Inorganica Chimica Acta 268 (1998) 69–76

Synthesis and reactivity of Ru(II) complexes containing the phosphino-amine $Ph_2PCH_2CH_2NMe_2$

Jin-Yu Shen [a], Christian Slugovc [a], Petra Wiede [b], Kurt Mereiter [b], Roland Schmid [a], Karl Kirchner [a,*]

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

Received 5 February 1997; revised 4 April 1997; accepted 29 April 1997

Abstract

$RuCl_3\cdot 3H_2O$ reacts with 2 equiv. of $Ph_2PCH_2CH_2NMe_2$ in the presence of Zn to the neutral complex $Ru(\kappa^2(P,N)\text{-}Ph_2PCH_2CH_2NMe_2)_2Cl_2$ (**1**). Alternatively, **1** is also obtained by the reaction of $RuCl_2(PPh_3)_3$ with 2 equiv. of $Ph_2PCH_2CH_2NMe_2$. Compound **1** crystallizes in the space group $P2_1$ (No. 4) with $a = 11.009(3)$, $b = 11.007(4)$, $c = 16.999(4)$ Å, $\beta = 106.22(2)°$ and $Z = 2$. The hemilabile nature of the $Ph_2PCH_2CH_2NMe_2$ ligand in **1** is revealed by the reaction with CO and $HC\equiv CPh$ affording complexes $Ru(\kappa^2(P,N)\text{-}Ph_2PCH_2CH_2NMe_2)(\kappa^1(P)\text{-}Ph_2PCH_2CH_2NMe_2)(Cl)_2(CO)$ (**2**) and $Ru(\kappa^2(P,N)\text{-}Ph_2PCH_2CH_2NMe_2)(\kappa^1(P)\text{-}Ph_2PCH_2CH_2NMe_2)(Cl)_2(=C=CHPh)$ (**3**). Halide abstraction from **1** with $NaBPh_4$ affords the five-coordinate cationic complex $[Ru(\kappa^2(P,N)\text{-}Ph_2PCH_2CH_2NMe_2)_2Cl]^+[BPh_4]^-$ (**4**) which crystallizes in the space group *Pbca* (No. 61) with $a = 21.806(4)$, $b = 19.683(4)$, $c = 26.405(5)$ Å, and $Z = 8$. Compound **4** reacts readily with CH_3CN, CO and $HC\equiv CR$ (R = Ph, $SiMe_3$, n-Bu) to give the cationic complexes $[Ru(\kappa^2(P,N)\text{-}Ph_2PCH_2CH_2NMe_2)_2(Cl)(CH_3CN)]^+$ (**5**), $[Ru(\kappa^2(P,N)\text{-}Ph_2PCH_2CH_2NMe_2)_2(Cl)(CO)]^+$ (**6**), and $[Ru(\kappa^2(P,N)\text{-}Ph_2PCH_2CH_2NMe_2)_2(Cl)(=C=CHR)]^+$ (**7–9**). Compound $[Ru(\kappa^2(P,N)\text{-}Ph_2PCH_2CH_2NMe_2)_2(Cl)(CO)]^+[BPh_4]^-$ (**6a**) one of the two stereoisomers **6a** and **6b** crystallizes in the space group $P\bar{1}$ (No. 2) with $a = 11.637(3)$, $b = 15.012(3)$, $c = 15.306(3)$ Å, $\alpha = 96.34(1)$, $\beta = 98.32(1)$, $\gamma = 98.73(1)°$ and $Z = 2$ and the isomeric compound **6b** crystallizes in the space group $P2_1/c$ (No. 14) with $a = 20.445(2)$, $b = 14.198(2)$, $c = 19.717(2)$ Å, $\beta = 94.66(1)°$ and $Z = 4$. **1** catalyzes the dimerization of $HC\equiv CPh$ to *Z*- and *E*-butenynes. © 1998 Elsevier Science S.A.

Keywords: Crystal structures; Catalytic dimerization; Ruthenium complexes; Phosphino-amine complexes

1. Introduction

Phosphinoethers, -esters, and -amines are hemilabile ligands that form a strong metal phosphorus and a weak metal oxygen or nitrogen bond with electron rich transition metal centers [1–6]. There is the ability in such assemblies to create or protect reversibly a vacant coordination site for incoming substrates. In actual fact, complexes with P–O and P–N bidentates have been found to facilitate several stoichiometric and catalytic transformations of organic molecules such as acetylene to vinylidene tautomerizations [3,5,7] or the conversion of a metal-$(\eta^2\text{-}CH_2{=}CH_2)$ to a metal-$(H)(\eta^1\text{-}CH{=}CH_2)$ unit [7]. Furthermore, such complexes appear to be effective catalyst precursors for olefin oligomerizations and polymerizations, carbonylations of methanol and methyl acetate, and hydrogenations [4].

Along these lines, we have been examining ruthenium complexes with hemilabile ligands for their efficiency in stoichiometrically and catalytically operating processes. Here we report on the synthesis and reactivity of the ruthenium complex $Ru(\kappa^2(P,N)\text{-}Ph_2PCH_2CH_2NMe_2)_2Cl_2$ (**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. X-ray structures of some of the new complexes are presented.

2. Experimental

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

---

[*] Corresponding author. Tel.: +43 1 58801-4620; fax: +43 1 5816668; e-mail: kkirch@fbch.tuwien.ac.at

0020-1693/98/$19.00 © 1998 Elsevier Science S.A. All rights reserved
PII S0020-1693(97)05721-6

$Ph_2PCH_2CH_2NMe_2$ and $RuCl_2(PPh_3)_3$ were prepared according to the literature [8,9]. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ 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 to H_3PO_4 (85%). Diffuse reflectance FT-IR spectra were recorded on a Mattson RS 2 spectrometer. Microanalysis were done by Microanalytical Laboratories, University of Vienna.

2.1. *Synthesis of Ru(κ^2(P,N)-$Ph_2PCH_2CH_2NMe_2$)$_2$$Cl_2$ (1)*

2.1.1. *Method (a)*

$RuCl_2(PPh_3)_3$ (2.00 g, 2.09 mmol) and $Ph_2PCH_2CH_2NMe_2$ (1.03 g, 4.01 mmol) were dissolved in toluene (20 ml) and the mixture was stirred for 20 h at room temperature. During that time the color changed from brown to red and a dark red precipitate was slowly formed, which was collected on a glass frit, washed with small amounts of toluene, diethyl ether, and then dried under vacuum. The crude product was purified by diffusion of diethyl ether into a solution of **1** in CH_2Cl_2. Yield: 1.25 g (87%).

2.1.2. *Method (b)*

To a solution of $RuCl_3 \cdot 3H_2O$ (262 mg, 1.00 mmol) in tetrahydrofuran (10 ml) $Ph_2PCH_2CH_2NMe_2$ (514 mg, 2.00 mmol) and Zn (160 mg, 2.44 mmol) was added and the mixture was stirred for 4 h at 65°C. Insoluble materials were removed by filtration. On removal of the solvent, a red solid was obtained which was purified by diffusion of diethyl ether into a solution of **1** in CH_2Cl_2. Yield: 550 mg (80%). *Anal.* Found: C, 55.91; H, 5.89; N, 3.96. Calc. for $C_{32}H_{40}Cl_2N_2P_2Ru$: C, 55.98; H, 5.87; N, 4.08%. NMR ($CDCl_3$, 20°C): δ_H, 7.29–7.00 (m, 20H), 3.05–2.80 (m, 8H), 2.82 (s, 12H). δ_C, 137.9 (t, J_{PC} = 21.4 Hz), 134.9 (t, J_{PC} = 4.3 Hz), 129.4, 127.6 (t, J_{PC} = 4.3 Hz), 62.4 (t, J_{PC} = 1.67 Hz, NCH_2), 50.9 (NMe_2), 32.7 (t, J_{PC} = 12.4 Hz, PCH_2). δ_P, 57.4.

