$[RuCp(PR_3)(CH_3CN)_2]PF_6$ (R = Ph, Me, Cy). Convenient Precursors for Mixed Ruthenium(II) and Ruthenium(IV) Half-Sandwich Complexes

Eva Rüba,† Walter Simanko,† Klaus Mauthner,† Kamran M. Soldouzi,† 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 April 7, 1999

The reaction of $[RuCp(CH_3CN)_3]PF_6$ (**1**) with the monodentate ligands PR_3 (R = Me, Ph, Cy) affords the cationic complexes $[RuCp(PR_3)(CH_3CN)_2]PF_6$ (**2a**−**c**) in high yields. The CH_3CN exchange kinetics has been studied by NMR, suggesting a dissociative mechanism. Due to van der Waals repulsive interactions between PCy_3 and the nitrile ligands, CH_3CN is particularly labile in **2c**. The chemistry of **2a**−**c** has been further investigated with respect to substitution and oxidative addition.

Introduction

The chemistry of cyclopentadienylruthenium complexes has been based largely on the precursors $RuCp(PPh_3)_2Cl$ and $RuCp(CO)_2Cl$.[1] However, the selective replacement of either PPh_3 or CO turned out to be very difficult, limiting the synthetic utility with respect to the introduction of reactive and thermally sensitive ligand systems. Therefore, more labile systems, including $[RuCp(CH_3CN)_3]^+$ (**1**),[2] RuCp(COD)Cl (COD = 1,5-cyclooctadiene),[3] and $RuCp(PPh_3)(\eta^2(O,O)\text{-}CH_3COO)$,[4] have been developed, making available the respective pseudo coordinatively unsaturated species $[RuCp]^+$,[5−7] RuCpCl,[3,8,9] and $[RuCp(PPh_3)]^+$ [10] under mild conditions. These intermediates react with potential, mostly chelating, ligands to give a variety of neutral and cationic cyclopentadienylruthenium(II) complexes.

Of the above complexes, we find the cationic complex **1** most promising for further study, since the CH_3CN ligands can be replaced in a controlled and stepwise fashion. Thus, using monodentate $P(OMe)_3$ under various conditions, any mixed complex $[RuCp(P(OMe)_3)(CH_3CN)_2]^+$, $[RuCp(P(OMe)_3)_2(CH_3CN)]^+$, and $[RuCp(P(OMe)_3)_3]^+$ is obtainable.[2] Recently, **1** has been converted to $[RuCp(\eta^1(P)\text{-}2\text{-}(PPh_2)\{C_6H_4CH_2(OR)_2\})(CH_3CN)_2]CF_3SO_3$ (R = Me, Et).[11] Thus, **1** might be a suitable starting material for providing mixed half-sandwich complexes of the type $[RuCp(L)(L')(L'')]^+$. In the present paper we report the synthesis, structure, and exchange kinetics of $[RuCp(L)(CH_3CN)_2]^+$ (L = PPh_3, PMe_3, PCy_3). In addition, the synthesis of a range of mixed Ru(II) and Ru(IV) half-sandwich complexes derived therefrom is described.

Experimental Section

General Information. All manipulations were performed under an inert atmosphere of argon by using Schlenk techniques. All chemicals were standard reagent grade and used without further purification. The solvents were purified according to standard procedures.[12] The deuterated solvents were purchased from Aldrich and dried over 4 Å molecular sieves. TLC was performed on Riedel-deHaen silica gel 60 F 254 TLC sheets (layer thickness 0.2 mm). For column chromatography, silica gel grade 60 (70−230 mesh, 60 Å), purchased from Merck, or neutral MN-aluminum oxide, purchased from Macherey-Nagel, was used. $[RuCp(CH_3CN)_3]PF_6$ (**1**) and was prepared according to the literature procedure.[2] ^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 H_3PO_4 (85%). Infrared spectra were recorded on a Perkin-Elmer 16PC FTIR spectrometer. Microanalyses were done by the Microanalytical Laboratories at the University of Vienna.

$[RuCp(PPh_3)(CH_3CN)_2]PF_6$ (2a). To a solution of **1** (247 mg, 0.568 mmol) in CH_2Cl_2 (8 mL) was added PPh_3 (149 mg, 0.568 mmol), and the mixture was stirred for 2 h at room temperature. After removal of the solvent, a yellow powder was obtained, which was collected on a glass frit, washed with Et_2O (3 × 5 mL), and dried under vacuum. Yield: 350 mg (94%). Anal. Calcd for $C_{27}H_{26}F_6N_2P_2Ru$: C, 49.47; H, 4.00; N, 4.27. Found: C, 49.56; H, 3.97; N, 4.13. ^1H NMR (δ, $CDCl_3$,

* To whom correspondence should be addressed. E-mail: kkirch@mail.zserv.tuwien.ac.at.
† Institute of Inorganic Chemistry.
‡ Institute of Mineralogy, Crystallography, and Structural Chemistry.

