Synthesis and Reactivity of RuCp*(κ^2(*P*,*N*)-$Ph_2PCH_2CH_2NMe_2$)Cl. Chelate-Assisted Methyl C−H Activation and Formation of the Novel Complex [RuCp*(κ^3(*P*,*N*,*C*)-$Ph_2PCH_2CH_2N(CH_2)Me$)Cl]BPh_4

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RuCp*(κ^2(*P*,*N*)-$Ph_2PCH_2CH_2NMe_2$)Cl (**1**) is afforded in 87% yield by the reaction of RuCp*(η^4-isoprene)Cl with 1 equiv of $Ph_2PCH_2CH_2NMe_2$ in CH_2Cl_2 as the solvent. The hemilabile nature of the $Ph_2PCH_2CH_2NMe_2$ ligand in **1** is revealed by the reaction with carbon monoxide, whereupon the neutral complex RuCp*(κ^1(*P*)-$Ph_2PCH_2CH_2NMe_2$)(Cl)(CO) (**2**) is obtained bearing the $Ph_2PCH_2CH_2NMe_2$ ligand in κ^1(P)-coordinated fashion. Chloride abstraction from **1** with $TlCF_3SO_3$ led to RuCp*(κ^2(*P*,*N*)-$Ph_2PCH_2CH_2NMe_2$)(η^1-OSO_2CF_3) (**3**), where $CF_3SO_3^-$ is directly bound to the metal center. Both **1** and **3** are convenient precursors for the synthesis of the cationic vinylidene complex [RuCp*(κ^2(*P*,*N*)-$Ph_2PCH_2CH_2NMe_2$)(=C=CHPh)]$^+$ (**4**). When chloride abstraction from **1** was performed with $NaBPh_4$ in CH_2Cl_2 instead of $TlCF_3SO_3$ in tetrahydrofuran as the solvent, the novel cationic Ru(IV) complex [RuCp*(κ^3(*P*,*N*,*C*)-$Ph_2PCH_2CH_2N(CH_2)Me$)Cl]$^+$ (**5**) was formed. This reaction likely proceeds via the cationic 16e$^-$ complex [RuCp*(κ^2(*P*,*N*)-$Ph_2PCH_2CH_2NMe_2$)]$^+$, which then readily undergoes methyl β-hydrogen elimination to give the cyclometalated cationic hydrido complex [RuCp*(κ^3(*P*,*N*,*C*)-$Ph_2PCH_2CH_2N(CH_2)Me$)H]$^+$. This latter complex is trapped in CH_2Cl_2 or CD_2Cl_2 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, $SiMe_3$, 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-CH_2=CH_2) to a metal−(H)(η^1-CH=CH_2) 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*(κ^2(*P*,*N*)-$Ph_2PCH_2CH_2NMe_2$)Cl (**1**). The hemilabile nature of the $Ph_2PCH_2CH_2NMe_2$ 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

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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. RuCp*(η^4-isoprene)Cl and $Ph_2PCH_2CH_2NMe_2$(pn) were prepared according to the literature.[3,4] ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}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. RuCp*(κ²(*P,N*)-Ph₂PCH₂CH₂NMe₂)Cl (1). To a solution of RuCp*(η^4-isoprene)Cl (2.00 g, 5.88 mmol) in CH_2Cl_2 (10 mL) was added $Ph_2PCH_2CH_2NMe_2$ (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 $C_{26}H_{35}ClNPRu$: C, 59.02; H, 6.68. Found: C, 59.37; H, 6.73. ^{1}H 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_{HP} = 1.6 Hz). ^{13}C{^{1}H} NMR (δ, $CDCl_3$, 20 °C): 135.9 (d, J_{CP} = 12.2 Hz), 132.5 (d, J_{CP} = 10.8 Hz), 129.5 (d, J_{CP} = 76.3 Hz), 128.4, 128.2, 81.8 (d, J_{CP} = 2.9 Hz, C_5Me_5), 61.5 (d, J_{CP} = 8.6 Hz, N*C*H₂), 55.2 (N*Me*), 53.3 (N*Me*), 32.0 (d, J_{CP} = 16.7 Hz, P*C*H₂), 10.5 (C_5*Me*₅). ^{31}P{^{1}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.