2.2. *Synthesis of Ru(κ^2(P,N)-$Ph_2PCH_2CH_2NMe_2$)(κ^1(P)-$Ph_2PCH_2CH_2NMe_2$)(Cl)$_2$(CO) (2)*

A solution of **1** (100 mg, 0.15 mmol) in CH_2Cl_2 (5 ml) was purged with CO for 5 min at room temperature, whereupon the color of the solution changed from red to orange. The solvent was removed under vacuum and the resulting solid was collected on a glass frit, washed with petroleum ether, and dried under vacuum. Yield: 72 mg (67%). (Found: C, 55.51; H, 6.60; N, 4.00). $C_{33}H_{40}Cl_2N_2OP_2Ru$ requires C, 55.47; H, 5.64; N, 3.92%. NMR ($CDCl_3$, 20°C): δ_H, 7.63–7.15 (m, 20H), 3.00 (s, 6H), 2.85–2.13 (m, 8H), 2.04 (s, 6H). d_C, 202.0 (dd, J_{PC} = 17.6 Hz, J_{PC} = 110.6 Hz, *CO*), 135.3–125.8, 61.3 (d, J_{PC} = 8.3 Hz, NCH_2), 54.5 (NMe_2), 54.1 (d, J_{PC} = 1.52 Hz, NCH_2), 50.6 (NMe_2), 30.6 (dd, J_{PC} = 20.6 Hz, J_{PC} = 1.5 Hz, PCH_2), 27.5 (d, J_{PC} = 29.8 Hz, PCH_2). δ_P, 36.6 (d, J_{PP} = 26.9 Hz), 19.3 (d, J_{PP} = 26.9 Hz). ν_{max}/(cm^{-1}) 1949s (CO).

2.3. *Synthesis of Ru(κ^2(P,N)-$Ph_2PCH_2CH_2NMe_2$)(κ^1(P)-$Ph_2PCH_2CH_2NMe_2$)(Cl)$_2$(=C=CHPh) (3)*

To a solution of **1** (70 mg, 0.10 mmol) in toluene (3 ml) HC≡CPh (27.5 µl, 0.25 mmol) was added and the mixture was stirred for 20 h at 80°C. Then the volume of the solution was reduced to about 1 ml and the resulting yellow precipitate was collected on glass frit, washed with diethyl ether, petroleum ether, and dried under vacuum. Yield: 36 mg (46%). *Anal.* Found: C, 60.78; H, 5.90; N, 3.52. Calc. for $C_{40}H_{46}Cl_2N_2P_2Ru$: C, 60.91; H, 5.88; N, 3.55%. NMR ($CDCl_3$, 20°C): δ_H, 8.06–6.70 (m, 25H), 2.76 (s, 6H), 3.04–2.64 (m, 8H), 2.31 (s, 6H). δ_C, 355.0 (dd, J_{PC} = 16.0 Hz, J_{PC} = 18.4 Hz, C_α), 138.5–126.0 (m, *Ph*), 112.1 (t, J_{PC} = 2.4 Hz, C_β), 61.3 (t, J_{PC} = 3.1 Hz, NCH_2), 55.5 (NMe_2), 54.6 (d, J_{PC} = 6.9 Hz, NCH_2), 50.6 (NMe_2), 30.0 (d, J_{PC} = 30.5 Hz, PCH_2), 25.4 (d, J_{PC} = 28.1 Hz, PCH_2). δ_P, 36.9 (d, J_{PP} = 28.1 Hz), 28.8 (d, J_{PP} = 28.1 Hz). ν_{max}/(cm^{-1}) 1616s (C=C).

2.4. *Synthesis of [Ru(κ^2(P,N)-$Ph_2PCH_2CH_2NMe_2$)$_2$Cl]BPh_4 (4)*

A solution of **1** (200 mg, 0.29 mmol) in CH_2Cl_2 (6 ml) was treated with $NaBPh_4$ (100 mg, 0.29 mmol) and the heterogeneous mixture was stirred for 60 h at room temperature. Insoluble materials were removed by filtration and the volatiles were removed under vacuum. The resulting purple–red solid was collected on a glass frit, washed with diethyl ether, and dried under vacuum. Yield: 270 mg (96%). *Anal.* Found: C, 69.03; H, 6.22; N, 2.78. Calc. for $C_{56}H_{60}BClN_2P_2Ru$: C, 69.31; H, 6.23; N, 2.89%. NMR ($CDCl_3$, 20°C): δ_H, 7.93–6.77 (m, 40H), 2.88–1.77 (m, 8H), 2.74 (m, 6H), 2.30 (s, 6H). δ_C, 164.6 (q, J_{BC} = 49.2 Hz), 136.7 (q, J_{BC} = 1.4 Hz), 134.2 (*Ph*), 133.7 (*Ph*), 132.2 (*Ph*), 130.0–129.3 (*Ph*), 127.9 (*Ph*), 127.7 (*Ph*), 126.2, 122.4, 66.5 (t, J_{PC} = 1.8 Hz, NCH_2), 58.0 (N*Me*), 52.7 (N*Me*), 32.2 (m, PCH_2). δ_P, 77.5.

2.5. *Synthesis of [Ru(κ^2(P,N)-$Ph_2PCH_2CH_2NMe_2$)$_2$(Cl)(CH_3CN)]BPh_4 (5)*

To a solution of **4** (50 mg, 0.05 mmol) in CH_2Cl_2 (3 ml), CH_3CN (2.7 µl, 0.05 mmol) was added, whereupon the solution became yellow immediately. The mixture was stirred for 15 min at room temperature and the solvent was removed under vacuum. The resulting yellow precipitate was collected on a glass frit, washed with ethanol, diethyl ether, and dried under vacuum. Yield: 32 mg (61%). *Anal.* Found: C, 68.83; H, 6.22; N, 4.20. Calc. for $C_{58}H_{63}BClN_3P_2Ru$: C, 68.88; H, 6.28; N, 4.15%. NMR ($CDCl_3$, 20°C): δ_H, 7.44–6.76 (m, 40H), 3.10–2.43 (m, 8H), 2.97 (m, 6H), 2.51 (s, 6H), 2.20 (s, 3H). δ_C, 164.2 (q, J_{BC} = 48.7 Hz), 136.0 (q, J_{BC} = 1.4 Hz), 134.0, 139.9–132.4, 132.4, 130.5, 130.1, 128.6, 127.7, 125.8 (CN), 126.2 (q, J_{BC} = 2.8 Hz), 122.4, 61.8 (NCH_2), 50.8 (N*Me*), 49.9 (N*Me*), 30.0 (t,

J_{PC} = 13.3 Hz, PCH_2), 4.6 (CH_3CN). δ_P, 53.7. $\nu_{max}/(cm^{-1})$ 2253w (CN).