(1) Bennett, M. A.; Bruce, M. I.; Matheson, T. W. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon: Oxford, U.K., 1982; Vol. 4, pp 775−796.
(2) Gill, T. P.; Mann, K. R. *Organometallics* **1982**, *1*, 485.
(3) (a) Albers, M. O.; Robinson, D. J.; Shaver, A.; Singleton, E. *Organometallics* **1986**, *5*, 2199. (b) Kirchner, K.; Mereiter, K.; Umfahrer, A.; Schmid, R. *Organometallics* **1994**, *13*, 1886.
(4) Daniel, T.; Mahr, N.; Barun, T.; Werner, H. *Organometallics* **1993**, *12*, 1475.
(5) Simanko, W.; Tesch, W.; Sapunov, V. N.; Schmid, R.; Kirchner, K.; Coddington, J.; Wherland, S. *Organometallics* **1998**, *17*, 5674.
(6) Slugovc, C.; Mereiter, K.; Schmid, R.; Kirchner, K. *Organometallics* **1999**, *18*, 1011.
(7) McNair, A. M.; Mann, K. R. *Inorg. Chem.* **1986**, *25*, 2519.
(8) Albers, M. O.; Liles, D. C.; Robinson, D. J.; Shaver, A.; Singleton, E. *Organometallics* **1987**, *6*, 2347.
(9) Kirchner, K.; Mereiter, K.; Umfahrer, A.; Schmid, R. *Organometallics* **1994**, *13*, 1886.
(10) Braun, T.; Gevert, O.; Werner, H. *J. Am. Chem. Soc.* **1995**, *117*, 7291.
(11) Grotjahn, D. B.; Lo, H. C. *Organometallics* **1996**, *15*, 2860.
(12) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon: New York, 1988.

10.1021/om990245o CCC: $18.00
Publication on Web 09/13/1999

20 °C): 7.47−7.28 (m, 15H, Ph), 4.43 (s, 5H, Cp), 2.12 (d, J_{HP} = 1.1 Hz, 6H, CH_3). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 20 °C): 133.7 (d, $^2J_{CP}$ = 11.1 Hz, 6C, $Ph^{2,6}$), 133.6 (d, $^1J_{CP}$ = 42.5 Hz, 3C, Ph^1), 130.5 (3C, Ph^4), 128.8 (d, $^3J_{CP}$ = 9.7 Hz, 6C, $Ph^{3,5}$), 127.7 (2C, N≡*C*), 77.1 (5C, Cp), 3.8 (2C, *C*H_3). $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$, 20 °C): 51.7 (PPh_3), −143.5 ($^1J_{PF}$ = 712.3 Hz, PF_6). IR (KBr, cm^{-1}): 2285 (m, ν_{CN}).

[RuCp(PMe$_3$)(CH$_3$CN)$_2$]PF$_6$ (2b). This complex has been prepared analogously to **2a** with **1** (100 mg, 0.230 mmol) and PMe_3 (24 μL, 0.230 mmol) as the starting materials. Yield: 100 mg (93%). Anal. Calcd for $C_{12}H_{20}F_6N_2P_2Ru$: C, 30.71; H, 4.30; N, 5.97. Found: C, 30.88; H, 4.46; N, 5.86. ^1H NMR (δ, CD_3NO_2, 20 °C): 4.52 (s, 5H, Cp), 2.38 (d, J_{HP} = 1.6 Hz, 6H, CH_3), 1.54 (d, $^2J_{HP}$ = 9.8 Hz, 9H, PMe_3). $^{13}C\{^1H\}$ NMR (δ, CD_3NO_2, 20 °C): 128.1 (2C, N≡*C*), 76.0 (d, J_{CP} = 2.3 Hz, 5C, Cp), 18.0 (d, $^2J_{CP}$ = 28.7 Hz, 3C, $P(CH_3)_3$), 3.7 (d, J_{CP} = 1.0 Hz, *C*H_3). $^{31}P\{^1H\}$ NMR (δ, CD_3NO_2, 20 °C): 5.4 (PMe_3), −145.9 ($^1J_{PF}$ = 712.0 Hz, PF_6). IR (KBr, cm^{-1}): 2276 (m, ν_{CN}).

[RuCp(PCy$_3$)(CH$_3$CN)$_2$]PF$_6$ (2c). This complex has been prepared analogously to **2a** with **1** (100 mg, 0.230 mmol) and PCy_3 (65 mg, 0.230 mmol) as the starting materials. Yield: 146 mg (94%). Anal. Calcd for $C_{27}H_{44}F_6N_2P_2Ru$: C, 48.14; H, 6.58; N, 4.16. Found: C, 48.33; H, 6.74; N, 3.99. ^1H NMR (δ, $CDCl_3$, 20 °C): 4.51 (s, 5H, Cp), 2.42 (s, 6H, *CH*$_3$), 2.03−1.77 (m, 18H, Cy), 1.42−1.17 (m, 15H, Cy). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 20 °C): 128.7 (2C, N≡*C*), 75.6 (d, J_{CP} = 2.0 Hz, 5C, Cp), 37.7 (bd, $^1J_{CP}$ = 18.1 Hz, 3C, Cy^1), 30.6 (s, 6C, Cy^4), 28.4 (bd, $^2J_{CP}$ = 10.5 Hz, 6C, $Cy^{2,6}$), 27.1 (bs, 3C, $Cy^{3,5}$), 4.6 (s, *C*H_3). $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$, 20 °C): 47.8 (PCy_3), −143.6 ($^1J_{PF}$ = 712.0 Hz, PF_6). IR (KBr, cm^{-1}): 2282, 2271 (m, ν_{CN}).

