

Synthesis and Reactivity of RuCp*($\kappa^2(P,N)$ -Ph₂PCH₂CH₂NMe₂)Cl. Chelate-Assisted Methyl C–H Activation and Formation of the Novel Complex [RuCp*($\kappa^3(P,N,C)$ - Ph₂PCH₂CH₂N(CH₂)Me)Cl]BPh₄

Klaus Mauthner,[†] Christian Slugovc,[†] Kurt Mereiter,[‡] Roland Schmid,[†] and
Karl Kirchner^{*,†}

*Institute of Inorganic Chemistry and Institute of Mineralogy, Crystallography, and Structural
Chemistry, Technical University of Vienna, Getreidemarkt 9, A-1060 Vienna, Austria*

Received December 10, 1996[®]

RuCp*($\kappa^2(P,N)$ -Ph₂PCH₂CH₂NMe₂)Cl (**1**) is afforded in 87% yield by the reaction of RuCp*(η^4 -isoprene)Cl with 1 equiv of Ph₂PCH₂CH₂NMe₂ in CH₂Cl₂ as the solvent. The hemilabile nature of the Ph₂PCH₂CH₂NMe₂ ligand in **1** is revealed by the reaction with carbon monoxide, whereupon the neutral complex RuCp*($\kappa^1(P)$ -Ph₂PCH₂CH₂NMe₂)(Cl)(CO) (**2**) is obtained bearing the Ph₂PCH₂CH₂NMe₂ ligand in $\kappa^1(P)$ -coordinated fashion. Chloride abstraction from **1** with TiClF₃SO₃ led to RuCp*($\kappa^2(P,N)$ -Ph₂PCH₂CH₂NMe₂)(η^1 -OSO₂CF₃) (**3**), where CF₃SO₃[−] is directly bound to the metal center. Both **1** and **3** are convenient precursors for the synthesis of the cationic vinylidene complex [RuCp*($\kappa^2(P,N)$ -Ph₂PCH₂CH₂NMe₂)(=C=CHPh)]⁺ (**4**). When chloride abstraction from **1** was performed with NaBPh₄ in CH₂-Cl₂ instead of TiClF₃SO₃ in tetrahydrofuran as the solvent, the novel cationic Ru(IV) complex [RuCp*($\kappa^3(P,N,C)$ -Ph₂PCH₂CH₂N(CH₂)Me)Cl]⁺ (**5**) was formed. This reaction likely proceeds via the cationic 16e[−] complex [RuCp*($\kappa^2(P,N)$ -Ph₂PCH₂CH₂NMe₂)]⁺, which then readily undergoes methyl β -hydrogen elimination to give the cyclometalated cationic hydrido complex [RuCp*($\kappa^3(P,N,C)$ -Ph₂PCH₂CH₂N(CH₂)Me)H]⁺. This latter complex is trapped in CH₂Cl₂ or CD₂Cl₂ as the chloro complex **5**. Preliminary results on the catalytic activity of **1** are also presented. Thus, **1** is shown to catalyze the dimerization and cyclotrimerization of some terminal alkynes HC≡CR. Whereas with R = Ph, SiMe₃, and *n*-Bu, isomeric mixtures of head-to-head and head-to-tail coupling products are obtained, in the case of R = COOEt, cyclotrimerization takes place exclusively. X-ray structures of complexes **1**, **3**, **4**, and **5** are presented.

Introduction

Late transition metal complexes containing hemilabile phosphino ethers, esters, and amines have been the subject of recent investigations.¹ Under appropriate conditions, these soft/hard assemblies are able to coordinate reversibly to a metal center, thus providing or protecting temporarily a vacant coordination site. Along these lines, complexes with P–O and P–N ligands have been found to facilitate several stoichiometric and catalytic transformations of organic molecules such as

acetylene-to-vinylidene tautomerizations^{1c,e,f} or the conversion of a metal-(η^2 -CH₂=CH₂) to a metal-(H)(η^1 -CH=CH₂) unit.² Furthermore, complexes of these types appear to be effective catalyst precursors for olefin oligomerizations and polymerizations, carbonylations of methanol and methyl acetate, and hydrogenations.^{1d}

Therefore, we have been investigating some ruthenium complexes with hemilabile ligands in order to examine their efficiency in stoichiometrically and catalytically operating processes. Here we report on the synthesis and reactivity of the ruthenium half-sandwich complex RuCp*($\kappa^2(P,N)$ -Ph₂PCH₂CH₂NMe₂)Cl (**1**). The hemilabile nature of the Ph₂PCH₂CH₂NMe₂ ligand in **1** is demonstrated, and a preliminary account of the catalytic activity of **1** is given. In addition, we describe a novel chelate-assisted oxidative addition of a methyl C–H bond. X-ray structures of some of the new complexes are presented.

Experimental Section

General Information. All manipulations were performed under an inert atmosphere of purified argon by using Schlenk techniques. All chemicals were standard reagent grade and

* To whom correspondence should be addressed. E-mail: kkirch@fbch.tuwien.ac.at.

[†] Institute of Inorganic Chemistry.

[‡] Institute of Mineralogy, Crystallography, and Structural Chemistry.

[®] Abstract published in *Advance ACS Abstracts*, April 1, 1997.

(1) (a) Lindner, E.; Hausteine, M.; Mayer, H. A.; Gierling, K.; Fawzi, R.; Steinmann, M. *Organometallics* **1995**, *14*, 2246. (b) Lindner, E.; Hausteine, M.; Fawzi, R.; Steinmann, M.; Wegner, P. *Organometallics* **1994**, *13*, 5021. (c) Lindner, E.; Geprägs, M.; Gierling, K.; Fawzi, R.; Steinmann, M. *Inorg. Chem.* **1995**, *34*, 6106. (d) Bader, A.; Lindner, E. *Coord. Chem. Rev.* **1991**, *108*, 27 and references therein. (e) Werner, H.; Stark, A.; Schulz, M.; Wolf, J. *Organometallics* **1992**, *11*, 1126. (f) Martin, M.; Gevert, O.; Werner, H. *J. Chem. Soc., Dalton Trans.* **1996**, 2275. (g) Braunstein, P.; Chauvin, Y.; Nähring, J.; Dusauesoy, Y.; Bayeul, D.; Tiripicchio, A.; Ugozzoli, F. *J. Chem. Soc., Dalton Trans.* **1995**, 851. (h) Braunstein, P.; Matt, D.; Nobel, D.; Bouaoud, S.-E.; Carlier, B.; Grandjean, D.; Lemoine, P. *J. Chem. Soc., Dalton Trans.* **1986**, 415.