2.6. *Synthesis of* $[Ru(\kappa^2(P,N)\text{-}Ph_2PCH_2CH_2NMe_2)_2(Cl)(CO)]BPh_4$ *(6a)*

A solution of **4** (54 mg, 0.06 mmol) in CH_2Cl_2 (6 ml) was purged with CO for 5 min at room temperature, whereupon the color of the solution changed from red to yellow. The volatiles were removed under reduced pressure and the resulting residue was recrystallized from CH_2Cl_2/methanol (1:1). **6a** was obtained as a yellow solid. Yield: 22 mg (39%). *Anal.* Found: C, 68.63; H, 6.14; N, 2.77. Calc. for $C_{57}H_{60}BClN_2OP_2Ru$: C, 68.57; H, 6.06; N, 2.81%. NMR ($CDCl_3$, 20°C): δ_H, 7.58–6.70 (m, 40H), 2.71 (s, 3H), 2.69 (s, 3H), 2.50–2.00 (m, 8H), 2.28 (s, 3H), 2.18 (s, 3H). δ_C, 200.0 (dd, J_{PC} = 15.2 Hz, J_{PC} = 103.2 Hz, CO), 164.2 (q, J_{BC} = 49.3 Hz) 136.5, 133.8–127.7, 125.9, 122.2, 65.2 (NCH_2), 64.0 (NCH_2), 60.8 (NMe), 60.6 (NMe), 58.1 (NMe), 57.7 (NMe), 30.1 (d, J_{CP} = 32.5 Hz, PCH_2), 27.0 (d, J_{CP} = 23.9 Hz, PCH_2). δ_P, 41.8 (d, J_{PP} = 28.1 Hz), 16.2 (d, J_{PP} = 28.1 Hz). $\nu_{max}/(cm^{-1})$ 1989s (CO).

2.7. *Synthesis of* $[Ru(\kappa^2(P,N)\text{-}Ph_2PCH_2CH_2NMe_2)_2(Cl)(CO)]BPh_4$ *(6b)*

In order to obtain crystals of **6a** for an X-ray diffraction analysis, a solution of **6a** (30 mg) in CH_2Cl_2/CH_3OH (1:1) was set aside for crystallization by vapor diffusion with diethyl ether. Within one day a small amounts of yellow and colorless crystals of **6a** and **6b**, respectively, were formed which were separated manually. NMR ($CDCl_3$, 20°C): δ_H, 7.63–6.67 (m, 40H), 3.00–1.98 (m, 8H), 2.67 (s, 6H), 2.58 (s, 6H). δ_C, 197.7 (t, J_{PC} = 15.2 Hz, CO), 163.5 (q, J_{BC} = 48.8 Hz), 141.2, 139.3, 137.6, 137.9, 137.0, 136.9, 136.4, 135.8, 135.0, 134.3, 133.4, 130.7 (q, J_{BC} = 3.1 Hz), 126.9, 67.6 (NCH_2), 59.6 (NMe), 55.2 (NMe), 34.7 (t, J_{PC} = 25.8 Hz, PCH_2). δ_P, 46.2. $\nu_{max}/(cm^{-1})$ 1948s (CO).

2.8. *Synthesis of* $[Ru(\kappa^3(P,N)\text{-}Ph_2PCH_2CH_2NMe_2)_2(Cl)(CO)]BPh_4$ *(6c)*

A solution of **6a** (50 mg) was stirred in 6 ml of CH_2Cl_2/MeOH (1:1) for 20 h at room temperature. Then, the volume of the solution was reduced to about 2 ml whereupon a white precipitate was formed, which was collected on glass frit, washed with diethyl ether, and dried under vacuum. Yield: 35 mg (70%). *Anal.* Found: C, 68.53; H, 6.10; N, 2.85. Calc. for $C_{57}H_{60}BClN_2OP_2Ru$: C, 68.57; H, 6.06; N, 2.81%. NMR ($CDCl_3$, 20°C): δ_H, 8.00–6.52 (m, 40H), 2.37 (s, 6H), 2.09 (s, 6H), 3.10–1.70 (m, 8H). δ_C, 201.1 (t, J_{PC} = 13.0 Hz, CO), 164.6 (q, J_{BC} = 49.6 Hz), 136.8 (q, J_{BC} = 1.5 Hz), 134.5, 133.8, 132.7, 132.0, 131.5, 130.2, 128.8, 126.1 (q, J_{BC} = 3.1 Hz), 122.3, 65.1 (NCH_2), 60.2 (NMe), 57.8 (NMe), 30.0 (t, J_{PC} = 22.1 Hz, PCH_2). δ_P, 34.9. $\nu_{max}/(cm^{-1})$ 1947s (CO).

2.9. *Synthesis of* $[Ru(\kappa^2(P,N)\text{-}Ph_2PCH_2CH_2NMe_2)_2(Cl)(=C=CHPh)]BPh_4$ *(7)*

To a solution of **4** (48 mg, 0.05 mmol) in CH_2Cl_2 (3 ml) HC≡CPh (5.4 μl, 0.05 mmol) was added and the mixture was stirred for 5 h at room temperature. On addition of diethyl ether a yellow precipitate was formed which was collected on a glass frit, washed with diethyl ether, and dried under vacuum. Yield: 32 mg (60%). *Anal.* Found: C, 71.56; H, 6.16; N, 2.58. Calc. for $C_{64}H_{66}BClN_2P_2Ru$: C, 71.67; H, 6.20; N, 2.61%. NMR ($CDCl_3$, 20°C): δ_H, 7.58–6.70 (m, 45H), 2.83 (s, 3H), 2.79 (s, 3H), 3.10–2.20 (m, 8H), 2.17 (s, 6H). δ_C, 358.3 (dd, J_{PC} = 14.4 Hz, J_{PC} = 20.9 Hz, C_α), 164.8 (q, J_{BC} = 49.0 Hz), 136.9, 135.3–127.0, 126.4, 122.6, 112.6 (t, J_{PC} = 4.8 Hz, C_β), 62.8 (NCH_2), 61.8 (NCH_2), 54.6 (NMe), 53.8 (NMe), 51.1 (NMe), 30.9 (d, J_{PC} = 31.3 Hz, PCH_2), 26.7 (d, J_{PC} = 28.9 Hz, PCH_2). δ_P, 38.1 (d, J_{PP} = 26.8 Hz), 32.3 (d, $^2J_{PP}$ = 26.8 Hz). $\nu_{max}/(cm^{-1})$ 1616s (C=C).

2.10. *Synthesis of* $[Ru(\kappa^2(P,N)\text{-}Ph_2PCH_2CH_2NMe_2)_2(Cl)(=C=CHSiMe_3)]BPh_4$ *(8)*

This complex has been prepared analogously to **7** but with **4** and HC≡$CSiMe_3$ as starting materials. Yield: 56%. *Anal.* Found: C, 68.63; H, 6.57; N, 2.73. Calc. for $C_{61}H_{70}BClN_2P_2RuSi$: C, 68.56; H, 6.60; N, 2.62%. NMR ($CDCl_3$, 20°C): δ_H, 7.90–6.55 (m, 40H), 2.99–2.00 (m, 8H), 2.47 (s, 6H), 2.30 (s, 6H), 0.02 (s, 9H). δ_C, 348.9 (t, = $^2J_{PC}$ = 16.1 Hz, C_α), 164.2 (q, $^1J_{BC}$ = 49.0 Hz), 136.4, 134.5, 134.3, 133.2, 131.7, 131.3, 128.8, 128.3, 125.8 (q, $^2J_{BC}$ = 2.4 Hz), 122.1, 92.2 (t, $^3J_{PC}$ = 1.6 Hz, C_β), 61.9 (NCH_2), 53.1 (NMe), 50.3 (NMe), 29.3 (t, $^1J_{PC}$ = 15.3 Hz, PCH_2), 1.8 ($SiMe_3$). δ_P, 42.7. $\nu_{max}/(cm^{-1})$ 1627s (C=C).

