1}), 136.4, 136.1 (d, $J(P,C) = 2.9$ Hz; tp), 135.8 (d, $^1J(P,C) = 50.5$ Hz; Ph^{1}), 135.3, 134.3 (d, $^2J(P,C) = 10.4$ Hz, 2C; Ph^{2,6}), 132.9 (d, $^2J(P,C) = 10.5$ Hz, 2C; Ph$^{2',6'}$), 131.5 (d, $^1J(P,C) = 44.8$ Hz; Ph$^{1'}$), 130.6 (d, $^4J(P,C) = 1.9$ Hz; Ph^{4}), 130.1 (d, $^4J(P,C) = 2.4$ Hz; Ph$^{4'}$), 128.9 (Ph^{R4}), 128.43 (d, $^3J(P,C) = 9.5$ Hz, 2C; Ph^{3,5}), 128.41 (d, $^3J(P,C) = 10.5$ Hz, 2C; Ph$^{3',5'}$), 127.8 (2C; Ph^{R3,5}), 126.8 (d, $^1J(P,C) = 39.1$ Hz; P*C*H=CH−CR=CH_2), 126.4 (2C; Ph^{R2,6}), 106.8 (d, $^4J(P,C) = 2.9$ Hz; tp), 106.2 (tp), 105.1 (tp), 103.8 (d, $^3J(P,C) = 6.6$ Hz; PCH=CH−*C*R=CH_2), 82.3 (d, $^4J(P,C) = 1.9$ Hz; PCH=CH−CR=*C*H_2); ^{31}P{^{1}H} NMR (101.26 MHz, $CDCl_3$, 25°C, H_3PO_4 (85%)): $\delta = 65.3$; $C_{32}H_{29}BClN_6PRu$ (675.9): calcd C 56.86, H 4.33, N 12.43; found C 56.40, H 4.56, N 11.04.

[Ru(tp)(κ^3(*P,C,C*)-η-(3,4)-diphenyl-(3-(phenylmethylen)-1,3-butadienyl)-phosphine)Cl] (**4c**): This complex was synthesized analogously to **4b** from **1** (100 mg, 0.218 mmol) and HC≡CCH$_2$Ph (200 μL). Yield: 50 mg (53%); ^{1}H NMR (250.13 MHz, $CDCl_3$, 25°C, TMS): $\delta = 8.01$ (d, $J = 2.0$ Hz, 1H; tp), 7.87 (d, $J = 2.5$ Hz, 1H; tp), 7.74 (d, $J = 2.3$ Hz, 1H; tp), 7.74 (d, $J = 2.5$ Hz, 1H; tp), 7.63 (d, $J = 2.2$ Hz, 1H; tp), 7.53 (dd, $^3J(H,H) = 8.7$ Hz, $^2J(P,H) = 25.6$ Hz, 1H; P*C*H=CH−CR=CH_2), 7.42–7.16 (m, 17H; Ph, tp), 7.05–6.98 (m, 2H; Ph), 6.70–6.63 (m, 2H; Ph), 6.37 (dd, $^3J(H,H) = 8.7$ Hz, $^3J(P,H) = 4.9$ Hz, 1H; PCH=CH−CR=CH_2), 6.29 (m, 1H; tp), 6.25 (vt, $J = 2.3$ Hz, 1H; tp), 6.05 (vt, $J = 2.2$ Hz, 1H; tp), 4.74 (s, 1H; PCH=CH−CR=CH_2), 4.46 (s, 1H; PCH=CH−CR=CH_2), 2.36 (m, 2H; diasterotopic CH_2); ^{13}C{^{1}H} NMR (62.86 MHz, $CDCl_3$, 25°C, TMS): $\delta = 160.3$ (d, $^2J(P,C) = 17.2$ Hz; PCH=*C*H−CR=CH_2), 146.4 (tp), 145.7 (d, $J(P,C) = 1.9$ Hz; tp), 141.2 (d, $J(P,C) = 2.8$ Hz; tp), 137.6 (tp), 136.4 (d, $^1J(P,C) = 49.1$ Hz, Ph^{1}), 135.9 (d, $J(P,C) = 2.9$ Hz; tp), 135.1, 134.6 (d, $^2J(P,C) = 9.5$ Hz, 2C; Ph^{2,6}), 132.1 (d, $^2J(P,C) = 9.5$ Hz, 2C; Ph$^{2',6'}$), 131.0 (d, $^1J(P,C) = 44.9$ Hz; Ph$^{1'}$), 130.5 (d, $^4J(P,C) = 2.3$ Hz; Ph^{4}), 129.9 (d, $^4J(P,C) = 2.3$ Hz; Ph$^{4'}$), 129.2 (2C; Ph^{R3,5}), 129.0 (2C; Ph^{R2,6}), 128.6 (d, $^3J(P,C) = 10$ Hz, 2C; Ph^{3,4}), 128.3 (d, $^3J(P,C) = 9.6$ Hz, 2C; Ph$^{3',5'}$), 126.8 (Ph^{R1}), 125.2 (d, $^1J(P,C) = 39.1$ Hz; P*C*H=CH−CR=CH_2), 106.5 (d, $^4J(P,C) = 2.9$ Hz; tp), 106.3, 106.2, 103.1 (d, $^3J(P,C) = 7.1$ Hz; PCH=CH−*C*R=CH_2), 83.8 (m, PCH=CH−CR=*C*H_2), 41.9 (CH_2R); ^{31}P{^{1}H} NMR (101.26 MHz, $CDCl_3$, 25°C, H_3PO_4 (85%)): $\delta = 64.2$; $C_{33}H_{31}BClN_6PRu$ (690.0): calcd C 57.45, H 4.53, N 12.18; found C 57.40, H 4.56, N 12.04.