[RuCp(η^2:η^2-COD)(PPh$_3$)]PF$_6$ (3a). A solution of **2a** (253 mg, 0.386 mmol) in 5 mL of acetone was treated with 1.5 equiv of COD (71 μL, 0.578 mmol), and the mixture was stirred for 1 h at room temperature. After reduction of the volume of the solution to about 2 mL, addition of Et_2O afforded a yellow powder, which was collected on a glass frit, washed with Et_2O (3 × 5 mL), and dried under vacuum. Yield: 0.244 mg (93%). Anal. Calcd for $C_{31}H_{32}F_6P_2Ru$: C, 54.63; H, 4.73. Found: C, 54.62; H, 4.88. ^1H NMR (δ, acetone-d_6, 20 °C): 7.70−7.53 (m, 15 H, Ph), 5.35 (m, 2H, COD), 5.08 (d, $^3J_{HP}$ = 1.0 Hz, 5H, Cp), 4.31 (m, 2H, COD), 2.60 (m, 2H, COD), 2.07 (m, 2H, COD), 1.55 (m, 2H, COD), 1.23 (m, 2H, COD). $^{13}C\{^1H\}$ NMR (δ, acetone-d_6, 20 °C): 135.7 (d, $^2J_{CP}$ = 9.3 Hz, 6C, $Ph^{2,6}$), 134.7 (d, $^1J_{CP}$ = 48.6 Hz, 3C, Ph^1), 131.9 (d, $^4J_{CP}$ = 2.8 Hz, 3C, Ph^4), 129.4 (d, $^3J_{CP}$ = 9.7 Hz, 6C, $Ph^{3,5}$), 89.9 (d, $^2J_{CP}$ = 1.0 Hz, 5C, Cp), 80.5 (d, $^2J_{CP}$ = 5.6 Hz, 2C, COD), 79.0 (d, $^2J_{CP}$ = 1.0 Hz, 2C, COD), 32.0 (2C, COD), 27.9 (d, $^3J_{CP}$ = 1.4 Hz, 2C, COD). $^{31}P\{^1H\}$ NMR (δ, acetone-d_6, 20 °C): 46.3 (*P*Ph_3), −142.7 ($^1J_{PF}$ = 707.0 Hz, *P*F_6).

[RuCp(η^2:η^2-COD)(PMe$_3$)]PF$_6$ (3b). To a solution of **2b** (70 mg, 0.149 mmol) in acetone (3 mL) was added COD (92 μL, 0.745 mmol), and the mixture was stirred for 2 h at room temperature. After removal of the solvent, a yellow powder was obtained, which was collected on a glass frit, washed with Et_2O (3 × 5 mL), and dried under vacuum. Yield: 60 mg (81%). Anal. Calcd for $C_{16}H_{26}F_6P_2Ru$: C, 38.79; H, 5.29. Found: C, 38.94; H, 5.44. ^1H NMR (δ, acetone-d_6, 20 °C): 5.35 (d, $^3J_{HP}$ = 1.1 Hz, 5H, Cp), 4.89 (m, 2H, COD), 4.75 (m, 2H, COD), 2.49 (m, 2H, COD), 2.35 (m, 2H, COD), 2.11−2.05 (m, 4H, COD), 1.92 (d, $^2J_{HP}$ = 9.7 Hz, 9H, PMe_3). $^{13}C\{^1H\}$ NMR (δ, acetone-d_6, 20 °C): 87.4 (d, $^2J_{CP}$ = 1.2 Hz, 5C, Cp), 77.2 (2C, COD), 75.9 (d, $^2J_{CP}$ = 5.5 Hz, 2C, COD), 32.2 (2C, COD), 29.3 (d, $^3J_{CP}$ = 2.4 Hz, 2C, COD), 20.5 (d, $^1J_{CP}$ = 31.7 Hz, 3C, P*Me*$_3$). $^{31}P\{^1H\}$ NMR (δ, acetone-d_6, 20 °C): 7.3 (*P*Me_3), −142.7 ($^1J_{PF}$ = 708.3 Hz, *P*F_6).

[RuCp(η^4-CH$_2$=CHCH=CH$_2$)(PMe$_3$)]PF$_6$ (3c). A solution of **2b** (100 mg, 0.213 mmol) in CH_2Cl_2 (3 mL) was saturated with 1,3-butadiene and then stirred for 2 h at room temperature. After removal of the solvent, a gray powder was obtained, which was collected on a glass frit, washed with Et_2O (3 × 5 mL), and dried under vacuum. Yield: 85 mg (90%). Anal. Calcd for $C_{12}H_{20}F_6P_2Ru$: C, 32.66; H, 4.57. Found: C, 33.01; H, 4.88. ^1H NMR (δ, acetone-d_6, 20 °C): 5.74 (m, 2H, CH_2=C*H*), 5.41 (d, $^3J_{HP}$ = 0.9 Hz, 5H, Cp), 3.12 (m, $^3J_{HHcis}$ = 7.2 Hz, 2H, CH_2=CH), 1.88 (d, $^2J_{HP}$ = 10.2 Hz, 9H, PMe_3), 0.25 (m, $^3J_{HHtrans}$ = 9.7 Hz, $^3J_{HP}$ = 14.6 Hz, 2H, CH_2=CH). $^{13}C\{^1H\}$ NMR (δ, acetone-d_6, 20 °C): 84.7 (5C, Cp), 80.9 (d, $^2J_{CP}$ = 2.2 Hz, 2C, CH_2=*C*H), 43.3 (d, $^2J_{CP}$ = 4.9 Hz, 2C, *C*H_2=CH), 19.8 (d, $^1J_{CP}$ = 37.2 Hz, 3C, P*Me*$_3$). $^{31}P\{^1H\}$ NMR (δ, acetone-d_6, 20 °C): 13.6 (*P*Me_3), −142.7 ($^1J_{PF}$ = 707.6 Hz, *P*F_6).