2.11. *Synthesis of* $[Ru(\kappa^2(P,N)\text{-}Ph_2PCH_2CH_2NMe_2)_2(Cl)(=C=CHBu^n)]BPh_4$ *(9)*

This complex has been prepared analogously to **7** but with **4** and HC≡CBu^n as the starting materials. Yield: 60%. *Anal.* Found: C, 70.66; H, 6.64; N, 2.73. Calc. for $C_{62}H_{70}BClN_2P_2Ru$: C, 70.75; H, 6.70; N, 2.66%. NMR ($CDCl_3$, 20°C): δ_H, 7.79–6.69 (m, 40H), 3.05–2.40 (m, 8H), 2.59 (s, 6H), 2.53 (s, 6H), 2.40–2.02 (m, 4H), 1.12 (q, 2H), 0.86 (t, 3H). δ_C, 351.5 (t, J_{PC} = 16.9 Hz, C_α), 164.3 (q, J_{BC} = 49.0 Hz), 136.5, 134.6, 134.3, 133.2, 131.5, 131.1, 128.8, 128.3, 125.8 (q, J_{BC} = 2.4. Hz), 122.0, 106.5 (C_β), 62.2 (NCH_2), 54.2 (NMe), 50.6 (NMe), 33.3 ($CH_2CH_2CH_2CH_3$), 29.5 (t, J_{PC} = 16.1 Hz, PCH_2), 22.3 ($CH_2CH_2CH_2CH_3$), 20.4 (s, $CH_2CH_2CH_2CH_3$), 14.1 (s, $CH_2CH_2CH_2CH_3$). δ_P, 43.4.

2.12. *Catalytic dimerization of HC≡CPh*

Phenylacetylene (215 μl) was added to a suspension of either **1** (2%) or **3** (2%) in toluene (4 ml). The sealed Schlenk tube was heated in an oil bath for 20 h at 111°C.

After that time the reaction mixture was evaporated to dryness and the coupling products were extracted with n-hexane. The solvent was again removed under vacuum affording an isomeric mixture of *Z*- and *E*-butynes in a 9:1 ratio in 70% isolated yield. The product distribution was determined by ^{1}H NMR spectroscopy.

2.13. X-ray structure determination for 1 · $CHCl_3$ · $(CH_3)_2CO$, 4 · $(C_2H_5)_2O$, 6a · CH_2Cl_2, and 6b · $2CH_2Cl_2$

Crystal data and experimental details are given in Table 1. X-ray data for **1**·$CHCl_3$·$(CH_3)_2CO$ were collected on a Philips PW 1100 four-circle diffractometer using graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation and the θ–2θ scan technique. Two other crystalline forms of this complex obtained from various solvents have been observed by us and by B. James (University of British Columbia, Vancouver; private communication). For **4**·$(C_2H_5)_2O$, **6a**·CH_2Cl_2, and **6b**·$2CH_2Cl_2$ 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 (empirical with program XABS2 [10a] for **1**·$CHCl_3$·$(CH_3)_2CO$ and with program SADABS [10b] for **4**·$(C_2H_5)_2O$, **6a**·CH_2Cl_2, and **6b**·$2CH_2Cl_2$ were applied. The structures were solved by direct methods [11a]. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included in idealized positions [11b]. The structures were refined against F^2.

3. Results and discussion

3.1. Synthesis of $Ru(\kappa^2(P,N)\text{-}Ph_2PCH_2CH_2NMe_2)_2Cl_2$ (1)

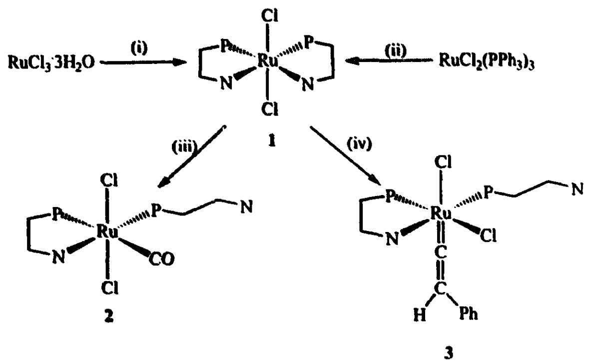
Treatment of $RuCl_3 \cdot 3H_2O$ with 2 equiv. of $Ph_2PCH_2CH_2NMe_2$ in the presence of Zn affords, on workup, the dark red complex $Ru(\kappa^2(P,N)\text{-}Ph_2PCH_2CH_2NMe_2)_2Cl_2$ (**1**) in 80% yield. Alternatively, **1** is also obtained by the reaction of $RuCl_2(PPh_3)_3$ with 2 equiv. of $Ph_2PCH_2CH_2NMe_2$ in 87% yield (Scheme 1). **1** is a thermally robust red solid which is stable to air both in the solid state and in solution.

Characterization of **1** was by elemental analysis, ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopy. The ^{31}P{^{1}H} NMR spectrum exhibits only one singlet at 57.4 ppm. In the

Table 1
Crystallographic data

	1·$(CH_3)_2CO$·$CHCl_3$	**4**·$(CH_3CH_2)_2O$	**6a**·CH_2Cl_2	**6b**·$2CH_2Cl_2$
Formula	$C_{36}H_{47}Cl_5N_2OP_2Ru$	$C_{60}H_{70}BClN_2OP_2Ru$	$C_{58}H_{62}BCl_3N_2OP_2Ru$	$C_{59}H_{64}BCl_5N_2OP_2Ru$
Formula weight	864.02	1044.45	1083.27	1168.19
Crystal size (mm)	0.32 × 0.35 × 0.40	0.43 × 0.20 × 0.18	0.36 × 0.19 × 0.11	0.35 × 0.25 × 0.18
Space group	$P2_1$ (No. 4)	*Pbca* (No. 61)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
a (Å)	11.009(3)	21.806(4)	11.637(3)	20.445(2)
b (Å)	11.007(4)	19.683(4)	15.012(3)	14.198(2)
c (Å)	16.999(4)	26.405(5)	15.306(3)	19.717(2)
α (°)			96.34(1)	
β (°)	106.22(2)		98.32(1)	94.66(1)
γ (°)			98.73(1)	
V (Å^3)	1978(1)	11333(4)	2591(1)	5704(2)
F(000)	888	4384	1124	2416
Z	2	8	2	4
ρ_{calc} (g cm^{-3})	1.451	1.224	1.388	1.360
T (K)	297	297	298	298
μ (mm^{-1}) (Mo Kα)	0.846	0.420	0.562	0.606
Absorption correction	empirical	empirical	empirical	empirical
Transmission factors min./max.	0.96/1.09	0.80/0.93	0.83/0.93	0.75/0.86
θmax (°)	25	25	25	25
Index ranges	$-13 \leq h \leq 12$ $-13 \leq k \leq 0$ $0 \leq l \leq 20$	$-25 \leq h \leq 25$ $-22 \leq k \leq 23$ $-30 \leq l \leq 31$	$-11 \leq h \leq 13$ $-17 \leq k \leq 17$ $-18 \leq l \leq 17$	$-23 \leq h \leq 24$ $-16 \leq k \leq 14$ $-17 \leq l \leq 23$
No. reflections measured	3858	125834	14890	31666
No. unique reflections	3668	9930	9015	9996
No. reflections $F > 4\sigma(F)$	3243	7261	6253	8107
No. parameters	426	626	617	675
$R(F)$ ($F > 4\sigma(F)$)	0.0338	0.0429	0.0534	0.0324
$R(F)$ (all data)	0.0430	0.0700	0.0959	0.0469
$wR(F^2)$ (all data)	0.0738	0.0970	0.1209	0.0811
Difference Fourier peaks min./max. (e Å^{-3})	−0.47/0.39	−0.28/0.40	−0.53/0.63	−0.30/0.55

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



Scheme 1. (i) $Ph_2PCH_2CH_2NMe_2$, Zn in tetrahydrofuran at 65°C. (ii) $Ph_2PCH_2CH_2NMe_2$ in toluene at room temperature. (iii) CO in CH_2Cl_2 for 5 min at room temperature. (iv) HC≡CPh in toluene at 80°C.