($R_{Ru}R_C/S_{Ru}S_C$)-[Ru(tp)(κ^3(*P,C,C*)-η-(1,2)-4-(diphenylphosphino)-(*N,N*-diethyl)-1-ferrocenyl-3-but-1-enamine)Cl] (**5a**): A suspension of **2** (100 mg, 0.158 mmol) in acetone (4 mL) was treated with HC≡C$C_{10}H_9$Fe (33 mg, 0.160 mmol) and refluxed for 5 h. The volume of the solution was reduced to about 0.5 mL, whereupon a precipitate was formed, which was collected on a glass frit, washed with methanol, and dried in vacuo. Yield: 78 mg (58%); ^{1}H NMR (250.13 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.55 (d, J = 1.8 Hz, 1H; tp), 7.60 (m, 2H; tp), 7.43–7.22 (m, 8H; tp, Ph), 7.07 (m, 2H; Ph), 6.63 (br m, 2H; Ph), 6.53 (d, J = 1.8 Hz, 1H; tp), 6.30 (m, 1H; tp), 6.21 (d, ^3J(H,H) = 11.2 Hz; −CH=C*H*−Fc), 5.82 (v t, J = 2.2 Hz, 1H; tp), 5.47 (v t, J = 2.2 Hz, J = 2.5 Hz; 1H; tp), 4.53 (m, 2H; −C*H*=CH−Fc, PCH_2CHN), 4.12 (s, 5H; Fc), 3.75 (m, 1H; PCH_2CHN), 3.57–3.50 (m, 4H; Fc′), 3.27–3.01 (m, 5H; NCH_2CH_3, PCH_2CHN), 1.34 (t, 6H; NCH_2CH_3); ^{13}C{^{1}H} NMR (62.86 MHz, $CDCl_3$, 25 °C, TMS): δ = 147.5 (tp), 145.1 (d, J = 2.3 Hz; tp), 144.9 (tp), 144.5 (tp), 136.5 (d, ^1J(C,P) = 40.5 Hz; Ph^1), 136.3 (tp), 135.8 (tp), 135.5 (d, J = 2.4 Hz; tp), 134.6 (d, ^2J(C,P) = 8.1 Hz, 2C; Ph^{2,6}), 133.4 (d, ^2J(C,P) = 8.6 Hz, 2C; Ph$^{2',6'}$), 131.4 (d, ^1J(C,P) = 39.6 Hz; Ph$^{1'}$), 130.2 (d, ^4J(C,P) = 1.9 Hz; Ph^4), 129.9 (d, ^4J(C,P) = 2.4 Hz; Ph$^{4'}$), 128.7 (d, ^3J(C,P) = 9.1 Hz, 2C; Ph^{3,5}), 128.0 (d, ^3J(C,P) = 9.5 Hz, 2C; Ph$^{3',5'}$), 106.0 (d, J = 1.9 Hz; tp), 105.6 (tp), 105.2 (tp), 88.8 (CHN−CH=CH−Fc^1), 87.4 (d, J = 2.2 Hz; CHN−CH=CH−Fc^1), 85.8 (CHN−CH=CH−Fc^1), 69.3 (5C, Fc), 68.2 (Fc′), 68.1 (Fc′), 67.3 (Fc′), 66.7 (Fc′), 63.9 (d, ^2J(C,P) = 14.3 Hz; PCH_2CHN), 44.5 (2C; NCH_2CH_3), 39.6 (d, ^1J(C,P) = 37.2 Hz; PCH_2CHN), 13.6 (2C; NCH_2CH_3); ^{31}P{^{1}H} NMR (101.26 MHz, $CDCl_3$, 25 °C, H_3PO_4 (85%)): δ = 40.5; $C_{39}H_{44}$BClFeN_7PRu (845.0): calcd C 55.44, H 5.25, N 11.60; found C 55.63, H 5.44, N 11.45.