(2) Werner, H.; Schulz, M.; Windmüller, B. *Organometallics* **1995**, *14*, 3659.

used without further purification. The solvents were purified according to standard procedures. The deuterated solvents were purchased from Aldrich and dried over 4 Å molecular sieves. $\text{RuCp}^*(\eta^4\text{-isoprene})\text{Cl}$ and $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{NMe}_2(\text{pn})$ were prepared according to the literature.^{3,4} ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded on a Bruker AC-250 spectrometer operating at 250.13, 62.86, and 101.26 MHz, respectively, and were referenced to SiMe_4 and H_3PO_4 (85%). FT-IR spectra were recorded on a Mattson RS 2 spectrometer. Microanalyses were done by Microanalytical Laboratories, University of Vienna.

Synthesis. $\text{RuCp}^*(\kappa^2(\text{P},\text{N})\text{-Ph}_2\text{PCH}_2\text{CH}_2\text{NMe}_2)\text{Cl}$ (1). To a solution of $\text{RuCp}^*(\eta^4\text{-isoprene})\text{Cl}$ (2.00 g, 5.88 mmol) in CH_2Cl_2 (10 mL) was added $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{NMe}_2$ (1.51 g, 5.88 mmol) dissolved in 35 mL of CH_2Cl_2 slowly within a period of 4 h. After being stirred for an additional hour, the volume of the solution was reduced to about 5 mL, and petroleum ether (30 mL) was added. A precipitate was formed which was collected on a glass frit, washed with petroleum ether, and dried under vacuum. Yield: 2.71 g (87%). Anal. Calcd for $\text{C}_{26}\text{H}_{35}\text{ClINPRu}$: C, 59.02; H, 6.68. Found: C, 59.37; H, 6.73. ^1H NMR (δ , CD_2Cl_2 , 20 °C): 7.90–7.10 (m, 10H), 2.88 (s, 3H), 2.83 (s, 3H), 2.80–1.70 (m, 4H), 1.41 (d, 15H, $J_{\text{HP}} = 1.6$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (δ , CDCl_3 , 20 °C): 135.9 (d, $J_{\text{CP}} = 12.2$ Hz), 132.5 (d, $J_{\text{CP}} = 10.8$ Hz), 129.5 (d, $J_{\text{CP}} = 76.3$ Hz), 128.4, 128.2, 81.8 (d, $J_{\text{CP}} = 2.9$ Hz, C_5Me_5), 61.5 (d, $J_{\text{CP}} = 8.6$ Hz, NCH_2), 55.2 (NMe), 53.3 (NMe), 32.0 (d, $J_{\text{CP}} = 16.7$ Hz, PCH_2), 10.5 (C_5Me_5). $^{31}\text{P}\{^1\text{H}\}$ NMR (δ , CDCl_3 , 20 °C): 60.9. Single crystals were obtained by slow diffusion of diethyl ether into a solution of **1** in CH_2Cl_2 .

$\text{RuCp}^*(\kappa^1(\text{P})\text{-Ph}_2\text{PCH}_2\text{CH}_2\text{NMe}_2)(\text{Cl})(\text{CO})$ (2). A solution of **1** (0.20 g, 0.378 mmol) in CH_2Cl_2 (5 mL) was saturated with CO and stirred for 24 h. On addition of diethyl ether (ca. 50 mL), a yellow precipitate was formed, which was collected on a glass frit, washed with diethyl ether, and dried under vacuum. Yield: 0.16 g (78%). Anal. Calcd for $\text{C}_{27}\text{H}_{35}\text{ClINOPRu}$: C, 58.21; H, 6.33. Found: C, 58.62; H, 6.37. ^1H NMR (δ , CDCl_3 , 20 °C): 7.60–7.38 (m, 10H), 2.50–2.10 (m, 4H), 2.14 (s, 6H), 1.48 (s, 15H). $^{13}\text{C}\{^1\text{H}\}$ NMR (δ , CDCl_3 , 20 °C): 207.1 (d, $J_{\text{CP}} = 20.8$ Hz, CO), 132.9–128.6 (Ph), 96.6 (C_5Me_5), 54.9 (d, $J_{\text{CP}} = 4.2$ Hz, NCH_2), 45.5 (NMe), 29.2 (d, $J_{\text{CP}} = 28.2$ Hz, PCH_2), 9.9 (C_5Me_5). $^{31}\text{P}\{^1\text{H}\}$ NMR (δ , CDCl_3 , 20 °C): 38.9. IR (diffuse reflectance, cm^{-1}): 1912 (s, ν_{CO}).

$\text{RuCp}^*(\kappa^2(\text{P},\text{N})\text{-Ph}_2\text{PCH}_2\text{CH}_2\text{NMe}_2)(\eta^1\text{-OSO}_2\text{CF}_3)$ (3). A solution of **1** (0.25 g, 0.473 mmol) in tetrahydrofuran (5 mL) was treated with TiCF_3SO_3 (0.17 g, 0.481 mmol) and stirred for 30 min, whereupon the solution turned dark red and a precipitate of TiCl was formed. Insoluble materials were removed by filtration, and the solution was evaporated to dryness, affording an orange solid, which was collected on a glass frit, washed with diethyl ether, and dried under vacuum. Yield: 0.24 g (80%). Anal. Calcd for $\text{C}_{27}\text{H}_{35}\text{F}_3\text{NO}_3\text{PSRu}$: C, 50.46; H, 5.49. Found: C, 50.62; H, 5.51. ^1H NMR (δ , CD_3NO_2 , 20 °C): 7.60–7.50 (m, 10H), 2.95–2.50 (m, 4H), 2.43 (s, 6H), 1.57 (d, 15H, $J_{\text{HP}} = 1.8$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (δ , CD_3NO_2 , 20 °C): 134.0–130.1 (Ph), 90.2 (C_5Me_5), 53.8 (NMe), 30.7 (d, $J_{\text{CP}} = 23.4$ Hz, PCH_2), 10.2 (d, $J_{\text{CP}} = 1.7$ Hz, C_5Me_5). The resonance of the NCH_2 carbon atom is superimposed by the solvent resonances. $^{31}\text{P}\{^1\text{H}\}$ NMR (δ , CD_2Cl_2 , 20 °C): 61.1. Single crystals suitable for X-ray crystallography were obtained by slow diffusion of diethyl ether into a solution of **3** in tetrahydrofuran.