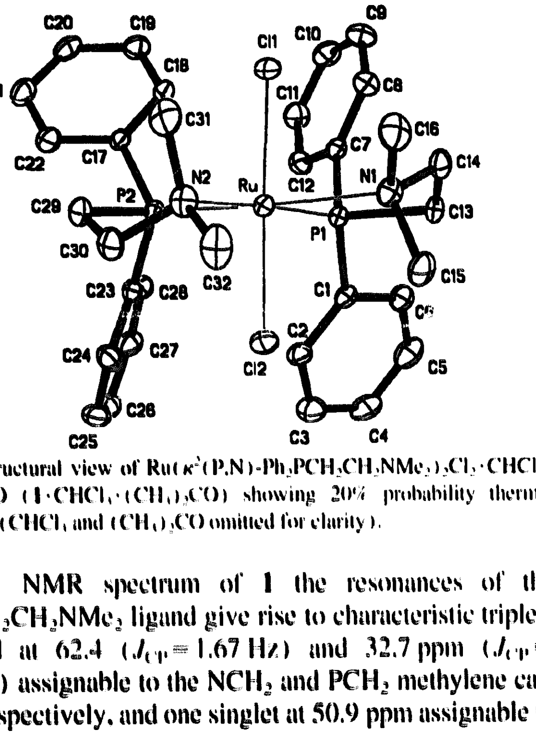


Fig. 1. Structural view of $Ru(\kappa^2(P,N)\text{-}Ph_2PCH_2CH_2NMe_2)_2Cl_2\cdot CHCl_3\cdot (CH_3)_2CO$ ($1\cdot CHCl_3\cdot (CH_3)_2CO$) showing 20% probability thermal ellipsoids ($CHCl_3$ and $(CH_3)_2CO$ omitted for clarity).

$^{13}C\{^1H\}$ NMR spectrum of **1** the resonances of the $Ph_2PCH_2CH_2NMe_2$ ligand give rise to characteristic triplets centered at 62.4 (J_{CP} = 1.67 Hz) and 32.7 ppm (J_{CP} = 11.2 Hz) assignable to the NCH_2 and PCH_2 methylene carbons, respectively, and one singlet at 50.9 ppm assignable to the methyl groups. An X-ray structure of $1\cdot CHCl_3\cdot (CH_3)_2CO$ is depicted in Fig. 1. Selected bond distances and angles are given in Table 2. The geometry about the metal center is distorted octahedral with the two phosphorus and nitrogen atoms in *cis* position and the two chloride atoms in *trans* position. The N(1)–Ru–N(2) and P(1)–Ru–P(2) angles are 95.7(2) and 99.6(1)°, while the P(1)–Ru–N(1) and P(2)–Ru–N(2) bond angles are smaller (82.7(2) and 82.1(1)°) probably due to the ring strain in the five-membered PC_2NRu ring systems. The Ru–Cl(1) and Ru–Cl(2) distances are 2.410(2) and 2.395(2) Å and the Cl(1)–Ru–Cl(2) angle is 172.1(1)°C. For comparison, in the related complex $Ru(\kappa^2(P,O)\text{-}Ph_2PCH_2CH_2OMe)_2Cl_2$ the Ru–Cl(1) and Ru–Cl(2) distances are 2.394(2) and 2.396(2) Å, respectively, with a Cl(1)–Ru–Cl(2) angle of 166.0(1)° [12]. The Ru–P and Ru–N distances are in the expected ranges.

3.2. *Reaction of 1 with CO and HC≡CPh*

The hemilabile nature of the $Ph_2PCH_2CH_2NMe_2$ ligand in **1** is revealed by the reaction with carbon monoxide and HC≡CPh. Thus, when **1** is stirred under a CO atmosphere for 5 min at ambient temperature, the Ru–N bond is cleaved resulting in the neutral complex $Ru(\kappa^2(P,N)\text{-}Ph_2PCH_2CH_2NMe_2)(\kappa^1(P)\text{-}Ph_2PCH_2CH_2NMe_2)(Cl)_2(CO)$ (**2**) in 67% isolated yield (Scheme 1). Characterization of **2** was again by a combination of elemental analysis, IR, ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy. In the IR spectrum the CO stretching frequency is observed at 1949 cm^{-1}. Owing to the presence of one chelating and one open chain $Ph_2PCH_2CH_2NMe_2$ ligand the $^{31}P\{^1H\}$ NMR spectrum of **2** exhibits an AB pattern. The small coupling constant of 26.9 Hz is in favor of a *cis* geometry of the phosphine atoms. In the $^{13}C\{^1H\}$ NMR spectrum the CO ligand exhibits a low-intensity resonance at 202.0 ppm (dd, J_{CP} = 17.6 Hz, J_{CP} = 110.6 Hz). This coupling pattern for the carbonyl carbon is originating from the two phosphine moieties *cis* and *trans* to the CO ligand. The ^{13}C resonances of the NCH_2 and NMe_2 moieties of the κ^1-(P) coordinated $Ph_2PCH_2CH_2NMe_2$ ligand are somewhat shifted to higher field compared with the κ^2-(P,N) coordinated one. Provided that the chlorine atoms are *trans* to each other the CO ligand would then be

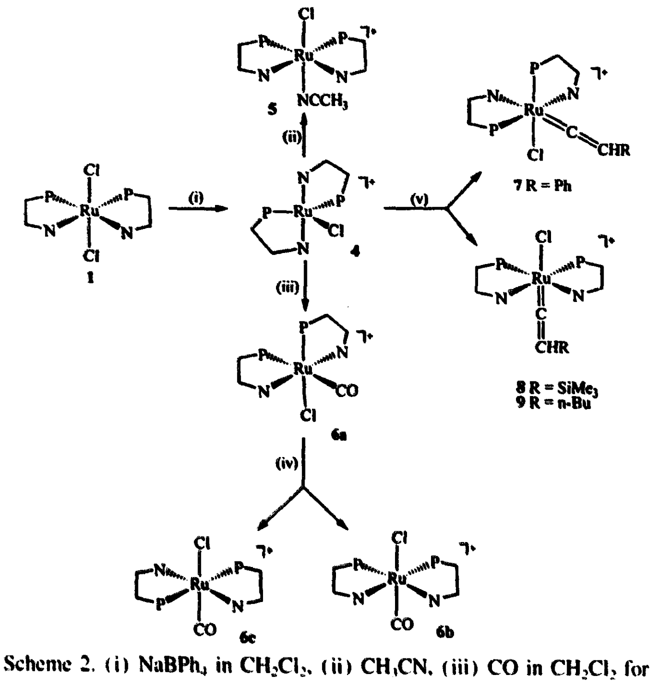
Table 2
Selected bond distances (Å) and angles (°) for complexes $1\cdot (CH_3)_2CO\cdot CHCl_3$, $4\cdot (CH_3CH_2)_2O$, $6a\cdot CH_2Cl_2$, and $6b\cdot 2CH_2Cl_2$