RuCp*(κ¹(*P*)-Ph₂PCH₂CH₂NMe₂)(Cl)(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 $C_{27}H_{35}ClNOPRu$: C, 58.21; H, 6.33. Found: C, 58.62; H, 6.37. ^{1}H 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}C{^{1}H} NMR (δ, $CDCl_3$, 20 °C): 207.1 (d, J_{CP} = 20.8 Hz, CO), 132.9−128.6 (Ph), 96.6 (C_5Me_5), 54.9 (d, J_{CP} = 4.2 Hz, N*C*H₂), 45.5 (N*Me*₂), 29.2 (d, J_{CP} = 28.2 Hz, P*C*H₂), 9.9 (C_5*Me*₅). ^{31}P{^{1}H} NMR (δ, $CDCl_3$, 20 °C): 38.9. IR (diffuse reflectance, cm^{-1}): 1912 (s, ν_{CO}).

RuCp*(κ²(*P,N*)-Ph₂PCH₂CH₂NMe₂)(η¹-OSO₂CF₃) (3). A solution of **1** (0.25 g, 0.473 mmol) in tetrahydrofuran (5 mL) was treated with $TlCF_3SO_3$ (0.17 g, 0.481 mmol) and stirred for 30 min, whereupon the solution turned dark red and a precipitate of TlCl 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 $C_{27}H_{35}F_3NO_3PSRu$: C, 50.46; H, 5.49. Found: C, 50.62; H, 5.51. ^{1}H 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_{HP} = 1.8 Hz). ^{13}C{^{1}H} NMR (δ, CD_3NO_2, 20 °C): 134.0−130.1 (Ph), 90.2 (C_5Me_5), 53.8 (N*Me*), 30.7 (d, J_{CP} = 23.4 Hz, P*C*H₂), 10.2 (d, J_{CP} = 1.7 Hz, C_5*Me*₅). The resonance of the N*C*H₂ carbon atom is superimposed by the solvent resonances. ^{31}P{^{1}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.

[RuCp*(κ²(*P,N*)-Ph₂PCH₂CH₂NMe₂)(=C=CHPh)](CF₃SO₃) (4). To a solution of **3** (0.20 g, 0.311 mmol) in tetrahydrofuran (5 mL) was added HC≡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 $C_{35}H_{41}F_3NO_3PSRu$: C, 56.44; H, 5.55. Found: C, 56.55; H, 5.56. ^{1}H NMR (δ, CD_2Cl_2, 20 °C): 7.70−6.80 (m, 15H), 4.26 (d, 1H, J_{HP} = 3.0 Hz), 3.50−2.70 (m, 4H), 2.83 (s, 3H), 2.77 (s, 3H), 1.63 (d, 15H, J_{HP} = 1.5 Hz). ^{13}C{^{1}H} NMR (δ, CD_2Cl_2, 20 °C): 347.8 (d, J_{CP} = 13.8 Hz, =*C*=CHPh), 134.0−125.5 (Ph), 117.4 (=C=*C*HPh), 101.6 (d, J_{CP} = 1.3 Hz, C_5Me_5), 66.0 (d, J_{CP} = 3.1 Hz, N*C*H₂), 62.4 (N*Me*), 55.6 (N*Me*), 30.4 (d, J_{CP} = 26.2 Hz, P*C*H₂), 10.3 (C_5*Me*₅). ^{31}P{^{1}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.