[RuCp(η^4-CH$_2$=C(Me)CH=CH$_2$)(PMe$_3$)]PF$_6$ (3d). To a solution of **2b** (110 mg, 0.234 mmol) in acetone (3 mL) was added isoprene (100 μL, 1 mmol), and the mixture was stirred for 2 h at room temperature. After removal of the solvent, a bright powder was obtained, which was collected on a glass frit, washed with Et_2O (3 × 5 mL), and dried under vacuum. Yield: 90 mg (84%). Anal. Calcd for $C_{13}H_{22}F_6P_2Ru$: C, 34.29; H, 4.87. Found: C, 34.42; H, 4.96. ^1H NMR (δ, acetone-d_6, 20 °C): 5.69 (m, 1H, CH_2=C*H*CMe=CH_2), 5.37 (d, $^3J_{HP}$ = 1.0 Hz, 5H, Cp), 3.13 (m, 1H, CH_2=CHCMe=CH_2), 3.03 (m, $^3J_{HHcis}$ = 7.4 Hz, 1H, CH_2=CHCMe=CH_2), 2.34 (s, 3H, CH_2=CHC*Me*=CH_2), 1.84 (d, $^2J_{HP}$ = 10.0 Hz, 9H, PMe_3), 0.16−0.06 (m, 2H, CH_2=CHCMe=CH_2). $^{13}C\{^1H\}$ NMR (δ, acetone-d_6, 20 °C): 102.3 (d, $^2J_{CP}$ = 2.2 Hz, 1C, CH_2=CH*C*Me=CH_2), 87.7 (5C, Cp), 81.9 (d, $^2J_{CP}$ = 1.2 Hz, 1C, CH_2=*CH**C*Me=CH_2), 45.2 (d, $^2J_{CP}$ = 5.5 Hz, 1C, *C*H_2=CHCMe=CH_2), 42.4 (d, $^2J_{CP}$ = 4.9 Hz, 1C, CH_2=CHCMe=*C*H_2), 24.9 (1C, CH_2=CHC*Me*=CH_2), 20.4 (d, $^1J_{CP}$ = 36.6 Hz, 3C, P*Me*$_3$). $^{31}P\{^1H\}$ NMR (δ, acetone-d_6, 20 °C): 13.5 (*P*Me_3), −142.7 ($^1J_{PF}$ = 707.8 Hz, *P*F_6).

[RuCp(PPh$_3$)(py)(CH$_3$CN)]PF$_6$ (4a). To a solution of **2a** (100 mg, 0.159 mmol) in acetone (3 mL) was added pyridine (12.9 μL, 0.159 mmol). The solution was stirred at room temperature for 1 h. The reaction mixture was evaporated to dryness, and the residue was redissolved in acetone (1 mL). Upon addition of Et_2O (4 mL), a bright yellow precipitate was formed, which was collected on a glass frit, washed with Et_2O (3 × 2 mL), and dried in vacuo. Yield: 90 mg (82%). Anal. Calcd for $C_{30}H_{28}F_6N_2P_2Ru$: C, 51.95; H, 4.07; N, 4.04. Found: C, 52.06; H, 4.33; N, 3.88. ^1H NMR (δ, $CDCl_3$, 20 °C): 8.54 (ddd, $^3J_{HH}$ = 4.9 Hz, $^4J_{HH}$ = 1.6, $^4J_{HP}$ = 1.4, 2H, $py^{2,6}$), 7.74−7.66 (m, 1H, py^4), 7.62−7.32 (m, 9H, $py,^{3,5}$ Ph), 7.17−7.07 (m, 8H, Ph), 4.44 (s, 5H, Cp), 2.14 (d, $^5J_{HP}$ = 1.4 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 20 °C): 157.0 (d, $^2J_{CP}$ = 2.4 Hz, 2C, $py^{2,6}$), 137.2 (s, 1C, py^4), 134.0 (d, $^1J_{CP}$ = 40.1 Hz, 3C, Ph^1), 133.8 (d, $^2J_{CP}$ = 11.2 Hz, 6C, $Ph^{2,6}$), 132.8 (d, $^3J_{CP}$ = 10.0 Hz, 1C, N≡*C*), 130.9 (d, $^4J_{CP}$ = 2.4 Hz, 3C, Ph^4), 129.3 (d, $^3J_{CP}$ = 10.0 Hz, 6C, $Ph^{3,5}$), 125.8 (s, 2C, $py^{3,5}$), 77.5 (d, $^2J_{CP}$ = 2.4 Hz, 5C, Cp), 4.30 (s, 1C, *C*H_3). $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$, 20 °C): 54.0 (*P*Ph_3), −143.4 ($^1J_{PF}$ = 712.1 Hz, *P*F_6).

[RuCp(PPh$_3$)(PMe$_3$)(CH$_3$CN)]PF$_6$ (4b). To a solution of **2b** (100 mg, 0.213 mmol) in acetone (3 mL) was added PPh_3 (56 mg, 0.213 mmol), and the mixture was stirred for 2 h at room temperature. After removal of the solvent, a yellow powder was obtained, which was collected on a glass frit, washed with Et_2O (3 × 5 mL), and dried under vacuum. Yield: 140 mg (95%). Anal. Calcd for $C_{28}H_{32}F_6NP_3Ru$: C, 48.70; H, 4.67; N, 2.03. Found: C, 48.88; H, 4.88; N, 1.91. ^1H NMR (δ, acetone-d_6, 20 °C): 7.52−7.39 (m, 15 H, Ph), 4.72 (s, 5H, Cp), 2.36 (vt, $^5J_{HP}$ = 1.8 Hz, $^5J_{HP}$ = 1.4 Hz, 3H, N≡C*C*H_3), 1.35 (dd, $^2J_{HP}$ = 9.5 Hz, $^4J_{HP}$ = 0.7 Hz, 9H, PMe_3). $^{13}C\{^1H\}$ NMR (δ, acetone-d_6, 20 °C): 137.5 (dd, $^1J_{CP}$ = 42.1 Hz, $^3J_{CP}$ = 1.5 Hz, 3C, Ph^1), 135.2 (d, $^2J_{CP}$ = 11.0 Hz, 6C, $Ph^{2,6}$), 131.8 (d, $^4J_{CP}$ = 2.4 Hz, 3C, Ph^4), 130.0 (d, $^3J_{CP}$ = 9.8 Hz, 6C, $Ph^{3,5}$), 130.0 (1C, N≡*C*CH$_3$), 83.0 (vt, $^4J_{CP}$ = 1.8 Hz, 5C, Cp), 21.1 (d, $^1J_{CP}$ = 29.9 Hz, $^3J_{CP}$ = 1.2 Hz, 3C, P*Me*$_3$), 4.7 (s, 1C, N≡*C*CH$_3$). $^{31}P\{^1H\}$ NMR (δ, acetone-d_6, 20 °C): 53.3 (d, $^2J_{PP}$ = 40.7 Hz, *P*Ph_3), 1.0 (d, $^2J_{PP}$ = 40.7 Hz, *P*Me_3), −142.7 ($^1J_{PF}$ = 707.0 Hz, *P*F_6).