($R_{Ru}R_C/S_{Ru}S_C$)-[Ru(tp)(κ^3(*P,C,C*)-η-(1,2)-1-(1-cyclohexenyl)-4-(diphenylphosphino)-(*N,N*-diethyl)-3-but-1-enamine)Cl] (**5b**): This complex was synthesized analogously to **5a** from **2** (100 mg, 0.158 mmol) and HC≡CC_6H_9 (33 mg, 0.160 mmol). Yield: 84 mg (72%); ^{1}H NMR (250.13 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.16 (d, J = 1.8 Hz, 1H; tp), 7.71 (d, J = 2.1 Hz, 1H; tp), 7.63 (d, J = 2.1 Hz, 1H; tp), 7.63 (d, J = 2.5 Hz, 1H; tp), 7.34–7.14 (m, 6H; Ph), 7.05–6.96 (m, 3H; Ph, tp), 6.89 (d, J = 1.8 Hz, 1H; tp), 6.39 (m, 2H; Ph), 6.23 (m, 1H; tp), 6.02 (m, 1H; *c*Hex^2), 5.96 (v t, J = 2.1 Hz, 1H; tp), 5.72 (d, ^3J(H,H) = 12.5 Hz; −CH=C*H*-*c*Hex), 5.68 (v t, J = 2.1 Hz, J = 2.5 Hz, 1H; tp), 4.23 (m, 1H; −C*H*=CH-*c*Hex), 3.75–3.60 (m, 2H; PCH_2CHN, PCH_2CHN), 3.36 (m, 1H; PCH_2CHN), 3.05 (m, 2H; NCH_2CH_3), 2.88 (m, 2H; NCH_2CH_3), 1.86 (m, 2H; *c*Hex), 1.30–0.71 (m, 5H; *c*Hex), 1.19 (t, 6H; NCH_2CH_3), −0.57 (m, 1H; *c*Hex); ^{13}C{^{1}H} NMR (62.86 MHz, $CDCl_3$, 25 °C, TMS): δ = 146.5 (d, J = 1.5 Hz; tp), 146.4 (d, J = 1.4 Hz; tp), 145.4 (d, J = 1.7 Hz; tp), 139.1 (*c*Hex^1), 136.6 (d, ^1J(C,P) = 40.7 Hz; Ph^1), 136.5 (tp), 136.3 (tp), 135.2 (d, J = 1.6 Hz; tp), 134.4 (d, ^2J(C,P) = 8.1 Hz, 2C; Ph^{2,6}), 133.2 (d, ^2J(C,P) = 8.2 Hz, 2C; Ph$^{2',6'}$), 130.1 (d, ^4J(C,P) = 2.3 Hz; Ph^4), 129.8 (d, ^4J(C,P) = 2.4 Hz; Ph$^{4'}$), 129.3 (*c*Hex^2), 128.9 (d, ^1J(C,P) = 42.2 Hz; Ph$^{1'}$), 128.7 (d, ^3J(C,P) = 9.0 Hz, 2C; Ph^{3,5}), 127.7 (d, ^3J(C,P) = 9.3 Hz, 2C; Ph$^{3',5'}$), 106.0 (2C; tp), 105.5 (d, J = 2.4 Hz; tp), 99.9 (−CH=C*H*-*c*Hex), 84.1 (d, J = 4.1 Hz; −CH=C*H*-*c*Hex), 66.9 (d, ^2J(C,P) = 22.7 Hz; PCH_2CHN), 44.8 (2C; NCH_2CH_3), 44.3 (d, ^1J(C,P) = 35.6 Hz; PCH_2CHN), 26.9 (*c*Hex), 23.2 (*c*Hex), 22.8 (2C; *c*Hex), 13.0 (2C; NCH_2CH_3); ^{31}P{^{1}H} NMR (101.26 MHz, $CDCl_3$, 25 °C, H_3PO_4 (85%)): δ = 42.3; $C_{35}H_{44}$BClN_7PRu (741.1): calcd C 56.72, H 5.98, N 13.23; found C 56.57, H 5.76, N 13.22.

($R_{Ru}R_C/S_{Ru}S_C$)-[Ru(tp)(κ^3(*P,C,C*)-η-(1,2)-4-(diphenylphosphino)-(*N,N*-diethyl)-1-phenyl-3-but-1-enamine)Cl] (**5c**): This complex was synthesized analogously to **5b** from **2** (100 mg, 0.158 mmol) and HC≡CPh (20 μL, 0.18 mmol). Yield: 95 mg (82%); ^{1}H NMR (250.13 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.15 (m,1H; tp), 7.69 (d, J = 2.4 Hz, 1H; tp), 7.58 (d, J = 2.4 Hz, 1H; tp), 7.38–7.21 (m, 8H), 7.09–7.03 (m, 3H), 6.93 (d, J = 1.9 Hz, 1H; tp), 6.86–6.70 (m, 3H), 6.52–6.42 (m, 3H), 6.00 (d, ^3J(H,H) = 12.7 Hz, 1H; PhC*H*=CH-), 5.95 (v t, J = 2.4 Hz, J = 2.0 Hz, 1H; tp), 5.91 (m, 1H; tp), 5.80 (v t, J = 2.4 Hz, 1H; tp), 4.75 (m, 1H; NCH−C*H*=CHPh), 4.01 (m, 1H; PCH_2CHN), 3.77 (m, 1H; PhCH=CH−C*H*N), 3.40 (m, 1H; PCH_2CHN), 3.07 (m, 2H; NCH_2CH_3), 2.88 (m, 2H; NCH_2CH_3), 1.17 (t, 6H; NCH_2CH_3); ^{13}C{^{1}H} NMR (62.86 MHz, $CDCl_3$, 25 °C, TMS): δ = 146.3 (tp), 145.5 (d, J = 1.9 Hz; tp), 145.3 (d, J = 2.4 Hz; tp), 144.3 (tp), 143.0 (Ph^{R1}), 136.7 (tp), 136.3 (tp), 136.1 (d, ^1J(C,P) = 39.1 Hz; Ph^1), 134.9 (tp), 134.5 (d, ^2J(C,P) = 8.1 Hz, 2C; Ph^{2,6}), 133.2 (d, ^2J(C,P) = 8.6 Hz, 2C; Ph$^{2',6'}$), 132.5 (d, ^1J(C,P) = 42.4 Hz; Ph$^{1'}$), 130.3 (d, ^4J(C,P) = 2.4 Hz; Ph^4), 130.0 (d, ^4J(C,P) = 1.9 Hz; Ph$^{4'}$), 128.8 (d, ^3J(C,P) = 8.6 Hz, 2C; Ph^{3,5}), 127.9 (2C; Ph^{R3,5}), 127.8 (d, ^3J(C,P) = 9.5 Hz, 2C; Ph$^{3',5'}$), 127.3 (2C; Ph^{R2,6}), 125.9 (Ph^{R4}), 106.2 (tp), 105.9 (tp), 105.7 (d, J = 1.9 Hz; tp), 91.2 (d, J = 2.2 Hz; −CH=CHPh), 90.6 (−CH=CHPh), 66.8 (d, ^2J(C,P) = 23.4 Hz; PCH_2CHN), 44.7 (2C; NCH_2CH_3), 43.7 (d, ^1J(C,P) = 42.9 Hz; PCH_2CHN), 13.1 (2C; NCH_2CH_3); ^{31}P{^{1}H} NMR (101.26 MHz, $CDCl_3$, 25 °C, H_3PO_4 (85%)): δ = 40.5; $C_{35}H_{40}$BClN_7PRu (737.1): calcd C 57.04, H 5.47, N 13.30; found C 57.32, H 5.69, N 13.14.