[RuCp*(κ³(*P,N,C*)-Ph₂PCH₂CH₂N(CH₂)Me)Cl]BPh₄ (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 $C_{50}H_{54}BClNPRu$: 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. ^{1}H NMR (δ, $CDCl_3$, 20 °C): 7.6−6.80 (m, 30H), 3.21 (d, 1H, J_{HP} = 9.5 Hz), 2.93 (s, 1H), 2.57 (s, 3H), 2.60−1.80 (m, 4H), 1.47 (d, 15H, J_{HP} = 1.5 Hz). ^{13}C{^{1}H} NMR (δ, CD_2Cl_2, 20 °C): 163.8 (q, J_{BC} = 49.3 Hz), 135.6, 133.1−128.3, 125.8, 121.9, 102.8 (d, J_{CP} = 2.3 Hz, C_5Me_5), 54.9 (N*C*H₂), 52.3 (d, J_{CP} = 5.5 Hz, N*C*H₂Ru), 50.0 (N*Me*), 22.0 (d, J_{CP} = 24.1 Hz, P*C*H₂), 9.8 (C_5*Me*₅). ^{31}P{^{1}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). ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}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 HC≡CCOOEt and Dimerization of HC≡CR (R = Ph, SiMe₃, 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 (R = 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 ^{1}H 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 Mo Kα (λ = 0.710 73 Å) radiation and the $\theta-2\theta$ scan technique. For **5**, a Siemens Smart CCD area detector diffractometer, graphite-monochromated Mo Kα 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 RuCp*(κ²(*P,N*)-Ph₂PCH₂CH₂NMe₂)Cl (1). RuCp*(κ²(*P,N*)-$Ph_2PCH_2CH_2NMe_2$)Cl (**1**) is obtained in 87% yield upon the reaction of RuCp*(η^4-isoprene)Cl with 1 equiv of $Ph_2PCH_2CH_2NMe_2$ in

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

	1	3	4	5
formula	$C_{26}H_{35}ClNPRu$	$C_{27}H_{35}F_3NO_3PRuS$	$C_{35}H_{41}F_3NO_3PRuS$	$C_{50}H_{54}BClNPRu$
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	$P2_12_12_1$ (No. 19)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P2_1$ (No. 4)
a, Å	19.152(3)	9.208(2)	8.720(4)	11.668(1)
b, Å	13.159(2)	10.659(3)	24.061(10)	13.450(1)
c, 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)		
V, Å^3	2618.8(8)	1458.6(6)	3565(3)	2181.8(3)
Z	4	2	4	2
ρ_{calc}, g cm^{-3}	1.342	1.463	1.387	1.290
T, 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	$0 \le h \le 22$	$0 \le h \le 10$	$0 \le h \le 8$	$-14 \le h \le 14$
	$0 \le k \le 15$	$-12 \le k \le 12$	$0 \le k \le 23$	$-17 \le k \le 12$
	$0 \le l \le 12$	$-17 \le l \le 18$	$-16 \le l \le 16$	$-17 \le l \le 17$
no. of reflns measd	2627	5147	3300	14651
no. of unique reflns	2627	5147	3319	6935
no. of reflns $F > 4\sigma(F)$	2441	4521	1991	6373
no. of params	277	335	368	506
$R(F)$ ($F > 4\sigma(F)$)[a]	0.0200	0.0274	0.0712	0.0248
$R(F)$ (all data)[a]	0.0238	0.0352	0.1340	0.0297
$wR(F^2)$ (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] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma(w(F_o^2)^2)]^{1/2}$.

CH_2Cl_2 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 ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopy.

The ^{1}H NMR spectrum of **1** in CD_2Cl_2 exhibits a doublet for the Cp* ring centered at 1.41 ppm (J_{HP} = 1.7 Hz). The NMe_2 group of the $Ph_2PCH_2CH_2NMe_2$ ligand displays two singlets at 2.88 (3H) and 2.83 ppm (3H), i.e., the methyl groups are diastereotopic. The ^{31}P-{^{1}H} NMR spectrum exhibits a singlet at 60.9 ppm. In the ^{13}C{^{1}H} NMR spectrum of **1**, the resonances of the $Ph_2PCH_2CH_2NMe_2$ 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 NCH_2 and PCH_2 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 $RuCp^*(Me_2NCH_2CH_2NMe_2)Cl$, 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 $Ph_2PCH_2CH_2NMe_2$ ligand in **1** is revealed by the 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 $RuCp^*(\kappa^1(P)\text{-}Ph_2PCH_2CH_2NMe_2)(Cl)(CO)$ (**2**) in 78% isolated yield (Scheme 1). Characterization of **2** was done by a combination of elemental analysis and IR, ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopy. In the IR spectrum, the CO stretching frequency is observed at 1912 cm^{-1}. In the ^{13}C{^{1}H} NMR spectrum, the CO ligand exhibits a characteristic low-intensity doublet centered at 207.1 ppm (J_{CP} = 20.8 Hz). Due to the η^1-(P) coordination of the $Ph_2PCH_2CH_2NMe_2$ ligand, the ^{13}C resonances of the NCH_2 and NMe_2 moieties are significantly shifted to higher field (ca. 7 ppm NCH_2, ca. 10 ppm NMe_2) compared to those of the η^2-(P)-coordinated $Ph_2PCH_2CH_2NMe_2$ ligand in **1**. Moreover, the methyl groups are no longer inequivalent showing now a singlet resonance in both the ^{1}H and ^{13}C{^{1}H} NMR spectra.