$[\text{RuCp}^*(\kappa^2(\text{P},\text{N})\text{-Ph}_2\text{PCH}_2\text{CH}_2\text{NMe}_2)(=\text{C}=\text{CHPh})](\text{CF}_3\text{SO}_3)$ (4). To a solution of **3** (0.20 g, 0.311 mmol) in tetrahydrofuran (5 mL) was added $\text{HC}\equiv\text{CPh}$ (51 μL , 0.464 mmol) by syringe, and the mixture was stirred for 15 min. On addition of diethyl ether, a red precipitate was formed, which was collected on a glass frit, washed with diethyl ether, and dried

under vacuum. Yield: 0.22 g (95%) as red crystals. Anal. Calcd for $\text{C}_{35}\text{H}_{41}\text{F}_3\text{NO}_3\text{PSRu}$: C, 56.44; H, 5.55. Found: C, 56.55; H, 5.56. ^1H NMR (δ , CD_2Cl_2 , 20 °C): 7.70–6.80 (m, 15H), 4.26 (d, 1H, $J_{\text{HP}} = 3.0$ Hz), 3.50–2.70 (m, 4H), 2.83 (s, 3H), 2.77 (s, 3H), 1.63 (d, 15H, $J_{\text{HP}} = 1.5$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (δ , CD_2Cl_2 , 20 °C): 347.8 (d, $J_{\text{CP}} = 13.8$ Hz, $=\text{C}=\text{CHPh}$), 134.0–125.5 (Ph), 117.4 ($=\text{C}=\text{CHPh}$), 101.6 (d, $J_{\text{CP}} = 1.3$ Hz, C_5Me_5), 66.0 (d, $J_{\text{CP}} = 3.1$ Hz, NCH_2), 62.4 (NMe), 55.6 (NMe), 30.4 (d, $J_{\text{CP}} = 26.2$ Hz, PCH_2), 10.3 (C_5Me_5). $^{31}\text{P}\{^1\text{H}\}$ NMR (δ , CDCl_3 , 20 °C): 65.4. Single crystals were obtained by slow diffusion of diethyl ether into a solution of **4** in CH_2Cl_2 .

$[\text{RuCp}^*(\kappa^3(\text{P},\text{N},\text{C})\text{-Ph}_2\text{PCH}_2\text{CH}_2\text{N}(\text{CH}_2)\text{Me})\text{Cl}]\text{BPh}_4$ (5). A solution of **1** (0.25 g, 0.472 mmol) in CH_2Cl_2 (5 mL) was treated with NaBPh_4 (0.178 g, 0.520 mmol), and the mixture was stirred for 24 h. Insoluble materials were removed by filtration. To the clear solution was added 25 mL of *n*-hexane, whereupon a yellow precipitate was formed, which was collected on a glass frit, washed with *n*-hexane, and dried under vacuum. Yield: 0.32 g (80%). Anal. Calcd for $\text{C}_{50}\text{H}_{54}\text{BCINPRu}$: C, 70.88; H, 6.42; N, 1.65; Cl, 4.18. Found: C, 71.09; H, 6.44; N, 1.70; Cl, 4.21. ^1H NMR (δ , CDCl_3 , 20 °C): 7.6–6.80 (m, 30H), 3.21 (d, 1H, $J_{\text{HP}} = 9.5$ Hz), 2.93 (s, 1H), 2.57 (s, 3H), 2.60–1.80 (m, 4H), 1.47 (d, 15H, $J_{\text{HP}} = 1.5$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (δ , CD_2Cl_2 , 20 °C): 163.8 (q, $J_{\text{BC}} = 49.3$ Hz), 135.6, 133.1–128.3, 125.8, 121.9, 102.8 (d, $J_{\text{CP}} = 2.3$ Hz, C_5Me_5), 54.9 (NCH₂), 52.3 (d, $J_{\text{CP}} = 5.5$ Hz, NCH_2Ru), 50.0 (NMe), 22.0 (d, $J_{\text{CP}} = 24.1$ Hz, PCH_2), 9.8 (C_5Me_5). $^{31}\text{P}\{^1\text{H}\}$ NMR (δ , CDCl_3 , 20 °C): 53.6. Single crystals were obtained by slow diffusion of diethyl ether into a solution of **5** in CH_2Cl_2 .

Reaction of **3 with CD_2Cl_2 .** A 5 mm NMR tube was charged with a solution of complex **3** (30 mg) in CD_2Cl_2 (0.5 mL). ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded, showing the slow formation of **5** (with CF_3SO_3^- as the counterion). The reaction was complete within about 5 h.

Catalytic Cyclotrimerization of $\text{HC}\equiv\text{CCOOEt}$ and Dimerization of $\text{HC}\equiv\text{CR}$ ($\text{R} = \text{Ph}$, SiMe_3 , and *n*-Bu). In a typical procedure, alkynes (0.3 M) were added to a suspension of **1** (2 mol %) in toluene (5 mL), and the sealed Schlenk tube was heated in an oil bath for 20 h ($\text{R} = \text{COOEt}$, Ph , SiMe_3 , *n*-Bu, CH_2OH) at 111 °C. After that time, the reaction mixture was evaporated to dryness under vacuum, and the coupling products were extracted with *n*-hexane. The solvent was again removed under vacuum, affording isomeric mixtures of coupling products. The product distribution was determined by ^1H NMR spectroscopy (see Supporting Information).

X-ray Structure Determination for **1, **3**, **4**, and **5**.** Crystal data and experimental details are given in Table 1. X-ray data for **1**, **3**, and **4** were collected on a Philips PW 1100 four-circle diffractometer using graphite-monochromated $\text{Mo K}\alpha$ ($\lambda = 0.71073$ Å) radiation and the θ – 2θ scan technique. For **5**, a Siemens Smart CCD area detector diffractometer, graphite-monochromated $\text{Mo K}\alpha$ radiation, a nominal crystal-to-detector distance of 3.85 cm, and 0.3° ω -scan frames were used. Corrections for Lorentz and polarization effects, for crystal decay, and for absorption (**5**) were applied. The structures were solved by Patterson or direct methods.⁵ All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included in idealized positions (**1**, **3**, **4**) or were refined without restraints (**5**).⁶ The structures were refined against F^2 .