($R_{Ru}S_C/S_{Ru}R_C$)-[Ru(tp)(κ^3(*P,C,C*)-η-(1,2)-1-(2-butyl)-4-(diphenylphosphino)-(*N,N*-diethyl)-3-but-1-enamine)Cl] (**5d**): This complex was synthesized analogously to **5b** from **2** (100 mg, 0.158 mmol) and HC≡C*n*Bu (19 μL, 0.18 mmol). Yield: 77 mg (69%); ^{1}H NMR (250.13 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.17 (d, J = 2.4 Hz, 1H; tp), 7.65 (m,3H; tp), 7.41–7.06 (m, 11H; Ph, tp), 6.73 (d, J = 2.4 Hz, 1H; tp), 6.27 (m, 1H; tp), 6.05 (v t, J = 2.4 Hz, 1H; tp), 5.75 (v t, J = 2.4 Hz, 1H; tp), 4.85 (s, 1H; −C*n*Bu=CH_2), 4.50 (s, 1H; −C*n*Bu=CH_2), 3.83 (m, 1H; PCH_2CHN), 3.02 (m, 2H; NCH_2CH_3), 2.82 (m, 2H; PCH_2CHN), 2.46 (m, 2H; NCH_2CH_3), 2.45 (m, 1H; *n*Bu), 1.64–0.52 (m, 5H; *n*Bu), 1.15 (t, 6H; NCH_2CH_3), 0.52 (t, 3H; *n*Bu); ^{13}C{^{1}H} NMR (62.86 MHz, $CDCl_3$, 25 °C, TMS): δ = 146.9 (tp), 145.8 (d, J = 2.3 Hz; tp), 142.0 (d, J = 2.3 Hz; tp), 136.8 (tp), 135.4 (d, J = 2.3 Hz; tp), 134.9 (tp), 134.2 (d, ^2J(C,P) = 7.9 Hz, 4C; Ph$^{2,2',6,6'}$), 133.6 (d, ^1J(C,P) = 41.6 Hz; Ph^1), 130.71 (d, ^1J(C,P) = 39.3 Hz; Ph$^{1'}$), 130.6 (d, ^4J(C,P) = 2.3 Hz; Ph^4), 129.8 (d, ^4J(C,P) = 2.3 Hz; Ph$^{4'}$), 129.1 (d, ^3J(C,P) = 9.3 Hz, 2C; Ph^{3,5}), 128.0 (d, ^3J(C,P) = 9.7 Hz, 2C; Ph$^{3',5'}$), 106.3 (CHN−C*n*Bu=CH_2), 106.2 (d, J = 2.3 Hz; tp), 106.0 (tp), 105.1 (tp), 75.9 (CHN−C*n*Bu=CH_2), 65.16 (d, ^2J(C,P) = 13.9 Hz; PCH_2CHN), 43.7 (2C; NCH_2CH_3), 37.7 (*n*Bu), 31.6 (*n*Bu), 23.7 (*n*Bu), 21.1 (d, ^1J(C,P) = 26.8 Hz; PCH_2CHN), 14.9 (2C; NCH_2CH_3), 14.3 (*n*Bu); ^{31}P{^{1}H} NMR (101.26 MHz, $CDCl_3$, 25 °C, H_3PO_4 (85%)): δ = 41.7; $C_{33}H_{44}$BClN_7PRu (717.1): calcd C 55.28, H 6.18, N 13.67; found C 55.44, H 6.32, N 13.45.