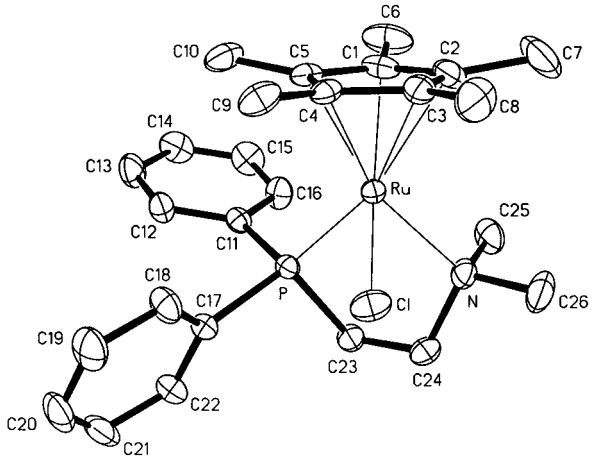

Figure 1. Stuctural view of $RuCp^*(\kappa^2(P,N)\text{-}Ph_2PCH_2CH_2NMe_2)Cl$ (**1**).

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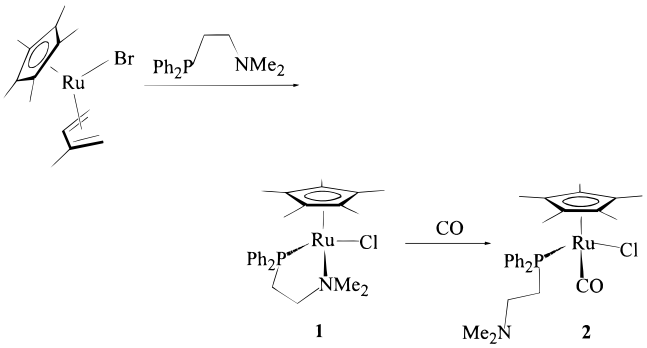
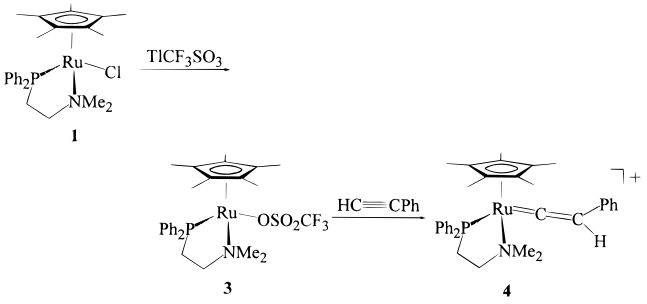
Table 2. Selected Bond Distances (Å) and Angles (deg) for Complexes 1, 3, 4, and 5

	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 $TlCF_3SO_3$ and HC≡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 $TlCF_3SO_3$ (1 equiv) affords, on workup, the expected neutral complex RuCp*(κ²(*P*,*N*)-$Ph_2PCH_2CH_2NMe_2$)(η¹-OSO_2CF_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 $^{13}C\{^1H\}$ 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) Å, respectively, with a P−Ru−N angle of 81.2(1)°. The $CF_3SO_3^-$ anion is coordinated via the oxygen atom in η¹-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 η¹-OSO_2CF_3 ligand are known and structurally characterized.[9−12]

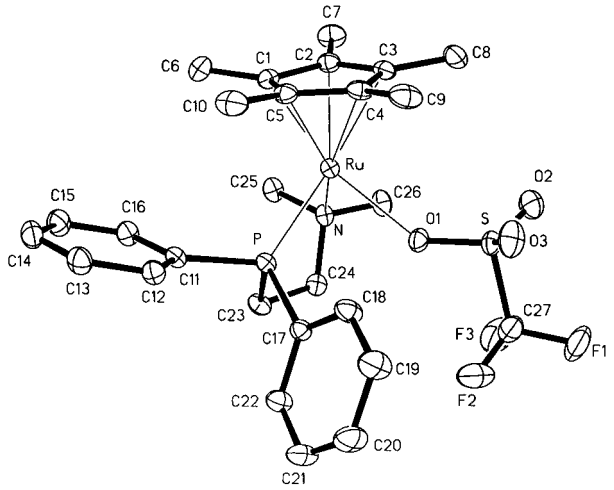


Figure 2. Structural view of RuCp*(κ²(*P*,*N*)-$Ph_2PCH_2CH_2NMe_2$)(η¹-OSO_2CF_3) (**3**).