Results and Discussion

Synthesis of $\text{RuCp}^*(\kappa^2(\text{P},\text{N})\text{-Ph}_2\text{PCH}_2\text{CH}_2\text{NMe}_2)\text{Cl}$ (1). $\text{RuCp}^*(\kappa^2(\text{P},\text{N})\text{-Ph}_2\text{PCH}_2\text{CH}_2\text{NMe}_2)\text{Cl}$ (**1**) is obtained in 87% yield upon the reaction of $\text{RuCp}^*(\eta^4\text{-isoprene})\text{Cl}$ with 1 equiv of $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{NMe}_2$ in

(3) Fagan, P. J.; Mahoney, W. S.; Calabrese, J. C.; Williams, I. D. *Organometallics* **1990**, 9, 1843.

(4) Smith, R. T.; Baird, M. C. *Inorg. Chim. Acta* **1982**, 62, 135.

(5) Sheldrick, G. M. *SHELXS86*, Program for the Solution of Crystal Structures, University of Göttingen, Germany, 1986.

(6) Sheldrick, G. M. *SHELXL93*, Program for Crystal Structure Refinement, University of Göttingen, Germany, 1993.

Table 1. Crystallographic Data for Complexes **1**, **3**, **4**, and **5**

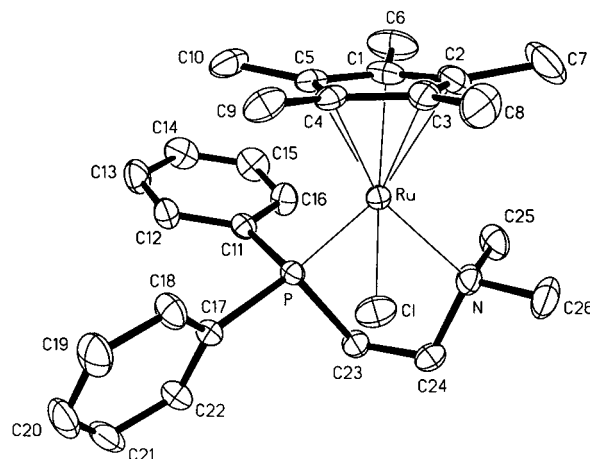
	1	3	4	5
formula	C ₂₆ H ₃₅ ClNPRu	C ₂₇ H ₃₅ F ₃ NO ₃ PRuS	C ₃₅ H ₄₁ F ₃ NO ₃ PRuS	C ₅₀ H ₅₄ BClNPRu
fw	529.04	642.66	744.79	847.24
cryst size, mm	0.55 × 0.50 × 0.48	0.25 × 0.35 × 0.60	0.10 × 0.10 × 0.20	0.50 × 0.30 × 0.26
space group	P2 ₁ 2 ₁ 2 ₁ (No. 19)	P1 (No. 2)	P2 ₁ /c (No. 14)	P2 ₁ (No. 4)
<i>a</i> , Å	19.152(3)	9.208(2)	8.720(4)	11.668(1)
<i>b</i> , Å	13.159(2)	10.659(3)	24.061(10)	13.450(1)
<i>c</i> , Å	10.391(2)	15.142(3)	17.483(8)	13.903(1)
α, deg		89.66(1)		
β, deg		85.19(1)	103.59(2)	90.56(1)
γ, deg		80.05(1)		
<i>V</i> , Å ³	2618.8(8)	1458.6(6)	3565(3)	2181.8(3)
<i>Z</i>	4	2	4	2
ρ _{calc} , g cm ⁻³	1.342	1.463	1.387	1.290
<i>T</i> , K	295	296	297	298
μ, mm ⁻¹ (Mo Kα)	0.774	0.711	0.593	0.492
absorption corr	none	none	none	empirical
transmiss factors, min/max				0.77/1.00
θ _{max} , deg	25	25	20	27
index ranges	0 ≤ <i>h</i> ≤ 22 0 ≤ <i>k</i> ≤ 15 0 ≤ <i>l</i> ≤ 12	0 ≤ <i>h</i> ≤ 10 -12 ≤ <i>k</i> ≤ 12 -17 ≤ <i>l</i> ≤ 18	0 ≤ <i>h</i> ≤ 8 0 ≤ <i>k</i> ≤ 23 -16 ≤ <i>l</i> ≤ 16	-14 ≤ <i>h</i> ≤ 14 -17 ≤ <i>k</i> ≤ 12 -17 ≤ <i>l</i> ≤ 17
no. of reflns measd	2627	5147	3300	14651
no. of unique reflns	2627	5147	3319	6935
no. of reflns <i>F</i> > 4σ(<i>F</i>)	2441	4521	1991	6373
no. of params	277	335	368	506
<i>R</i> (<i>F</i>) (<i>F</i> > 4σ(<i>F</i>)) ^a	0.0200	0.0274	0.0712	0.0248
<i>R</i> (<i>F</i>) (all data) ^a	0.0238	0.0352	0.1340	0.0297
<i>wR</i> (<i>F</i> ²) (all data) ^a	0.0468	0.0671	0.1906	0.0593
diff Four peaks, min/max, e Å ⁻³	-0.29/0.21	-0.33/0.44	-0.43/0.52	-0.36/0.37

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|, wR = [\sum (w(F_o^2 - F_c^2)^2) / \sum (w(F_o^2)^2)]^{1/2}.$$

CH₂Cl₂ as the solvent. **1** is a thermally robust orange solid which is stable to air in the solid state but decomposes in solution when exposed to air. Characterization of **1** was done by a combination of elemental analysis and ¹H, ¹³C{¹H}, and ³¹P{¹H} NMR spectroscopy.