($R_{Ru}R_C/S_{Ru}S_C$)-[Ru(tp)(κ^3(*P,C,C*)-η-(1,2)-4-(diphenylphosphino)-(*N,N*-di(methylethyl))-1-phenyl-3-but-1-enamine)Cl] (**6a**): A solution of [Ru(tp)(COD)Cl] (142 mg, 0.310 mmol) and $Ph_2PCH_2CH_2NiPr_2$ (97 mg, 0.310 mmol) in DMF (3 mL) was refluxed for 2 h. The solvent was removed under vacuum, and the residue was dissolved in acetone (5 mL). After addition of HC≡CPh (35 μL, 0.34 mmol), the solution was refluxed for 1 h. The volume of the solution was then reduced to about 0.5 mL. Addition of methanol gave analytically pure **6a**. Yield: 197 mg (83%); ^{1}H NMR (250.13 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.15 (m, 1H; tp), 7.68 (d, J = 2.5 Hz, 1H; tp), 7.59 (d, J = 2.1 Hz, 1H; tp), 7.37 (d, J = 2.1 Hz; 1H; tp) 7.30–7.24 (m, 7H; Ph, tp), 7.10–7.00 (m, 3H; Ph, tp), 6.90–6.67 (m, 4H; Ph), 6.50–6.45 (m, 3H; tp), 6.00 (d, ^3J(H,H) = 12.5 Hz, 1H; PhC*H*=CH-), 5.94 (v t, J = 2.5 Hz, 1H; tp), 5.91 (m, 1H; tp), 5.81 (v t, J = 2.1 Hz, 1H; tp), 5.02 (m, 1H; NCH−C*H*=CHPh), 4.43 (m, 1H; PCH_2CHN), 3.67 (m, 1H; PhCH=CH−C*H*N), 3.51 (m, 2H; $NCH(CH_3)_2$), 2.96 (m, 1H; PCH_2CHN), 1.23 (d, 6H; $NCH(CH_3)_2$), 1.15 (d, 6H; $NCH(CH_3)_2$); ^{13}C{^{1}H} NMR (62.86 MHz, $CDCl_3$, 25 °C, TMS): δ = 146.3 (d, J = 1.6 Hz; tp), 145.6 (d, J = 2.1 Hz; tp), 145.4 (d, J = 2.6 Hz; tp), 144.3 (tp), 136.7 (tp), 136.6 (d, ^1J(C,P) = 39.1 Hz; Ph^1), 136.3 (tp), 135.8 (tp), 134.9 (Ph^{R1}), 134.6 (d, ^2J(C,P) = 7.9 Hz, 2C; Ph^{2,6}), 133.5 (d, ^2J(C,P) = 8.3 Hz, 2C; Ph$^{2',6'}$), 132.8 (d, ^1J(C,P) = 42.1 Hz; Ph$^{1'}$), 130.2 (d, ^4J(C,P) = 2.4 Hz; Ph^4), 129.7 (d, ^4J(C,P) = 2.4 Hz; Ph$^{4'}$), 128.8 (d, ^3J(C,P) = 8.3 Hz, 2C; Ph^{3,5}), 127.8 (2C; Ph^{R3,5}), 127.7 (d, ^3J(C,P) = 8.6 Hz, 2C; Ph$^{3',5'}$), 126.9 (2C; Ph^{R2,6}), 125.5 (Ph^{R4}), 106.2 (tp), 105.9 (tp), 105.7 (d, J = 2.4 Hz; tp), 93.4 (d, J = 4.2 Hz; −CH=CHPh), 90.1 (−CH=CHPh), 60.4 (d, ^2J(C,P) = 25.4 Hz; PCH_2CHN), 45.6 (2C; $NCH(CH_3)_2$), 42.4 (d, ^1J(C,P) = 32.4 Hz; PCH_2CHN), 24.1 (2C; $NCH(CH_3)_2$), 23.3 (2C; $NCH(CH_3)_2$); ^{31}P{^{1}H} NMR (101.26 MHz, $CDCl_3$, 25 °C, H_3PO_4 (85%)): δ = 33.5; $C_{37}H_{44}$BClN_7PRu (765.1): calcd C 58.08, H 5.80, N 12.81; found C 58.19, H 5.67, N 12.13.

($R_{Ru}R_C/S_{Ru}S_C$)-[Ru(tp)(κ^3(*P,C,C*)-η-(1,2)-1-(1-cyclohexenyl)-4-(diphenylphosphino)-(*N,N*-di(methylethyl))-3-but-1-enamine)Cl] (**6b**): This complex was synthesized analogously to **6a** from [Ru(tp)(COD)Cl] (138 mg, 0.30 mmol), $Ph_2PCH_2CH_2NiPr_2$ (95 mg, 0.30 mmol), and HC≡CC_6H_9 (36 μL, 0.34 mmol). Yield: 178 mg (80%); ^{1}H NMR (250.13 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.16 (d, J = 2.3 Hz, 1H; tp), 7.71 (d, J = 2.3 Hz, 1H; tp), 7.62 (d, J = 2.7 Hz, 1H; tp), 7.59 (d, J = 2.3 Hz, 1H; tp) 7.35–7.17 (m, 6H; Ph), 7.02 (m, 2H; Ph), 6.95 (d, J = 1.9 Hz, 1H; tp), 6.91 (d, J = 2.3 Hz, 1H; tp), 6.38 (m, 2H; Ph), 6.23 (m, 1H; tp), 5.96 (m, 1H; cHex^2), 5.95 (v t, J = 2.3 Hz, 1H; tp), 5.71 (d, ^3J(H,H) = 12.7 Hz, 1H; −CH=C*H*c*H*ex), 5.70 (v t, J = 2.3 Hz, 1H; tp), 4.51 (dd, ^3J(H,H) = 12.7 Hz, ^3J(H,H) = 4.8 Hz, 1H; NCH−C*H*=CH*c*Hex), 4.81 (m, 1H; PCH_2CHN), 3.60–3.42 (m, 3H; PCH_2CHN, $NCH(CH_3)_2$), 2.92 (m, 1H; PCH_2CHN), 1.84 (m, 2H; *c*Hex), 1.22 (d, 6H; $NCH(CH_3)_2$), 1.18 (d, 6H; $NCH(CH_3)_2$), 1.01–0.71 (m, 5H; *c*Hex), −0.57 (m, 1H; *c*Hex); ^{13}C{^{1}H} NMR (62.86 MHz, $CDCl_3$, 25 °C,