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 HC≡CPh in the presence of $TlCF_3SO_3$ in CH_2Cl_2 yields the cationic vinylidene complex [RuCp*(κ²(*P*,*N*)-$Ph_2PCH_2CH_2NMe_2$)(=C=CHPh)]⁺ (**4**) in high yield as an air-stable red solid. Similarly, treatment of **3** with 1 equiv of HC≡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 $^{13}C\{^1H\}$ NMR spectrum, a marked low-field resonance at 347.8 ppm (d, $J_{CP} = 13.8$ 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 ($J_{HP} = 3.0$ 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 $Ph_2PCH_2CH_2NMe_2$ 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

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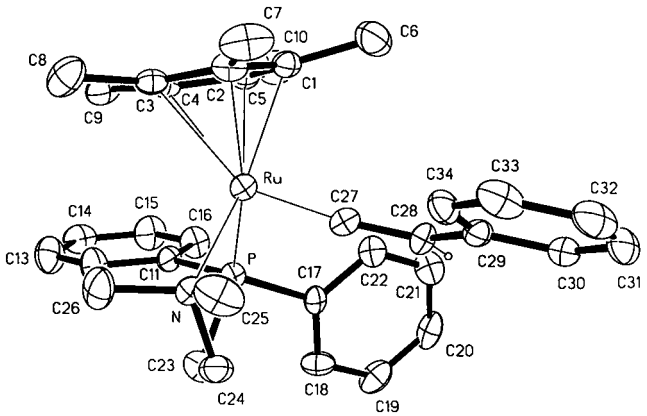
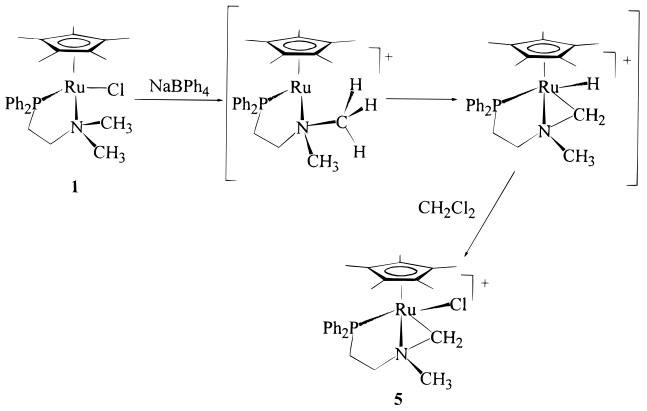


Figure 3. Structural view of [RuCp*(κ^2(*P*,*N*)-$Ph_2PCH_2CH_2NMe_2$)(=C=CHPh)]CF_3SO_3 (**4**) ($CF_3SO_3^-$ omitted for clarity).

Scheme 3



instance, in [RuCp(PMe_3)$_2$(=C=CHMe)]$^+$ and [RuCp($Ph_2PCH_2CH_2PPh_2$)(=C=CPh(C_7H_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 $NaBPh_4$ and CH_2Cl_2. Next we performed chloride abstraction from **1** with $NaBPh_4$ instead of $TlCF_3SO_3$ in CH_2Cl_2 as the solvent. Instead of the expected cationic complex [RuCp*(κ^2(*P*,*N*)-$Ph_2PCH_2CH_2NMe_2$)]$^+$, however, the novel cationic Ru(IV) complex [RuCp*(κ^3(*P*,*N*,*C*)-$Ph_2PCH_2CH_2N(CH_2)Me$)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, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy.