	$1\cdot (CH_3)_2CO\cdot CHCl_3$	$4\cdot (CH_3CH_2)_2O$	$6a\cdot CH_2Cl_2$	$6b\cdot 2CH_2Cl_2$
Ru–P(1)	2.255(2)	2.253(1)	2.478(1)	2.323(1)
Ru–P(2)	2.251(2)	2.214(1)	2.363(1)	2.324(1)
Ru–N(1)	2.402(4)	2.193(2)	2.237(4)	2.333(2)
Ru–N(2)	2.377(6)	2.201(3)	2.229(4)	2.357(2)
Ru–Cl(1)	2.410(2)	2.391(1)	2.427(2)	2.407(1)
Ru–Cl(2)	2.395(2)			
Ru–C(33)			1.984(6)	1.847(3)
P(1)–Ru–P(2)	99.6(1)	96.4(1)	102.2(1)	100.1(1)
N(1)–Ru–N(2)	95.7(2)	176.6(1)	175.9(1)	95.5(1)
Cl(1)–Ru–Cl(2)	172.1(1)			
P(1)–Ru–N(1)	82.7(2)	82.2(1)	82.5(1)	82.3(1)
P(2)–Ru–N(2)	82.1(1)	80.7(1)	83.1(1)	82.4(1)

trans to the phosphorus atom of the κ^2-(P,N) coordinated $Ph_2PCH_2CH_2NMe_2$ ligand (as drawn in Scheme 1). Two other possible structures with the chlorine atoms in *cis* position, however, cannot be ruled out with the data at hand. All attempts to grow a crystal of **2** suitable for an X-ray diffraction analysis have failed. It is worth noting that the related complex Ru(κ^2(P,O)-$Ph_2PCH_2CH_2OMe)_2Cl_2$ reacts with CO to a mono and a dicarbonyl species both with a *trans*-P,P configuration [12], while Ru(κ^2(P,O)-*i*-$Pr_2PCH_2CH_2OMe)_2$-Cl_2 yields only the dicarbonyl complex [7]. In contrast, **1** does not give a dicarbonyl complex with two κ^1-(P) coordinated $Ph_2PCH_2CH_2NMe_2$ ligands. In these type of complexes, therefore, the Ru–N bond is stronger than the Ru–O bond.

The reaction of **1** with HC≡CPh in toluene at 80°C yields the neutral vinylidene complex Ru(κ^2(P,N)-$Ph_2PCH_2CH_2$-NMe_2)(κ^1(P)-$Ph_2PCH_2CH_2NMe_2$)$(Cl)_2$(=C=CHPh) (**3**) in 46% yield as an air-stable yellow solid (Scheme 1). The $^{31}P\{^1H\}$ NMR spectrum of **3** displays an AB pattern showing two doublets centered at 36.9 and 28.8 ppm. As above, the small coupling constant of 28.1 Hz is consistent with a *cis*-P,P arrangement. Characteristic $^{13}C\{^1H\}$ NMR spectroscopic features comprise a marked low-field resonance at 355.0 ppm (dd, J_{CP} = 16.0 Hz, J_{CP} = 18.4 Hz) and a resonance at 112.1 ppm (t, J_{CP} = 2.4 Hz) assignable to the α- and β-carbons of the vinylidene moiety, respectively. This coupling pattern of the vinylidene C_α carbon atom results from the two phosphines *cis* to the vinylidene unit. Noteworthy, in the ^1H NMR spectrum the C_β-hydrogen could not be observed. The spectroscopic data, however, do not allow to distinguish whether the vinylidene moiety is bound *trans* to the chlorine or *trans* to the nitrogen atom. In analogy to a recent X-ray structure of the related complex Ru(κ^2(P,O)-$Ph_2PCH_2CH_2OMe$)-(κ^1(P)-$Ph_2PCH_2CH_2OMe$)$(Cl)_2$(=C=CHPh) [3] showing the vinylidene moiety *trans* to the chlorine atom, we favor a similar structure for complex **3** (as drawn in Scheme 1). This in accord with the bonding types, since vinylidene is a π acceptor and chloride is a π donor, whereas the amine moiety has no π-bonding abilities.

3.3. Reaction of 1 with NaBPh₄



Scheme 2. (i) $NaBPh_4$ in CH_2Cl_2, (ii) CH_3CN, (iii) CO in CH_2Cl_2 for 5 min, (iv) in CH_2Cl_2/CH_3OH (1:1) for 20 h, (v) HC≡CR (R = Ph, $SiMe_3$, n-Bu) in CH_2Cl_2 at room temperature.

When a solution of complex **1** in CH_2Cl_2 is treated with 1 equiv. of $NaBPh_4$ for 60 h at ambient temperature the five-coordinate cationic complex $[Ru(\kappa^2(P,N)$-Ph_2PCH_2-$CH_2NMe_2)_2Cl]^+$ (**4**) was obtained as a purple–red solid (Scheme 2). **4** is moderately air-sensitive both in the solid state and in solution. Characterization was by elemental analysis, ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy. The $^{31}P\{^1H\}$ NMR spectrum of **4** displays a singlet 77.5 ppm in agreement with two equivalent $Ph_2PCH_2CH_2NMe_2$ ligands. The ^1H and $^{13}C\{^1H\}$ NMR spectra bear no unusual features and it is sufficient to mention that the NMe_2 groups give rise to two singlets, i.e. the methyl groups are diastereotopic. While there are several reports of five coordinate cationic ruthenium(II) complexes of the type $[Ru(PP)_2Cl]^+$ (PP = diphosphine) [13–15], there are only a few examples with five-coordinate ruthenium complexes with phosphine–amine ligands such as Ru(pn)$(Cl)_2(PR_3)$ (pn = *o*-diphenylphosphino-*N*,*N*-dimethylaniline, R = *p*-tolyl) [16].

In order to establish unequivocally the ligand arrangement around the metal center the structure of **4** has been determined by X-ray crystallography. A structural view of **4** is depicted in Fig. 2. Important bond distances and angles are given in Table 2. The coordination geometry around the ruthenium atom is best described as a distorted trigonal bipyramid with the phosphine and chloride atoms in the equatorial position and the nitrogen atoms occupying the axial position. The N(1)–Ru–N(2) angle is 176.6(1)°. The bite angles of the chelating ligands are 82.2(1) and 80.7(1)°, respectively. The two phosphorus atoms in the equatorial plane form a relatively small P–Ru–P angle of only 96.4(1)°. This value is comparable with the respective P–Ru–P angles in the related cationic complexes $[Ru(Ph_2PCH_2CH_2PPh_2)_2Cl]^+$

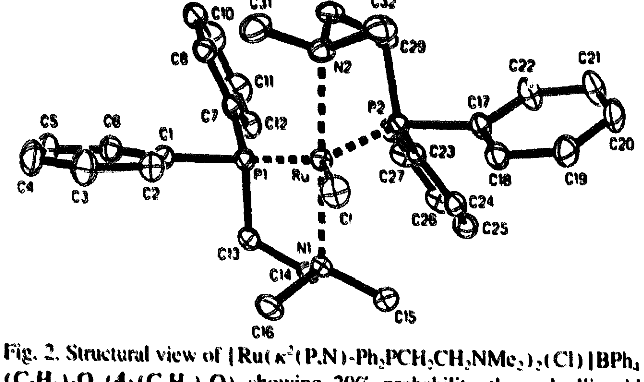


Fig. 2. Structural view of $[Ru(\kappa^2(P,N)$-$Ph_2PCH_2CH_2NMe_2)_2(Cl)]BPh_4$·$(C_2H_5)_2O$ (**4**·$(C_2H_5)_2O$) showing 20% probability thermal ellipsoids (BPh_4 and diethyl ether omitted for clarity).