The ¹H NMR spectrum of **1** in CD₂Cl₂ exhibits a doublet for the Cp* ring centered at 1.41 ppm (*J*_{HP} = 1.7 Hz). The NMe₂ group of the Ph₂PCH₂CH₂NMe₂ ligand displays two singlets at 2.88 (3H) and 2.83 ppm (3H), i.e., the methyl groups are diastereotopic. The ³¹P{¹H} NMR spectrum exhibits a singlet at 60.9 ppm. In the ¹³C{¹H} NMR spectrum of **1**, the resonances of the Ph₂PCH₂CH₂NMe₂ ligand give rise to characteristic doublets centered at 61.5 (*J*_{CP} = 8.6 Hz) and 32.0 ppm (*J*_{CP} = 16.7 Hz), assigned to the NCH₂ and PCH₂ methylene protons, respectively, and two singlets at 55.2 and 55.3 ppm, assigned to the methyl groups. The resonance of the ring carbon atoms of Cp* appears as a doublet centered at 81.8 ppm (*J*_{CP} = 2.9 Hz), indicative of the +II oxidation state of ruthenium. In addition, **1** was characterized by X-ray crystallography. A structural view of **1** is depicted in Figure 1. Selected bond distances and angles are given in Table 2. **1** adopts the usual "three-legged" piano stool structure. The Ru–P and Ru–N distances are 2.289(1) and 2.260(2) Å, respectively, with a P–Ru–N angle of 81.4(1)° (in RuCp*(Me₂NCH₂CH₂NMe₂)Cl, the Ru–N distances are 2.262(4) and 2.295(4) Å).⁷ The Ru–Cl distance of 2.441(1) Å is in the range observed for other half-sandwich ruthenium complexes in the same the formal oxidation state.⁸

Reaction of 1 with CO. The hemilabile nature of the Ph₂PCH₂CH₂NMe₂ ligand in **1** is revealed by the

**Figure 1.** Structural view of RuCp*(κ²(P,N)-Ph₂PCH₂CH₂-NMe₂)Cl (**1**).

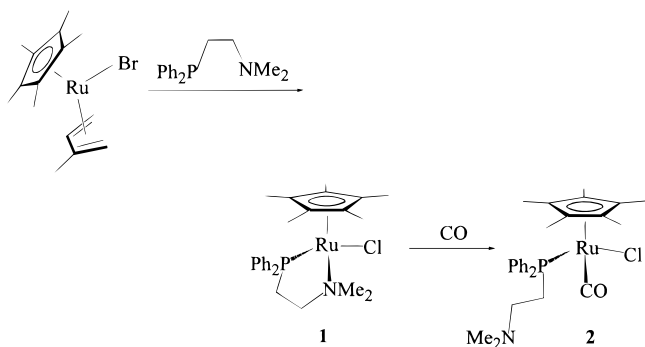
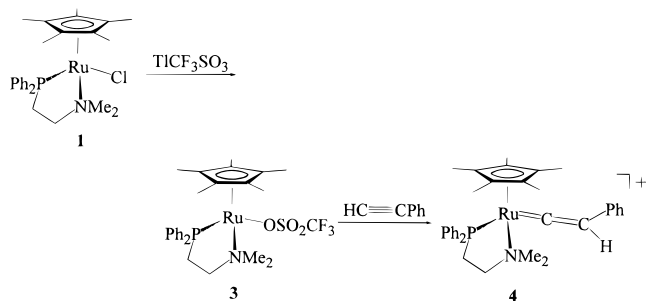
reaction with carbon monoxide. Thus, when **1** is stirred under a CO atmosphere for 24 h at ambient temperature, the Ru–N bond is cleaved to afford the neutral complex RuCp*(κ¹(P)-Ph₂PCH₂CH₂NMe₂)(Cl)(CO) (**2**) in 78% isolated yield (Scheme 1). Characterization of **2** was done by a combination of elemental analysis and IR, ¹H, ¹³C{¹H}, and ³¹P{¹H} NMR spectroscopy. In the IR spectrum, the CO stretching frequency is observed at 1912 cm⁻¹. In the ¹³C{¹H} NMR spectrum, the CO ligand exhibits a characteristic low-intensity doublet centered at 207.1 ppm (*J*_{CP} = 20.8 Hz). Due to the η¹-(P) coordination of the Ph₂PCH₂CH₂NMe₂ ligand, the ¹³C resonances of the NCH₂ and NMe₂ moieties are significantly shifted to higher field (ca. 7 ppm NCH₂, ca. 10 ppm NMe₂) compared to those of the η²-(P)-coordinated Ph₂PCH₂CH₂NMe₂ ligand in **1**. Moreover, the methyl groups are no longer inequivalent showing now a singlet resonance in both the ¹H and ¹³C{¹H} NMR spectra.

(7) Wang, M. H.; Englert, U.; Koelle, U. *J. Organomet. Chem.* **1993**, 453, 127.

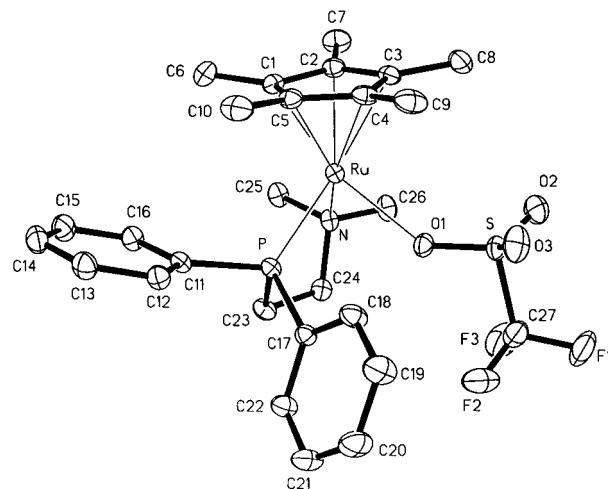
(8) de Rios, I. los; Tenorio, M. J.; Padilla, J.; Puerta, M. C.; Valerga, P. *J. Chem. Soc., Dalton Trans.* **1996**, 377.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Complexes 1, 3, 4, and 5

	1	3	4	5
Ru—C(1–5) _{av}	2.180(4)	2.182(3)	2.268(7)	2.250(3)
Ru—P	2.289(1)	2.319(1)	2.330(4)	2.350(1)
Ru—N	2.260(2)	2.256(2)	2.217(10)	2.122(2)
Ru—Cl	2.441(1)			2.373(1)
Ru—O(1)		2.277(2)		
Ru—C(27)			1.81(2)	
Ru—C(25)				2.085(2)
N—C(25)	1.465(5)	1.480(3)	1.51(2)	1.396(4)
N—C(26)	1.495(5)	1.481(3)	1.46(2)	1.480(4)
P—Ru—N	81.4(1)	81.2(1)	81.4(3)	82.6(1)
P—Ru—Cl	89.5(1)			87.7(1)
N—Ru—Cl	84.5(1)			84.2(1)
N—Ru—O(1)		79.4(1)		
P—Ru—O(1)		84.5(1)		
P—Ru—C(27)			90.7(4)	
P—Ru—C(25)				85.6(1)
Ru—C(27)—C(28)			173(1)	