0947-6539/98/0410-2048 $ 17.50+.50/0 *Chem. Eur. J.* **1998**, *4*, No. 10

TMS): $\delta = 146.5$ (d, $J = 1.4$ Hz; tp), 146.4 (d, $J = 1.4$ Hz; tp), 145.5 (d, $J = 1.8$ Hz; tp), 140.1 (*c*Hex[1]), 137.0 (d, $^3J(C,P) = 40.2$ Hz; Ph[1]), 136.5 (tp), 136.2 (tp), 135.1 (d, J = 1.8 Hz; tp), 134.5 (d, $^2J(C,P) = 8.3$ Hz, 2C; Ph[2,6]), 133.4 (d, $^2J(C,P) = 8.3$ Hz, 2C; Ph[2',6']), 133.3 (d, $^1J(C,P) = 41.2$ Hz; Ph[1']), 130.0 (d, $^4J(C,P) = 2.3$ Hz; Ph[4]), 129.6 (d, $^4J(C,P) = 2.8$ Hz; Ph[4']), 128.6 (d, $^3J(C,P) = 8.8$ Hz; Ph[3,5]), 128.3 (*c*Hex[2]), 127.6 (d, $^3J(C,P) = 9.2$ Hz; Ph[3',5']), 106.0 (2C; tp), 105.5 (d, $J = 2.3$ Hz; tp), 98.8 (−CH=*C*Hex), 85.8 (d, $J = 4.6$ Hz; −*C*H=CHex), 60.4 (d, $^2J(C,P) = 25.4$ Hz; PCH_2CHN), 45.5 (2C; $NCH(CH_3)_2$), 42.9 (d, $^1J(C,P) = 31.9$ Hz; PCH_2CHN), 26.9 (*c*Hex), 24.2 (2C; $NCH(CH_3)_2$), 23.3 (*c*Hex), 23.1 (2C; $NCH(CH_3)_2$), 23.0 (*c*Hex), 22.9 (*c*Hex); $^{31}P\{^1H\}$ NMR (101.26 MHz, $CDCl_3$, 25 °C, H_3PO_4 (85 %)): $\delta = 34.9$; $C_{37}H_{48}BClN_7PRu$ (769.1) calcd C 57.78, H 6.29, N 12.75; found C 58.01, H 6.15, N 12.31.

($R_{Ru}S_C/S_{Ru}R_C$)-[Ru(tp)(κ^3(*P*,*C*,*C*)-η-(1,2)-1-(2-butyl)-4-(diphenylphosphino)-(*N*,*N*-di(methylethyl))-3-but-1-en-amine)Cl] (**6c**): This complex was synthesized analogously to **6a** from [Ru(tp)(COD)Cl] (155 mg, 0.34 mmol), $Ph_2PCH_2CH_2NiPr_2$ (106 mg, 0.34 mmol), and HC≡C*n*Bu (39 μL, 0.38 mmol). Yield: 194 mg (77 %); ^1H NMR (250.13 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 8.18$ (d, $J =$ 2.2 Hz, 1H; tp), 7.68 (d, $J = 2.5$ Hz, 1H; tp), 7.66 (m, 2H; tp), 7.37–7.14 (m, 11H; Ph, tp), 6.82 (d, $J = 2.2$ Hz, 1H; tp), 6.27 (m, 1H; tp), 6.04 (vt, $J = 2.2$ Hz, $J = 2.5$ Hz, 1H; tp), 5.80 (vt, $J = 2.2$ Hz, $J = 2.5$ Hz, 1H; tp), 4.88 (s, 1H; −C*n*Bu=CH_2), 4.44 (s, 1H; −C*n*Bu=CH_2), 3.81 (m, 1H; PCH_2CHN), 3.71–3.30 (m, 2H; $NCH(CH_3)_2$), 2.97–2.62 (m, 2H; PCH_2CHN, *n*Bu), 1.86 (m, 1H; PCH_2CHN), 1.51–1.26 (m, 1H; *n*Bu), 1.21 (d, 6H; $NCH(CH_3)_2$), 1.11 (d, 6H; $NCH(CH_3)_2$), 0.96–0.53 (m, 3H; *n*Bu), 0.41 (t, 3H; *n*Bu), 0.40–0.26 (m, 1H; *n*Bu); $^{13}C\{^1H\}$ NMR (62.86 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 147.5$ (tp), 145.7 (d, $J = 1.8$ Hz; tp), 142.2 (d, $J = 2.3$ Hz; tp), 136.8 (tp), 135.4 (d, J = 3.2 Hz; tp), 135.0 (tp), 134.1 (d, $^2J(C,P) =$ 7.9 Hz, 4C; Ph[2,2',6,6']), 134.0 (d, $^1J(C,P) = 36.5$ Hz; Ph[1]), 130.7 (d, $^4J(C,P) = 1.8$ Hz; Ph[4]), 130.69 (d, $^1J(C,P) =$ 39.3 Hz; Ph[1']), 129.6 (d, $^4J(C,P) = 2.3$ Hz; Ph[4']), 128.9 (d, $^3J(C,P) = 9.2$ Hz, 2C; Ph[3,5]), 127.9 (d, $^3J(C,P) = 9.2$ Hz, 2C; Ph[3',5']), 109.8 (CHN−*C*Bu=CH_2), 106.2 (d, $J = 2.8$ Hz; tp), 106.0 (tp), 105.2 (tp), 74.6 (CHN−C*n*Bu=*C*H_2), 59.6 (d, $^2J(C,P) = 14.3$ Hz, PCH_2CHN), 44.9 (2C; $NCH(CH_3)_2$), 36.6 (*n*Bu), 35.0 (d, $^1J(C,P) = 40.0$ Hz; PCH_2CHN), 30.4 (*n*Bu), 23.8 (*n*Bu), 23.6 (2C; $NCH(CH_3)_2$), 23.0 (2C; $NCH(CH_3)_2$), 14.2 (*n*Bu); $^{31}P\{^1H\}$ NMR (101.26 MHz, $CDCl_3$, 25 °C, H_3PO_4 (85 %)): $\delta = 43.6$; $C_{35}H_{48}BClN_7PRu$ (745.1): calcd C 56.42, H 6.49, N 13.16; found C 56.64, H 6.22, N 13.05.