Accordingly, the ^1H and $^{13}C\{^1H\}$ 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 $Ph_2PCH_2CH_2NMe_2$ ligand as follows. There is a substantial down-field shift for the PCH_2 carbon atom from about 31 ppm in complexes **1**−**4** to 22.0 ppm (d, J_{CP} = 24.1 Hz) in **5**. Furthermore, the $^{13}C\{^1H\}$ 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 N*C*H_2CH_2P, N*Me*, and Ru*C*H_2N carbon atoms, respectively. The ^1H NMR spectrum of **5** exhibits a doublet resonance centered at 3.21 ppm (1H, J_{HP} = 9.5 Hz) and two singlet resonances at 2.93 (1H) and 2.57 ppm (3H), assignable to the geminal methylene protons of a Ru*C*H_2N unit and a NMe group. Surprisingly, no coupling is observed between the two geminal hydrogen atoms of the metal-coordinated CH_2 moiety; moreover, only one of the two CH_2 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.

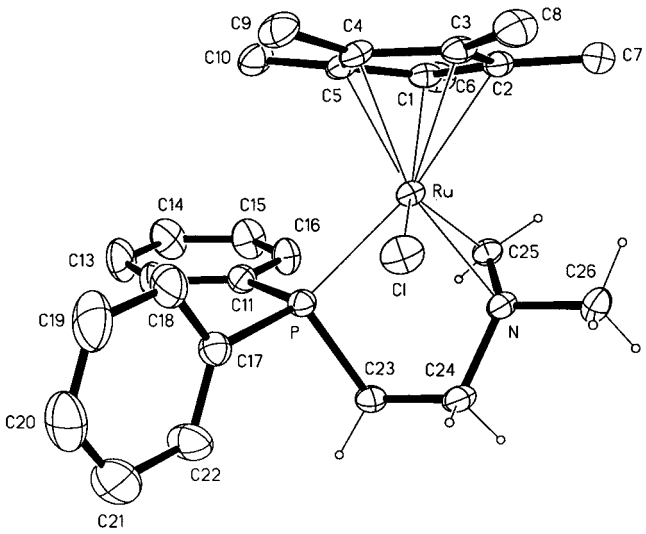
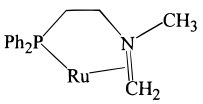
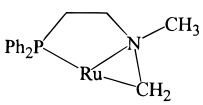


Figure 4. Structural view of [RuCp*(κ^3(*P*,*N*,*C*)-$Ph_2PCH_2CH_2N(CH_2)Me$)Cl]BPh_4 (**5**) (BPh_4^- omitted for clarity).

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 $Ph_2PCH_2CH_2N(Me)CH_2$ as the legs. The $Ph_2PCH_2CH_2N(Me)CH_2$ 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 sp^2 and sp^3, and the bonding situation of the $Ph_2PCH_2CH_2N(Me)CH_2$ ligand might be best described as intermediate between the two limiting forms **I** and **II**.



I



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 $NaBPh_4$ in either CH_2Cl_2 or CD_2Cl_2 as the solvents. Likewise, **3** is quantitatively

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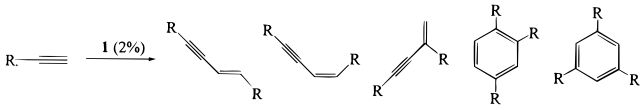
converted in CD_2Cl_2 to **5**, as monitored by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. In both cases, we assume that the cationic 16e⁻ complex [RuCp*(κ²(*P*,*N*)-$Ph_2PCH_2CH_2NMe_2$)]⁺ is intermediarily formed. Methyl β-hydrogen elimination results in the formation of the cyclometalated cationic hydrido complex [RuCp*(κ³(*P*,*N*,*C*)-$Ph_2PCH_2CH_2N(CH_2)Me$)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^i_2 ligand in a dinuclear ruthenium complex[17] and the activation of tertiary amines by osmium cluster complexes.[18] It should further be mentioned that similar intramolecular β-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 HC≡CR (R = Ph, $SiMe_3$, and *n*-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 R = 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 intermediarily 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 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 $RuTp(PPh_3)_2Cl$ (Tp = trispyrazolylborate) and $RuCp^*(PR_3)H_3$ (R = Ph, Me, and Cy).[21,22] In the case of the cyclotrimerization, the reaction presumably proceeds via a different pathway, likely involving metallacyclic 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.

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



	I	II	III	IV	V	
R						conversion
Ph	57	43				63
$SiMe_3$		83	17			20
n-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.

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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

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