Scheme 1**Scheme 2**

Reaction of 1 with TiCF_3SO_3 and $\text{HC}\equiv\text{CPh}$. Substitution of the Cl atom in **1** for the weakly nucleophilic CF_3SO_3^- anion was investigated with the intention of generating a reactive complex bearing a weakly coordinating ligand occupying a latent coordination site. In fact, chloride abstraction from **1** with TiCF_3SO_3 (1 equiv) affords, on workup, the expected neutral complex $\text{RuCp}^*(\kappa^2(\text{P},\text{N})\text{-Ph}_2\text{PCH}_2\text{CH}_2\text{NMe}_2)(\eta^1\text{-OSO}_2\text{CF}_3)$ (**3**), where CF_3SO_3^- is directly bound to the metal center (Scheme 2). This formulation corresponds with both the elemental analysis and the close similarities between the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of the 18e^- complex **1**. A structural view of **3** is depicted in Figure 2. Important bond distances and angles are shown in Table 2. The overall geometry of the complex is very similar to that observed for other three-legged piano stool complexes. The Cp^* ring is essentially planar, with C—C bond distances in the range 1.402(4)–1.453(4) Å, giving a mean value of 1.433 Å. The Ru—C distances range from 2.147(3) to 2.233(3) Å (mean 2.182 Å). The Ru—P and Ru—N distances are 2.319(1) and 2.256(2)

**Figure 2.** Structural view of $\text{RuCp}^*(\kappa^2(\text{P},\text{N})\text{-Ph}_2\text{PCH}_2\text{CH}_2\text{NMe}_2)(\eta^1\text{-OSO}_2\text{CF}_3)$ (**3**).

Å, respectively, with a P—Ru—N angle of 81.2(1)°. The CF_3SO_3^- anion is coordinated via the oxygen atom in η^1 -fashion, with the Ru—O(1) distance and the Ru—O(1)—S angle being 2.277(2) Å and 141.4(1)°, respectively. Note that only a few ruthenium complexes with the $\eta^1\text{-OSO}_2\text{CF}_3$ ligand are known and structurally characterized.^{9–12}

Both **1** and **3** turned out to be excellent precursors for the synthesis of cationic vinylidene complexes as depicted in Scheme 2. The reaction of **1** with $\text{HC}\equiv\text{CPh}$ in the presence of TiCF_3SO_3 in CH_2Cl_2 yields the cationic vinylidene complex $[\text{RuCp}^*(\kappa^2(\text{P},\text{N})\text{-Ph}_2\text{PCH}_2\text{CH}_2\text{NMe}_2)(=\text{C}=\text{CHPh})]^+$ (**4**) in high yield as an air-stable red solid. Similarly, treatment of **3** with 1 equiv of $\text{HC}\equiv\text{CPh}$ in CH_2Cl_2 affords **4** in essentially quantitative yield as monitored by ^1H NMR spectroscopy, attesting to the labile nature of the CF_3SO_3^- ligand. The molecular structure of **4** has been determined as shown in Figure 3, with selected bond distances and angles given in Table 2. The characteristic NMR spectroscopic features comprise, in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, a marked low-field resonance at 347.8 ppm (d, $J_{\text{CP}} = 13.8$ Hz) and a signal at 117.4 ppm assignable to the α - and β -carbons of the vinylidene moiety, respectively. The C_β -hydrogen atom gives rise to a doublet centered at 4.26 ppm ($J_{\text{HP}} = 3.0$ Hz). The ring carbon resonance of the Cp^* ring is low-field shifted, appearing at 102.6 ppm (the respective resonances in **1** and **3** appear at 81.8 and 90.2 ppm, respectively), indicative of a higher oxidation state of ruthenium. This is not surprising in view of the strong π -acidity of the vinylidene ligand. Finally, the resonances of the $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{NMe}_2$ ligand are in the expected ranges.

The overall three-legged piano stool structure of **4** is very similar to those of **1** and **3**. The Ru—C(27) bond distance is 1.81(2) Å, somewhat shorter than those in other cationic vinylideneruthenium complexes.¹³ For

(9) Gemel, C.; Kalt, D.; Mereiter, K.; Sapunov, V. N.; Schmid, R.; Kirchner, K. *Organometallics* **1997**, *16*, 427.

(10) Sutter, J.-P.; James, S. L.; Steenwinkel, P.; Karlen, T.; Grove, D. M.; Veldman, N.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *Organometallics* **1996**, *15*, 941.

(11) Kraakman, M. J. A.; Klerk-Engels, B. de; de Lange, P. P. M.; Vrieze, K.; Smeets, W. J. J.; Spek, A. L. *Organometallics* **1992**, *11*, 3774.

(12) Plosser, P. W.; Gallucci, J. C.; Wojcicki, A. *Inorg. Chem.* **1992**, *31*, 2376.

(13) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197.

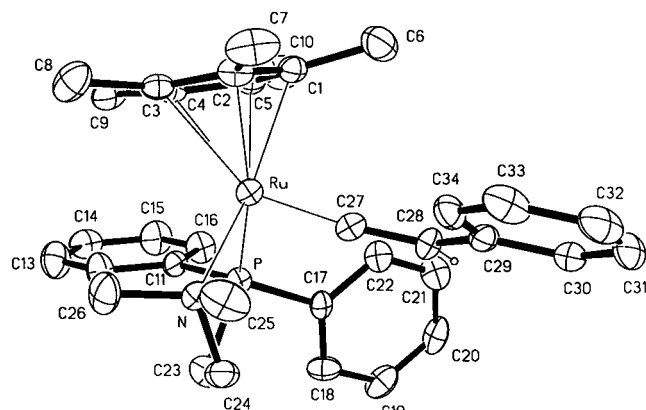
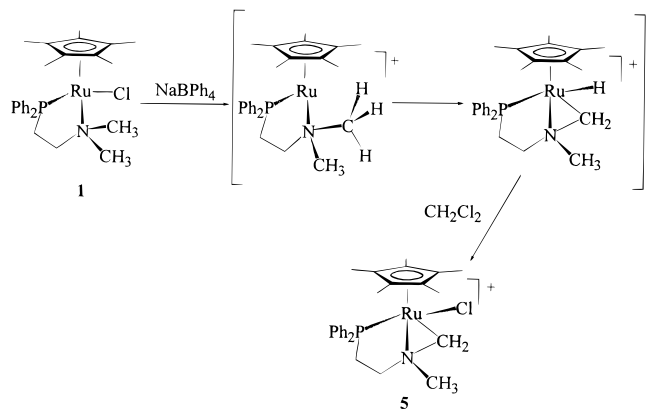