Crystallographic structure determinations: Crystallographic data, and the collection and refinement parameters are given in Table 3. Crystals of **5a** were obtained by diffusion of diethylether into CH_2Cl_2 solutions. Crystals of **6b** and **6c** were obtained by slow evaporation of a 1:1 mixture of CH_3NO_2/MeOH (v/v). For **5a** and **6b** X-ray data were collected on a Siemens Smart CCD area detector diffractometer (graphite monochromated $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, 0.3° ω-scan frames). For **6c** a Philips PW1100 four-circle diffractometer with graphite monochromated $Mo_{K\alpha}$ radiation and the $\theta - 2\theta$ scan technique was used. Corrections for Lorentz and polarization effects, for crystal decay, and in the case of **5a** and **6b** also for absorption, were applied. The structures were solved by direct or Patterson methods.[20] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were inserted into idealized positions and were refined riding on the atoms to which they were bonded. The structures were refined against F^2.[21] Compound **6c** is remarkable as it contains two independent complexes with very similar conformations that differ only in the orientation of the *n*-butyl side chain.

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-101 407. 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).

Table 3. Crystallographic data for complexes **5a**, **6b**, and **6c**.

	5a	**6b**	**6c**
formula	$C_{39}H_{44}BClFeN_7PRu$	$C_{37}H_{48}BClN_7PRu$	$C_{35}H_{48}BClN_7PRu$
M_f	844.96	769.12	745.10
crystal system	monoclinic	orthorhombic	triclinic
space group	*Pc* (no. 3)	$P2_12_12_1$ (no. 19)	$P\bar{1}$ (no. 2)
a [Å]	7.923(3)	7.886(2)	12.111(5)
b [Å]	11.020(4)	12.143(3)	15.816(5)
c [Å]	21.672(8)	38.874(12)	20.514(8)
α [°]	90	90	104.89(2)
β [°]	94.20(2)	90	102.70(2)
γ [°]	90	90	90.10(2)
V [Å^3]	1887(1)	3723(2)	3698(2)
Z	2	4	4
crystal dimensions [mm]	0.20 × 0.12 × 0.08	0.32 × 0.08 × 0.02	0.40 × 0.35 × 0.15
crystal color, habit	orange, prism	yellow, needle	yellow, plate
ρ_{calcd} [g cm^{-3}]	1.487	1.372	1.339
$\mu(Mo_{K\alpha})$ [mm^{-1}]	0.937	0.572	0.574
T [K]	298(2)	301(2)	293(2)
abs corr	empirical	empirical	none
F(000)	868	1600	1552
transmission factors (min/max)	0.93–0.82	0.83–0.84	–
θ_{max} [°]	27.0	25.0	23.0
index ranges	$-10 \le h \le 10$ $-14 \le k \le 14$ $-27 \le l \le 27$	$-9 \le h \le 9$ $-14 \le k \le 14$ $-17 \le l \le 46$	$-13 \le h \le 0$ $-17 \le k \le 17$ $-21 \le l \le 22$
reflections collected	23 895	18 702	9849
unique reflections	8200	6533	9849
no. of reflections [$F > 4\sigma(F)$]	6670	4183	7465
no. of parameters	465	434	830
*R*1 [$F > 4\sigma(F)$][a]	0.036	0.059	0.069
*R*1 (all data)[a]	0.055	0.120	0.095
*wR*2 (all data)[a]	0.063	0.089	0.154
diff Fourier peaks min/max [e Å^{-3}]	−0.30/0.28	−0.40/0.41	−0.67/1.04

[a] $R1 = \Sigma\,||F_o| - |F_c||/\Sigma\,|F_o|$, $wR2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma(w(F_o^2)^2)]^{1/2}$.

Acknowledgments: Financial support by the Jubiläumsfond der Österreichischen Nationalbank is gratefully acknowledged (Project No. 6474).

Received: April 16, 1998 [F1099]

[1] a) H. E. Selnau, J. S. Merola, *J. Am. Chem. Soc.* **1991**, *113*, 4008; b) R. Wiedmann, P. Steinert, M. Schäfer, H. Werner, *J. Am. Chem. Soc.* **1993**, *115*, 9864; c) H. Werner, R. Wiedmann, P. Steinert, J. Wolf, *Chem. Eur. J.* **1997**, *3*, 127; d) P.-C. Ting, Y.-C. Lin, G.-H. Lee, M.-C. Cheng, Y. Wang, *J. Am. Chem. Soc.* **1996**, *118*, 6433; e) C. Bianchini, P. Innocenti, M. Peruzzini, A. Romerosa, F. Zanobini, *Organometallics* **1996**, *15*, 272; f) S.-M. Yang, M. C.-W. Chan, K.-K. Cheung, C.-M. Che, S.-M. Peng, *Organometallics* **1997**, *16*, 2819; g) Y. Wang, M. G. Finn, *J. Am. Chem. Soc.* **1995**, *117*, 8045.

[2] a) R. Beckhaus, *Angew. Chem.* **1997**, *109*, 695; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 686; b) R. Beckhaus, J. Sang, T. Wagner, B. Ganter, *Organometallics* **1996**, *15*, 1176; c) H. G. Alt, H. E. Engelhardt, M. D. Rausch, L. B. Kool, *J. Organomet. Chem.* **1987**, *329*, 61.