[RuCp(PPh$_3$)(PCy$_3$)(CH$_3$CN)]PF$_6$ (4c). This complex has been prepared analogously to **4b** with **2a** and PCy_3 as the starting materials: Yield: 93%. Anal. Calcd for $C_{43}H_{56}F_6NP_2$-

Ru: C, 59.78; H, 6.53; N, 1.62. Found: C, 59.81; H, 6.66; N, 1.76. ^{1}H NMR (δ, acetone-d_6, 20 °C): 7.50 (m, 15 H, Ph), 4.78 (s, 5H, Cp), 2.47 (vt, $^5J_{HP}$ = 1.4 Hz, 3H, N≡C*CH$_3$*), 2.10−1.0 (m, 33H, PCy$_3$). ^{13}C{^{1}H} NMR (δ, acetone-d_6, 20 °C): 137.5−129,0 (18C, Ph), 132.7 (1C, N≡*C*), 81.5 (vt, $^4J_{CP}$ = 2.0 Hz, 5C, Cp), 39.5−27.0.1 (18C, P*Cy$_3$*), 4.5 (s, 1C, *C*H$_3$). ^{31}P{^{1}H} NMR (δ, acetone-d_6, 20 °C): 44.6 (d, $^2J_{PP}$ = 33.1 Hz, *P*Ph$_3$), 39.6 (d, $^2J_{PP}$ = 33.1 Hz, *P*Cy$_3$), −142.6 ($^1J_{PF}$ = 707.5 Hz, *P*F$_6$).

[RuCp(PPh$_3$)(AsPh$_3$)(CH$_3$CN)]PF$_6$ (4d). This complex has been prepared analogously to **4b** with **2a** and AsPh$_3$. Yield: 96%. Anal. Calcd for $C_{43}H_{38}F_6NP_2AsRu$: C, 56.09; H, 4.16. Found: C, 56.13; H, 4.05. ^{1}H NMR (δ, acetone-d_6, 20 °C): 7.53−7.09 (m, 30H, *Ph*), 4.58 (s, 5H, *Cp*), 2.17 (d, J_{PH} = 1.54 Hz, 3H, *CH$_3$*). ^{13}C{^{1}H} NMR (δ, acetone-d_6, 20 °C): 139−129 (36C, *Ph*), 130 (s, 1C, *C*N), 81.6 (d, J_{CP} = 2 Hz, 5C, *Cp*), 4.3 (s, 1C, *CH$_3$*). ^{31}P{^{1}H} NMR (δ, acetone-d_6, 20 °C): 46.5 (*P*Ph$_3$), −143.4 (*P*F$_6$).

[RuCp(η^2:η^2-COD)(CH$_3$CN)]PF$_6$ (5a). To a solution of **1** (187 mg, 0.430 mmol) in CH_2Cl_2 (8 mL) was added COD (80 μL, 0.648 mmol), and the mixture was stirred for 2 h at room temperature. After removal of the solvent, a yellow powder was obtained, which was collected on a glass frit, washed with Et_2O (3 × 5 mL), and dried under vacuum. Yield: 192 mg (97%). Anal. Calcd for $C_{15}H_{20}F_6NPRu$: C, 39.13; H, 4.38; N, 3.04. Found: C, 39.36; H, 4.17; N, 2.83. ^{1}H NMR (δ, acetone-d_6, 20 °C): 5.67 (m, 2H, COD), 5.29 (s, 5H, Cp), 4.37 (m, 2H, COD), 2.68 (s, 3H, N≡C), 2.42 (m, 2H, COD), 2.30−2.05 (m, 6H, COD). ^{13}C{^{1}H} NMR (δ, acetone-d_6, 20 °C): 133.2 (1C, N≡C), 86.8 (2C, COD), 85.5 (2C, COD), 85.4 (5C, Cp), 32.3 (2C, COD), 28.00 (2C, COD), 4.33 (1C, N≡C*CH$_3$*).