(95.0(1)°) and [Ru(Cy$_2$PCH$_2$CH$_2$PCy$_2$)$_2$Cl]$^+$ (93.1(1)°). The angles between Cl–Ru–P(1) and Cl–Ru–P(2) are 138.8(1) and 124.8(1)°. The deviation from 120° appears to be electronic rather than steric in origin. An explanation for this distortion has been given in the literature [17,18].

3.4. *Reaction of 4 with CH$_3$CN, CO, and HC≡CR (R = Ph, SiMe$_3$, n-Bu)*

On treatment with CH$_3$CN, **4** affords on workup the cationic complex [Ru(κ^2(P,N)-Ph$_2$PCH$_2$CH$_2$NMe$_2$)$_2$(Cl)(CH$_3$CN)]$^+$(**5**) in 61% yield (Scheme 2). The ^{31}P{^{1}H} NMR spectrum of **5** displays a singlet at 53.7 ppm consistent with the phosphorus and nitrogen atoms being in equatorial positions adopting presumably an all *cis* (as drawn in Scheme 2) configuration with the CH$_3$CN ligand *trans* to the chlorine atom in axial position. The ^{1}H and ^{13}C{^{1}H} NMR spectra bear no remarkable features. In the IR spectrum of **5** the ν(CN) band is observed at 2253 cm^{-1}, in line with many other ruthenium CH$_3$CN complexes in this oxidation state.

Likewise, **4** reacts readily with CO to give the cationic complex [Ru(κ^2(P,N)-Ph$_2$PCH$_2$CH$_2$NMe$_2$)$_2$(Cl)(CO)]$^+$ (**6a**) in 39% yield. **6a** is configurationally unstable in solution and slowly isomerizes to both **6b** and **6c** (Scheme 2). In the IR spectrum the CO stretching frequency is observed at 1989 cm^{-1}. The ^{31}P{^{1}H} NMR spectrum of **6a** displays an AX pattern showing two doublets centered at 41.8 and 16.2 ppm. The small coupling constant of 28.1 Hz is consistent with a *cis*-P,P configuration. The ^{13}C{^{1}H} NMR spectrum of **6a** displays a low-field doublet of doublets centered at 200.0 ppm ($^2J_{PC}$ = 15.2 Hz, $^2J_{PC}$ = 103.2 Hz) assignable to the carbon atom of the CO ligand. This coupling pattern is characteristic of two phosphine moieties lying *cis* and *trans* to the CO ligand. Both ^{1}H and ^{13}C{^{1}H} NMR data indicate that the two Ph$_2$PCH$_2$CH$_2$NMe$_2$ ligands in **6a** are inequivalent giving rise to four singlets for the methyl groups.

The structure of **6a** has been confirmed by X-ray crystallography. Crystals of **6a** were grown by diffusion of diethyl ether into a solution of **6a** in CH$_2$Cl$_2$/CH$_3$OH (1:1). After 1 day, small amounts of yellow crystals **6a** together with colorless crystals **6b** were formed which could be separated manually. A structural view of **6a** is depicted in Fig. 3. Important bond distances and angles are reported in Table 2. The configuration around the metal center corresponds to a distorted octahedron with the two phosphorus atoms in *cis* position and the two nitrogen atoms in *trans* position. The N(1)–Ru–N(2) angle is 175.9(1)°. The P(1)–Ru–N(1) and P(2)–Ru–N(2) bond angles are 82.5(2) and 83.1(1)°, respectively, similar to the respective angles in complex **1**. The Ru–Cl(1) and Ru–C(33) distances are 2.427(2) and 1.984(6) Å and the Ru–C(33)–O(1) angle is 172.9(6)°C. Ru–P(1) distance (2.478(1) Å) is significantly longer than the Ru–P(2) distance (2.363(1) Å) owing to the different *trans*-influences of the CO (*trans* to P(1)) and Cl (*trans* to P(2)) ligands.

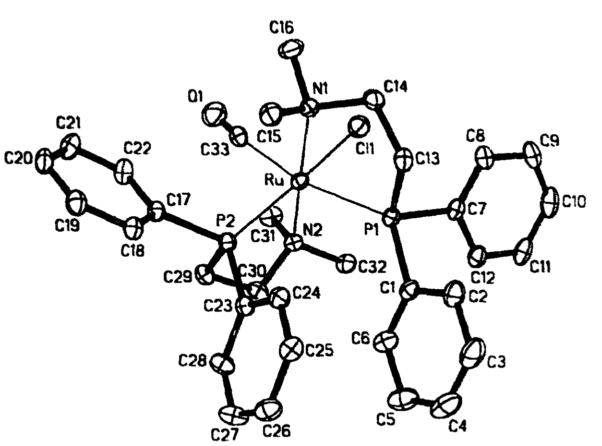


Fig. 3. Structural view of [Ru(κ^2(P,N)-Ph$_2$PCH$_2$CH$_2$NMe$_2$)$_2$(Cl)(CO)]-BPh$_4$·CH$_2$Cl$_2$ (**6a**·CH$_2$Cl$_2$) showing 20% probability thermal ellipsoids (BPh$_4$ and CH$_2$Cl$_2$ omitted for clarity).

In contrast to **6a**, the CO ligand in **6b** is bound *trans* to the chlorine atom as established by ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectroscopy. In the ^{13}C{^{1}H} NMR spectrum the CO carbon atom gives rise to a characteristic low-field triplet resonating at 197.7 (J_{PC} = 15.2 Hz). The small coupling constant is diagnostic for the phosphorus atoms in *cis* position with respect to the CO ligand. This is also consistent with the ^{31}P{^{1}H} NMR spectrum exhibiting only one signal. In the IR spectrum of **6b** the CO stretching frequency is found at 1948 cm^{-1} which is typical of a *trans* Cl–Ru–CO arrangement [12]. A structural view of **6b** is shown in Fig. 4. Selected bond distances and angles are given in Table 2. The overall slightly distorted octahedral structure of **6b** is very similar to that of **1** with the two phosphorus and nitrogen atoms in *cis* position and the chloride and CO ligands in *trans* position. The Ru–Cl(1) and Ru–C(33) distances are 2.407(1) and 1.847(3) Å and the Cl(1)–Ru–C(33) angle is 175.9(1)°C. The Ru–P and Ru–N distances as well as the angles about the metal center are in the expected ranges.

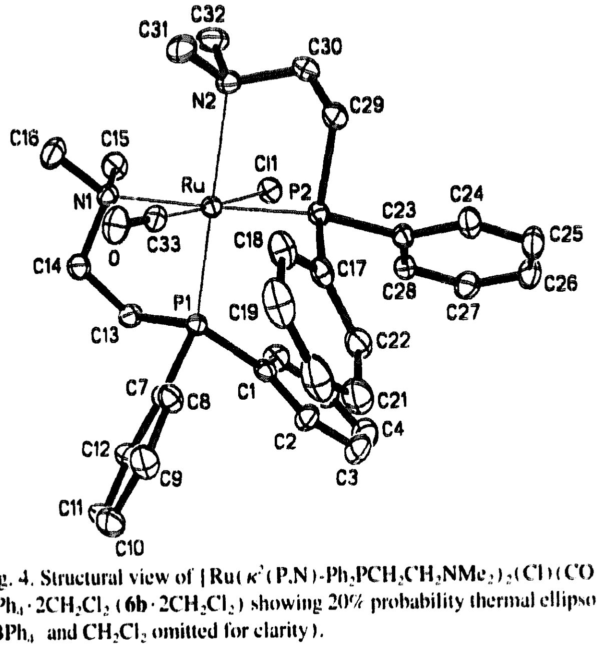


Fig. 4. Structural view of [Ru(κ^2(P,N)-Ph$_2$PCH$_2$CH$_2$NMe$_2$)$_2$(Cl)(CO)]-BPh$_4$·2CH$_2$Cl$_2$ (**6b**·2CH$_2$Cl$_2$) showing 20% probability thermal ellipsoids (BPh$_4$ and CH$_2$Cl$_2$ omitted for clarity).