[3] C. A. Merlic, M. E. Pauly, *J. Am. Chem. Soc.* **1996**, *118*, 11 319; H. M. Lee, J. Yao, G. Jia, *Organometallics* **1997**, *16*, 3927.

[4] B. M. Trost, J. A. Flygare, *J. Am. Chem. Soc.* **1992**, *114*, 5476.

[5] B. M. Trost, G. Dyker, R. Kulawiec, *J. Am. Chem. Soc.* **1990**, *112*, 7809.

[6] a) Y. Wakatsuki, H. Yamazaki, N. Kumegawa, T. Satoh, J. Y. Satoh, *J. Am. Chem. Soc.* **1991**, *113*, 9604; b) C. Slugovc, K. Mereiter, E. Zobetz, R. Schmid, K. Kirchner, *Organometallics* **1996**, *15*, 5275; c) C. Slugovc, D. Doberer, C. Gemel, R. Schmid, K. Kirchner, B. Winkler, F. Stelzer, *Monatsh. Chem.* **1998**, *129*, 221; d) C. S. Yi, N. Liu, *Organometallics* **1996**, *15*, 3968.

[7] M. I. Bruce, B. C. Hall, N. N. Zaitseva, B. W. Skelton, A. H. White, *J. Organomet. Chem.* **1996**, *522*, 307.

[8] C. Slugovc, P. Wiede, K. Mereiter, R. Schmid, K. Kirchner, *Organometallics* **1997**, *16*, 2768.
[9] a) H. Werner, M. Schulz, B. Windmüller, *Organometallics* **1995**, *14*, 3659; b) J.-Y. Shen, C. Slugovc, P. Wiede, K. Mereiter, R. Schmid, K. Kirchner, *Inorg. Chim. Acta* **1998**, *268*, 69.
[10] C. Gemel, G. Trimmel, C. Slugovc, S. Kremel, K. Mereiter, R. Schmid, K. Kirchner, *Organometallics* **1996**, *15*, 3998.
[11] a) N.-Y. Sun, S. J. Simpson, *J. Organomet. Chem.* **1992**, *434*, 341; b) N. W. Alcock, I. D. Burns, K. S. Claire, A. F. Hill, *Inorg. Chem.* **1992**, *31*, 2906; c) N. W. Alcock, A. F. Hill, R. B. Melling, *Organometallics* **1991**, *10*, 3898; d) A. F. Hill, *J. Organomet. Chem.* **1990**, *395*, C35; e) M. M. de V. Steyn, E. Singleton, S. Hietkamp, D. C. Liles, *J. Chem. Soc. Dalton Trans.* **1990**, 2991; f) A. M. McNair, D. C. Boyd, K. R. Mann, *Organometallics* **1986**, *5*, 303; g) G. Trimmel, C. Slugovc, P. Wiede, K. Mereiter, V. N. Sapunov, R. Schmid, K. Kirchner, *Inorg. Chem.* **1997**, *36*, 1076.
[12] a) M. I. Bruce, *Chem. Rev.* **1991**, *91*, 197; b) C. Slugovc, V. N. Sapunov, P. Wiede, K. Mereiter, R. Schmid, K. Kirchner, *J. Chem. Soc. Dalton Trans.* **1997**, 4209; c) I. de los Rios, M. J. Tenorio, M. C. Puerta, P. Valerga, *J. Am. Chem. Soc.* **1997**, *119*, 6529.
[13] C. Gemel, G. Kickelbick, R. Schmid, K. Kirchner, *J. Chem. Soc. Dalton Trans.* **1997**, 2119.
[14] a) C. S. Yi, N. Liu, A. L. Rheingold, L. M. Liable-Sands, I. A. Guzei, *Organometallics* **1997**, *16*, 3729; b) C. S. Yi, N. Liu, A. L. Rheingold, L. M. Liable-Sands, *Organometallics* **1997**, *16*, 3910.
[15] a) V. Cadierno, M. P. Gamasa, J. Gimeno, M. C. Lopez-Gonzazez, J. Borge, S. Garcia-Granda, *Organometallics* **1997**, *16*, 4453; b) P. Crochet, B. Demerseman, M. I. Vallejo, M. P. Gamasa, J. Gimeno, J. Borge, S. Garcia-Granda, *Organometallics* **1997**, *16*, 5406.
[16] R. D. Adams, A. Davison, J. P. Selegue, *J. Am. Chem. Soc.* **1979**, *101*, 7232.
[17] a) A. M. McNair, D. C. Boyd, K. R. Mann, *Organometallics* **1986**, *5*, 303; b) M. A. Halcrow, B. Chaudret, S. Trofimenko, *J. Chem. Soc. Chem. Commun.* **1993**, 465.
[18] D. D. Perrin, W. L. F. Armarego, *Purification of Laboratory Chemicals*, 3rd ed., Pergamon, New York, **1988**.
[19] a) R. T. Smith, M. C. Baird, *Inorg. Chim. Acta* **1982**, *62*, 135; b) G. K. Anderson, R. Kumar, *Inorg. Chem.* **1984**, *23*, 4064.
[20] G. M. Sheldrick, SHELXS-97: Program for the Solution of Crystal Structures, University of Göttingen (Germany) **1997**.
[21] G. M. Sheldrick, SHELXL-97: Program for Crystal Structure Refinement, University of Göttingen (Germany) **1997**.

  0947-6539/98/0410-2050 $ 17.50+.50/0