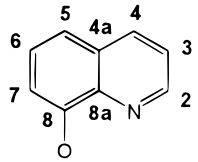
[RuCp(η^4-CH$_2$=CHCH=CH$_2$)(CH$_3$CN)]PF$_6$ (5b). A solution of **1** (2.98 g, 6.86 mmol) in CH_2Cl_2 (300 mL) was saturated with 1,3-butadiene and was then stirred at room temperature for 24 h. During that time the solution was purged several times with 1,3-butadiene. On removal of the solvent, a bright yellow solid was obtained, which was collected on a glass frit, washed with Et_2O, and dried under vacuum. Yield: 2.38 g (85%). Anal. Calcd for $C_{11}H_{14}F_6NPRu$: C, 32.52; H, 3.47; N, 3.45. Found: C, 32.41; H, 3.30; N, 3.50. ^{1}H NMR (δ, acetone-d_6, 20 °C): 5.88 (m, 2H), 5.41 (s, 5H), 4.13 (d, 2H, J = 7.5 Hz), 2.64 (s, 3H), 1.52 (d, 2H, J = 9.8 Hz).^{13}C{^{1}H} NMR (δ, acetone-d_6, 20 °C): 136.1 (1C, N≡C), 89.9 (2C, CH$_2$=*C*H), 85.4 (5C, Cp), 53.4 (2C, CH=*C*H$_2$), 5.1 (1C, CH$_3$).

[RuCp(Me$_2$NCH$_2$CH$_2$NMe$_2$)(CH$_3$CN)]PF$_6$ (5c). 1 (349 mg, 0.803 mmol) and Me$_2$NCH$_2$CH$_2$NMe$_2$ (112.1 mg, 0.964 mmol) in Et_2O (15 mL) were stirred at room temperature for 15 h. After evaporation of the solvent, the pale yellow residue was dried in vacuo. Yield: 350 mg (93%). Anal. Calcd for $C_{13}H_{24}F_6N_3PRu$: C, 33.34; H, 5.16; N, 8.97. Found: C, 33.38; H, 5.19; N, 9.09. ^{1}H NMR (δ, acetone-d_6, −30 °C): 4.10 (s, 5H), 3.29 (s, 6H), 2.75 (s, 6H), 2.69 (m, 2H), 2.63 (s, 3H), 2.42 (m, 2H). ^{3}C{^{1}H} NMR (δ, acetone-d_6, −30 °C): CN not observed, 68.5 (s, 5C, Cp), 62.6 (s, 2C, NCH$_3$), 59.0 (s, 2C, CH$_2$), 54.7 (s, 2C, NCH$_3$), 4.6 (CH$_3$). IR (KBr, cm^{-1}): 2254 (s, ν_{CN}).

[RuCp(Ph$_2$PCH$_2$CH$_2$NMe$_2$)(CH$_3$CN)]PF$_6$ (5d). A solution of **1** (145 mg, 0.334 mmol) was treated with Ph$_2$PCH$_2$CH$_2$NMe$_2$ (87 mg, 0.334 mmol) in acetone (3 mL). After the mixture was stirred for 1 h, the product was precipitated by addition of Et_2O (25 mL). Yield: 185 mg (91%). Anal. Calcd for $C_{23}H_{28}F_6N_2P_2Ru$: C, 45.32; H, 4.63; N, 4.60. Found: C, 45.38; H, 4.89; N, 4.39. ^{1}H NMR (δ, CD_3NO_2, 20 °C): 7.18−7.42 (m, 10H, Ph), 4.47 (s, 5H, Cp), 3.07 (s, 3H, NMe), 3.02 (s, 3H, NMe), 2.62−2.30 (m, 4H), 1.96 (s, 3H, Me). ^{13}C{^{1}H} NMR (δ, CD_3NO_2, 20 °C): 139.1 (d, $^1J_{CP}$ = 47.6 Hz, 1C, Ph^1), 135.0 (d, $^2J_{CP}$ = 11.6 Hz, 2C, Ph^{2,6}), 132.5 (d, $^2J_{CP}$ = 11.1 Hz, 2C, Ph$^{2',6'}$), 131.9 (d, $^4J_{CP}$ = 2.3 Hz, 1C, Ph^4), 131.3 (d, $^4J_{CP}$ = 2.3 Hz, 1C, Ph$^{4'}$), 131.2 (d, $^1J_{CP}$ = 41.6 Hz, 1C, Ph$^{1'}$), 130.2 (d, $^3J_{CP}$ = 10.2 Hz, 2C, Ph^{3,5}), 130.05 (d, $^3J_{CP}$ = 10.2 Hz, 2C, Ph$^{3',5'}$), 130.0 (d, $^3J_{CP}$ = 8.3 Hz, 1C, N*C*), 76.9 (d, $^2J_{CP}$ = 2.8 Hz, 5C, Cp), 64.0 (d, $^2J_{CP}$ = 6.5 Hz, PCH$_2$*C*H$_2$N), 58.7 (1C, N*Me$_2$*), 57.8 (1C, N*Me$_2$*), 30.0 (d, $^1J_{CP}$ = 22.2 Hz, P*C*H$_2$CH$_2$N), 3.6 (1C, N≡C*CH$_3$*). ^{31}P{^{1}H} NMR (δ, CD_3NO_2, 20 °C): 66.3 (PPh$_2$), −145.9 ($^1J_{PF}$ = 711.7 Hz, PF$_6$).

RuCp(acac)(CO) (6a). To a solution of **1** (100 mg, 0.230 mmol) in CH_2Cl_2 (5 mL) were added acetylacetone (23.6 μL, 0.230 mmol) and NEt_3 (32 μL, 0.230 mmol), and the reaction mixture was stirred at room temperature for 30 min. Subsequently, CO was bubbled through the solution for 1 min, whereupon the reaction mixture changed from dark brown to yellow. The solvent was removed under reduced pressure, and the residue was dissolved in 3 mL of Et_2O. Insoluble materials were removed by filtration. The filtrate was evaporated to dryness, resulting in a dark yellow oil which slowly transforms into small shiny crystals. Yield: 55 mg (81%). Anal. Calcd for $C_{11}H_{12}O_3Ru$: C, 45.05; H, 4.12. Found: C, 45.08; H, 4.21. ^{1}H NMR (δ, $CDCl_3$, 20 °C): 5.31 (s, 1H, MeCOC*H*COMe), 4.92 (s, 5H, Cp), 1.92 (s, 6H, *Me*COCHCO*Me*). ^{13}C{^{1}H} NMR (δ, $CDCl_3$, 20 °C): 204.9 (1C, *C*O), 189.2 (2C, Me*C*OCH*C*OMe), 102.0 (1C, MeCO*C*HCOMe), 80.1 (5C, Cp), 27.6 (2C, *Me*COCHCO*Me*). IR (CH_2Cl_2, cm^{-1}): 1949 (s, ν_{CO}).