Figure 3. Structural view of $[\text{RuCp}^*(\kappa^2(\text{P},\text{N})\text{-Ph}_2\text{PCH}_2\text{CH}_2\text{NMe}_2)(=\text{C}=\text{CHPh})]\text{CF}_3\text{SO}_3$ (**4**) (CF_3SO_3^- omitted for clarity).

Scheme 3



instance, in $[\text{RuCp}(\text{PMe}_3)_2(=\text{C}=\text{CHMe})]^+$ and $[\text{RuCp}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)(=\text{C}=\text{CPh}(\text{C}_7\text{H}_7))]^+$, the Ru–C distances are 1.845(7) and 1.848(9) Å, respectively.^{14,15} The Ru=C=C group is nearly linear, the angle Ru–C(27)–C(28) being 173(1)°.

Reaction of 1 with NaBPh₄ and CH₂Cl₂. Next we performed chloride abstraction from **1** with NaBPh₄ instead of TlCF₃SO₃ in CH₂Cl₂ as the solvent. Instead of the expected cationic complex $[\text{RuCp}^*(\kappa^2(\text{P},\text{N})\text{-Ph}_2\text{PCH}_2\text{CH}_2\text{NMe}_2)]^+$, however, the novel cationic Ru(IV) complex $[\text{RuCp}^*(\kappa^3(\text{P},\text{N},\text{C})\text{-Ph}_2\text{PCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{Me})\text{Cl})]^+$ (**5**) was formed in 80% yield (Scheme 3). This complex is air stable both in solution and in the solid state. Characterization was done by elemental analysis and ¹H, ¹³C{¹H}, and ³¹P{¹H} NMR spectroscopy.

Accordingly, the ¹H and ¹³C{¹H} NMR spectra of **5** are quite different from those of complexes **1–4** and are inconsistent with the presence of a bidentate P,N-coordinated Ph₂PCH₂CH₂NMe₂ ligand as follows. There is a substantial down-field shift for the PCH₂ carbon atom from about 31 ppm in complexes **1–4** to 22.0 ppm (*d*, *J*_{CP} = 24.1 Hz) in **5**. Furthermore, the ¹³C{¹H} NMR spectrum of **5** exhibits two singlets at 54.9 and 50.0 ppm and a doublet centered at 52.3 ppm (*J*_{CP} = 5.5 Hz), assignable to NCH₂CH₂P, NMe, and RuCH₂N carbon atoms, respectively. The ¹H NMR spectrum of **5** exhibits a doublet resonance centered at 3.21 ppm (1H, *J*_{HP}

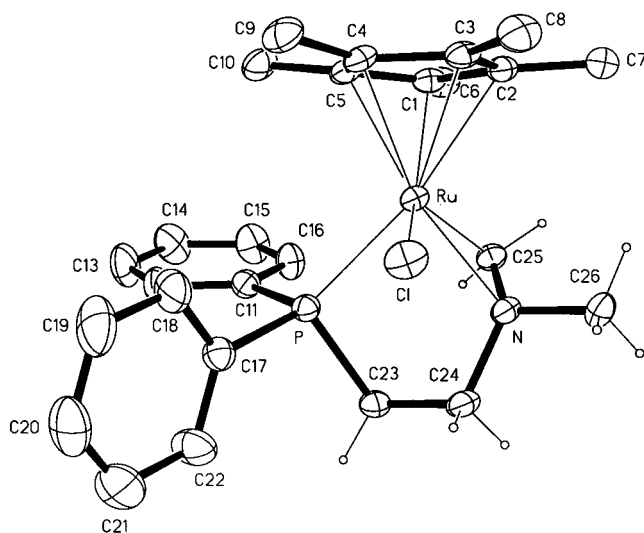
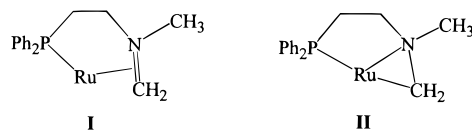


Figure 4. Structural view of $[\text{RuCp}^*(\kappa^3(\text{P},\text{N},\text{C})\text{-Ph}_2\text{PCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{Me})\text{Cl})]\text{BPh}_4$ (**5**) (BPh_4^- omitted for clarity).

= 9.5 Hz) and two singlet resonances at 2.93 (1H) and 2.57 ppm (3H), assignable to the geminal methylene protons of a RuCH₂N unit and a NMe group. Surprisingly, no coupling is observed between the two geminal hydrogen atoms of the metal-coordinated CH₂ moiety; moreover, only one of the two CH₂ protons is coupled to the phosphorus atom of the chelating ligand. The ring carbon resonance of the Cp* ring is low-field shifted with respect to **1**, appearing at 102.8 ppm (*d*, *J*_{CP} = 2.3 Hz), consistent with a higher oxidation state of the metal center.

The structural identity of **5** was unequivocally proven by X-ray crystallography. The result is depicted in Figure 4 with important bond distances and angles given in Table 2. Accordingly, **5** adopts a four-legged piano stool conformation, with Cl and the novel tridentate ligand Ph₂PCH₂CH₂N(Me)CH₂ as the legs. The Ph₂PCH₂CH₂N(Me)CH₂ moiety is coordinated via P, N, and C. The Ru–P, Ru–N, and Ru–C(25) distances are 2.350(1), 2.122(2), and 2.085(2) Å, respectively. The bond distances at the nitrogen atom are 1.396(4) Å to C(25), 1.495(4) Å to C(24), and 1.480(4) Å to C(26). This is consistent with a double bond between N and C(25). However, both the nitrogen and the C(25) atoms show distinctly pyramidal environments with respect to their bonding partners (Figure 4). N deviates by 0.277(3) Å from the plane C(24)–C(25)–C(26), and C(25) deviates by 0.249(14) Å from the plane H(25a)–H(25b)–N (hydrogen atoms refined in positional parameters), both pointing toward Ru. Thus, hybridization of N and C(25) is between sp² and sp³, and the bonding situation of the Ph₂PCH₂CH₂N(Me)CH₂ ligand might be best described as intermediate between the two limiting forms **I** and **II**.