When a solution of **6a** in CH_2Cl_2/CH_3OH (1:1) is stirred for 20 h at room temperature and the volume of the solution is then reduced to about one third, a white precipitate of **6c** has been obtained in 70% yield. Owing to some minor differences found in the IR and NMR spectroscopic data between **6b** and **6c** it is reasonable to assume that in **6c** a *trans*-P,P and a *trans*-N,N rather than an all *cis* configuration is adopted. Unfortunately, several attempts to grow crystals suitable for an X-ray analysis failed.

Treatment of **4** with 1 equiv of $HC\equiv CR$ (R = Ph, $SiMe_3$, n-Bu) results in the formation of the cationic vinylidene complexes $[Ru(\kappa^2(P,N)\text{-}Ph_2PCH_2CH_2NMe_2)_2(Cl)(=C=CHR)]^+$ (**7–9**) (Scheme 2). All of these complexes are air-stable both in the solid state and in solution. Characterization was by elemental analysis, IR, ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy.

The $^{31}P\{^1H\}$ NMR spectrum of **7** reveals two doublets centered at 38.1 and 32.3 ppm with a small coupling constant of 26.8 Hz indicating *cis*-P,P configuration and inequivalence of the phosphino-amine ligands. The $^{13}C\{^1H\}$ NMR spectrum displays the highly deshielded vinylidene C_α resonance as a doublet of doublets centered at 358.3 ppm (J_{CP} = 14.4 Hz, J_{CP} = 20.9 Hz). This coupling pattern places the two phosphine atoms in *cis* position with respect to the vinylidene unit and *trans* to one of the two nitrogen atoms of the $Ph_2PCH_2CH_2NMe_2$ ligands.

In contrast to **7**, the $^{31}P\{^1H\}$ NMR spectrum of **8** and **9** exhibits just one signal being diagnostic of two equivalent phosphorus atoms. In the $^{13}C\{^1H\}$ NMR spectrum of **8** and **9** the low-field triplet resonance of the C_α carbon of the vinylidene moiety is observed at 348.9 (J_{CP} = 16.1 Hz) and 351.5 ppm (J_{CP} = 16.9 Hz), respectively. This coupling pattern derives from two equivalent phosphines which are both *cis* to the vinylidene unit. However, we cannot distinguish whether the phosphorus atoms are *trans* or *cis* to one another.

3.5. Catalytic coupling of phenylacetylene with 1 and 3

Reaction of **1** or **3** with a 50-fold excess of $HC\equiv CPh$ in toluene at reflux for 20 h results in an isomeric mixture of *Z*- and *E*-butenynes in a 9:1 ratio in 70% isolated yield (30% unreacted $HC\equiv CPh$, as seen by TLC). Conversion with unchanged product distribution decreases by temperature and reaction ceases below 90°C. Other terminal alkynes $HC\equiv CR$ ($R = Bu^n$, Bu^t, CH_2OH, $SiMe_3$) gave no dimerization reaction under above mentioned conditions. For mechanistic details, it seems likely that the catalytic dimerization is initiated by a neutral vinylidene complex (**3** or a possible isomer thereof) by HCl elimination to afford a 16e alkynyl catalyst. Such an elimination might be facilitated owing to the basic NMe_2 group. In fact, it has been shown recently that neutral vinylidene complexes undergo 1,3-HCl eliminations upon treatment with base to give 16e alkynyl intermediates which were trapped in the presence of potential ligands such as CO, pyridine or CH_3CN [19]. The occurrence of such intermediates has also been surmised in the coupling reaction of terminal acetylenes catalyzed by $RuTp(PPh_3)_2Cl$ (Tp = trispyrazolylborate) and $RuCp^*(PR_3)H_3$ (R = Ph, Me, Cy) [20,21].

4. Supplementary material

Listings of atomic coordinates, anisotropic temperature factors, complete bond lengths and angles, and least-squares planes for complexes **1**, **4**, **6a** and **6b** can be obtained from the authors on request. Corresponding data have been deposited with the Cambridge Structural Database.

Acknowledgements

J.Y.S thanks the 'Fonds zur Förderung der wissenschaftlichen Forschung' for a Lise-Meitner Postdoctoral Research Fellowship (Project No. M00311-CHE).

References

[1] E. Lindner, M. Haustein, H.A. Mayer, K. Gierling, R. Fawzi and M. Steinmann, Organometallics, 14 (1995) 2246.

[2] E. Lindner, M. Haustein, R. Fawzi, M. Steinmann and P. Wegner, Organometallics, 13 (199) 5021.

[3] E. Lindner, M. Geprägs, K. Gierling, R. Fawzi and M. Steinmann, Inorg. Chem., 34 (1995) 6106.

[4] A. Bader and E. Lindner, Coord. Chem. Rev., 108 (1991) 27 and Refs. therein.

[5] H. Werner, A. Stark, M. Schulz and J. Wolf, Organometallics, 11 (1992) 1126.

[6] M. Martin, O. Gevert and H. Werner, J. Chem. Soc., Dalton Trans., (1996) 2275.

[7] H. Werner, M. Schulz and B. Windmüller, Organometallics, 14 (1995) 3659.

[8] P.S. Hallman, T.A. Stephenson and G. Wilkinson, Inorg. Synth., 12 (1970) 237.

[9] R.T. Smith and M.C. Baird, Inorg. Chim. Acta, 62 (1982) 135.

[10] (a) S. Parkin, XABS2: program for empirical absorption correction, Lawrence Livermore National Laboratory, 1995; (b) G.M. Sheldrick, SADABS: program for empirical absorption correction for Siemens Smart diffractometer data, University of Göttingen, Germany, 1996.

[11] (a) G.M. Sheldrick, SHELXS86: program for the solution of crystal structures, University of Göttingen, Germany, 1986; (b) G.M. Sheldrick, SHELXL93: program for crystal structure refinement, University of Göttingen, Germany, 1993.

[12] E. Lindner, U. Schober, R. Fawzi, W. Hiller, U. Englert and P. Wegner, Chem. Ber., 120 (1987) 1621.

[13] J.C. Briggs, C.A. McAuliffe and G. Dyer, J. Chem. Soc., Dalton Trans., (1984) 423.

[14] A. Mezzetti, A. Del Zotto, P. Rigo and N.B. Pahor, J. Chem. Soc., Dalton Trans., (1989) 1045.

[15] B. Chin, A.J. Lough, R.H. Morris, C.T. Schweitzer and C. D'Agostino, Inorg. Chem., 33 (1994) 6278.

[16] D.C. Mudalige, S.J. Rettig, B.R. James and W.R. Cullen, J. Chem. Soc., Chem. Commun., (1993) 830.

[17] I.E. Rachidi, O. Eisenstein and Y. Jean, New J. Chem., 14 (1990) 671.

[18] D.L. Thorn and R. Hoffman, New J. Chem., 3 (1979) 39.

[19] M.I. Bruce, B.C. Hall, N.N. Zaitseva, B.W. Skelton and A.H. White, J. Organomet. Chem., 522 (1996) 307.

[20] C. Slugovc, K. Mereiter, E. Zobetz, R. Schmid and K. Kirchner, Organometallics, 15 (1996) 5275.

[21] C.S. Yi and N. Liu, Organometallics, 15 (1996) 3968.