RuCp(oxinate)(CO) (6b). To a solution of **1** (150 mg, 0.345 mmol) in CH_2Cl_2 (5 mL) was added potassium 8-quinolin-8-olate (oxinate) (74 mg, 0.345 mmol), and the reaction mixture was stirred at room temperature for 30 min. Subsequently, CO was bubbled through the solution for 1 min, whereupon the reaction mixture changed from dark brown to yellow. The solvent was evaporated under reduced pressure. The residue was redissolved in 3 mL of Et_2O, and insoluble materials were removed by filtration. The filtrate was evaporated to dryness, resulting in a dark yellow oil. The product was purified by column chromatography (silica gel). The column was eluted with CH_2Cl_2 until the solution was colorless and then with acetone, at which point the first brown band was collected. The solvent was removed under reduced pressure, resulting in a dark yellow oil, which was dried under vacuum. Yield: 50 mg (43%). Anal. Calcd for $C_{15}H_{11}NO_2Ru$: C, 53.25; H, 3.28; N, 4.14. Found: C, 53.44; H, 3.35; N, 3.80. ^{1}H NMR (δ, $CDCl_3$, 20 °C): 8.59 (dd, $^3J_{HH}$ = 4.8 Hz, $^4J_{HH}$ = 1.2 Hz, 1H, H^2), 8.06 (dd, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 1.2 Hz, 1H, H^4), 7.35 (dd, dd, $^3J_{HH}$ = 8.0 Hz, $^3J_{HH}$ = 7.6 Hz, 1H, H^6), 7.15 (dd, $^3J_{HH}$ = 8.4 Hz, $^3J_{HH}$ = 4.8 Hz, 1H, H^3), 6.99 (d, $^3J_{HH}$ = 8.0 Hz, 1H, H^5), 6.81 (d, $^3J_{HH}$ = 8.0 Hz, 1H, H^7), 5.03 (s, 5H, Cp). ^{13}C{^{1}H} NMR (δ, $CDCl_3$, 20 °C): 202.5 (1C, *C*O), 171.6 (1C, C^8), 152.5 (1C, C^2), 146.8 (1C, C^{8a}), 137.5 (1C, C^4), 131.0 (1C, C^{4a}), 130.7 (1C, C^6), 121.9 (1C, C^3), 115.6 (1C, C^5), 110.4 (1C, C^7), 81.6 (5C, Cp).



RuCp(5-Cl-oxinate)(CO) (6c). To a solution of **1** (100 mg, 0.230 mmol) in CH_2Cl_2 (5 mL) was added 5-chloroquinolin-8-olate (5-Cl-oxinate), potassium salt (50 mg, 0.230 mmol), and the reaction mixture was stirred at room temperature for 30 min. Subsequently, CO was bubbled through the solution for 1 min, whereupon the reaction mixture changed from dark brown to yellow. The solvent was evaporated under reduced pressure. The residue was extracted with 100 mL of Et_2O. The filtrate was evaporated to dryness, resulting in a dark yellow oil, which was dried under vacuum. Yield: 45 mg (52%). Anal. Calcd for $C_{15}H_{10}ClNO_2Ru$: C, 48.33; H, 2.70; N, 3.76. Found: C, 48.51; H, 2.85; N, 3.83. DC: R_f(CH_2Cl_2/acetone 1/1 (v/v)) = 0.72). ^{1}H NMR (δ, $CDCl_3$, 20 °C): 8.66 (d, $^3J_{HH}$ = 4.7 Hz, 1H, H^2), 8.38 (d, $^3J_{HH}$ = 8.6 Hz, 1H, H^4), 7.40 (s, 1H, H^6), 7.28 (dd, $^3J_{HH}$ = 8.6 Hz, $^3J_{HH}$ = 4.7 Hz, 1H, H^3), 6.90 (s, $^3J_{HH}$ = 8.0 Hz, 1H, H^7), 5.04 (s, 5H, Cp). ^{13}C{^{1}H} NMR (δ, $CDCl_3$, 20 °C): 201.9 (1C, *C*O), 170.7 (1C, C^8), 152.8 (1C, C^2), 147.0 (1C, C^{8a}), 134.8 (1C, C^4), 130.1 (1C, C^{4a}), 128.1 (1C, C^6), 122.6 (1C, C^3),

115.0 (1C, C^5), 112.1 (1C, C^7), 81.6 (5C, Cp). IR (CH_2Cl_2, cm^{-1}): 1946 (s, ν_{CO}).

Author: Assignment of C^2 for the 152.8 ppm resonance OK?