A possible mechanism to account for the formation of **5** is suggested in Scheme 3. **5** is formed after halide abstraction in **1** with NaBPh₄ in either CH₂Cl₂ or CD₂Cl₂ as the solvents. Likewise, **3** is quantitatively

(14) Bruce, M. I.; Wong, F. S.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1982**, 2203.

(15) Bruce, M. I.; Humphrey, M. G.; Koutsantonis, G. A.; Liddell, M. J. *J. Organomet. Chem.* **1987**, 326, 247.

converted in CD_2Cl_2 to **5**, as monitored by ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy. In both cases, we assume that the cationic $16e^-$ complex $[\text{RuCp}^*(\kappa^2(\text{P},\text{N})\text{-Ph}_2\text{PCH}_2\text{CH}_2\text{NMe}_2)]^+$ is intermediately formed. Methyl β -hydrogen elimination results in the formation of the cyclometalated cationic hydrido complex $[\text{RuCp}^*(\kappa^3(\text{P},\text{N},\text{C})\text{-Ph}_2\text{PCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{Me})\text{H})]^+$, which, although not detected by NMR spectroscopy, is trapped in CH_2Cl_2 or CD_2Cl_2 as the chloro complex **5**. It is worth noting that activation of C–H bonds adjacent to nitrogen is rare, in contrast to those adjacent to phosphorus.¹⁶ Known examples include only the activation of a NPr_2 ligand in a dinuclear ruthenium complex¹⁷ and the activation of tertiary amines by osmium cluster complexes.¹⁸ It should further be mentioned that similar intramolecular $\beta\text{-C-H}$ eliminations are believed to be involved in the chemical vapor deposition of amino and amido transition metal complexes and in hydrodenitrogenation chemistry.¹⁹

Catalytic Cyclotrimerization and Dimerization of Terminal Acetylenes. Reaction of **1** with an excess of $\text{HC}\equiv\text{CR}$ ($\text{R} = \text{Ph}$, SiMe_3 , and $n\text{-Bu}$) in toluene at reflux for 20 h results typically in isomeric mixtures of head-to-head- and head-to-tail-coupled dimers in low to moderate yields (Table 3). Both conversion and selectivity vary drastically with the substituent. In the case of $\text{R} = \text{COOEt}$, however, exclusively cyclotrimerization was observed, affording a 1:1 mixture of 1,2,4- and 1,3,5-benzenetricarboxylic acid esters in 96% yield (Table 3). For the mechanism of this process, it seems likely that the catalytic dimerization of terminal alkynes is initiated by a neutral vinylidene complex which is intermediately formed. Subsequent HCl elimination affords a $16e^-$ alkynyl catalyst. Such an elimination might be facilitated due to the basic NMe_2 group. In fact, it has been shown recently that neutral vinylidene complexes undergo 1,3-HCl eliminations on treatment with base

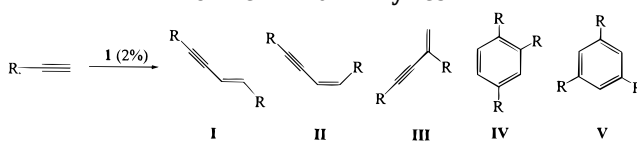
(16) Crabtree, R. *Angew. Chem.* **1993**, 105, 828. (b) Crabtree, R. *Chem. Rev.* **1985**, 85, 245.

(17) Kuhlman, R.; Folting, K.; Caulton, K. G. *Organometallics* **1995**, 14, 3188.

(18) Adams, R. D.; Tanner, J. T. *Appl. Organomet. Chem.* **1992**, 6, 449.

(19) (a) Hoffman, D. M. *Polyhedron* **1994**, 13, 1169. (b) Fix, R. M.; Gordon, R. G.; Hoffman, D. M. *Chem. Mater.* **1990**, 2, 235.

Table 3. Conversion and Product Distribution of the Catalytic Dimerization and Cyclotrimerization of Terminal Alkynes^a



R	I	II	III	IV	V	conversion
Ph	57	43				63
SiMe_3		83	17			20
$n\text{-Bu}$	40	18	42			11
COOEt				50	50	96

^a Reactions were performed in boiling toluene for 20 h. Yields are for isolated products. Product distribution has been determined by ^1H NMR spectroscopy. All values are in percent.

to give $16e^-$ alkynyl intermediates, which are trapped in the presence of potential ligands such as CO, pyridine, or CH_3CN .²⁰ Such intermediates have also been suggested in the coupling reaction of terminal acetylenes catalyzed by $\text{RuTp}(\text{PPh}_3)_2\text{Cl}$ ($\text{Tp} = \text{trispyrazolylborate}$) and $\text{RuCp}^*(\text{PR}_3)_3$ ($\text{R} = \text{Ph}$, Me , and Cy).^{21,22} In the case of the cyclotrimerization, the reaction presumably proceeds via a different pathway, likely involving metallocyclic intermediates. At present, however, the mechanism of both reactions can only be speculated upon. Further work is in progress and will be reported in a forthcoming paper.

Acknowledgment. Financial support by the “Jubiläumsfond der Österreichischen Nationalbank” is gratefully acknowledged (Project 5305).

Supporting Information Available: Listings of atomic coordinates, anisotropic temperature factors, complete bond lengths and angles, and least-squares planes for complexes **1**, **3**, **4**, and **5** (42 pages). Ordering information is given on any current masthead page.

OM9610408

(20) Bruce, M. I.; Hall, B. C.; Zaitseva, N. N.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1996**, 522, 307.

(21) Slugovc, C.; Mereiter, K.; Zöbets, E.; Schmid, R.; Kirchner, K. *Organometallics* **1996**, 15, 5275.

(22) Yi, C. S.; Liu, N. *Organometallics* **1996**, 15, 3968.