[RuCp(η^3-CH_2CHCH_2)(CH_3CN)Br]PF_6 (7). To a solution of **1** (300 mg, 0.690 mmol) in 6 mL of acetone was slowly added CH_2═$CHCH_2Br$ (59.7 μL, 0.690 mmol). The mixture was stirred at room temperature for 1 h. The solvent was then removed in vacuo and the residue redissolved in CH_2Cl_2 (1 mL). On addition of Et_2O (5 mL) an orange precipitate was formed, which was collected on a glass frit, washed with Et_2O (4 × 1 mL), and dried in vacuo. Yield: 297 mg (91%). Anal. Calcd for $C_{10}H_{13}BrF_6NPRu$: C, 25.38; H, 2.77; N, 2.96. Found: C, 25.55; H, 2.86; N, 2.95. ^{1}H NMR (δ, $CDCl_3/CD_3NO_2$ 1/1 (v/v), 20 °C): 5.87 (s, 5H, Cp), 5.02 (m, 1H, C*H*), 4.67 (dd, $^3J_{HHcis}$ = 6.3 Hz, $^2J_{HH}$ = 3.2 Hz, 1H, CH_2), 4.16 (dd, $^3J_{HHcis}$ = 5.8 Hz, $^2J_{HH}$ = 3.2 Hz, 1H, CH_2), 4.01 (d, $^3J_{HHtrans}$ = 11.3 Hz, 1H, CH_2), 3.85 (d, $^3J_{HHtrans}$ = 11.0 Hz, 1H, CH_2-CHCH_2), 2.41 (s, 3H, N≡CCH_3). ^{13}C{^{1}H} NMR (δ, $CDCl_3/CD_3NO_2$ 1/1 (v/v), 20 °C): 132.8 (N≡*C*), 99.7 (*C*H), 94.5 (5C, Cp), 69.1 (*C*H_2), 61.9 (*C*H_2), 4.1 (*C*H_3). ^{31}P{^{1}H} NMR (δ, $CDCl_3/CD_3NO_2$ 1/1 (v/v), 20 °C): −140.4 ($^1J_{PF}$ = 710.0 Hz, *P*F_6).

[RuCp(η^3-CH_2CHCH_2)(PPh_3)Br]PF_6 (8a). A solution of **2a** (278 mg, 0.424 mmol) in acetone (8 mL) was treated with CH_2═$CHCH_2Br$ (74 μL, 0.848 mmol), and the mixture was stirred for 1 h, whereupon the color changed from yellow to orange. The solvent and unreacted CH_2═$CHCH_2Br$ were removed under reduced pressure. The resulting dark orange powder was washed with Et_2O and dried under vacuum. Yield: 242 mg (85%). Anal. Calcd for $C_{26}H_{25}BrF_6P_2Ru$: C, 44.97; H, 3.63. Found: C, 45.08; H, 3.51. ^{1}H NMR (δ, $CDCl_3/CD_3NO_2$ 1/1 (v/v), 20 °C): 7.41−7.25 (m, 15H, Ph), 5.86 (s, 5H, Cp), 4.75−4.65 (m, 2H, CH_2C*H*), 4.08−3.94 (m, 1H, CH_2), 3.79−3.72 (m, 1H, CH_2), 3.61 (d, $^3J_{HHtrans}$ = 11.2 Hz, 1H, CH_2). ^{13}C{^{1}H} NMR (δ, $CDCl_3$, 20 °C): 134.9−129.0 (m, 15C, Ph), 97.7 (d, $^2J_{CP}$ = 1.6 Hz, 1C, *C*H), 94.6 (d, $^2J_{CP}$ = 1.1 Hz, 5C, Cp), 68.4 (d, $^2J_{CP}$ = 3.8 Hz, 1C, *C*H_2), 55.5 (d, $^2J_{CP}$ = 2.7 Hz, 1C, *C*H_2). ^{31}P{^{1}H} NMR (δ, $CDCl_3/CD_3NO_2$ 1/1 (v/v), 20 °C): 33.7 (*P*Cy_3), −143.3 ($^1J_{PF}$ = 710.2 Hz, *P*F_6).

[RuCp(η^3-CH_2CHCH_2)(PMe_3)Br]PF_6 (8b). This complex has been prepared analogously to **8a** with **2b** as the starting material. Yield: 94%. Anal. Calcd for $C_{11}H_{19}BrF_6P_2Ru$: C, 26.00; H, 3.77. Found: C, 26.22; H, 3.95. ^{1}H NMR (δ, acetone-d_6, 20 °C): 6.07 (s, 5H, Cp), 4.54 (dd, 1H, $^3J_{HH}$ = 11.1 Hz, $^2J_{HH}$ = 2.1 Hz, CH_2), 4.50−4.34 (m, 1H, C*H*), 4.28−4.21 (m, 1H, CH_2), 3.92−3.81 (m, 1H, CH_2), 3.38 (d, $^3J_{HHtrans}$ = 10.4 Hz, 1H, CH_2). ^{13}C{^{1}H} NMR (δ, acetone-d_6, 20 °C): 97.5 (s, 1C, *C*H), 94.4 (d, $^2J_{CP}$ = 1.1 Hz, 5C, Cp), 63.0 (d, $^2J_{CP}$ = 3.3 Hz, 1C, *C*H_2), 54.2 (d, $^2J_{CP}$ = 3.3 Hz, 1C, *C*H_2). ^{31}P{^{1}H} NMR (δ, acetone-d_6, 20 °C): 10.0 (*P*Me_3), −142.7 ($^1J_{PF}$ = 707.6 Hz, *P*F_6).

[RuCp(η^3-CH_2CHCH_2)(PCy_3)Br]PF_6 (8c). To a solution of **2c** (207 mg, 0.307 mmol) in acetone (4 mL) was slowly added $BrCH_2CH$═CH_2 (36.6 μL mg, 0.307 mmol). The reaction mixture was stirred at room temperature for 1 h, whereupon the color changed from yellow to orange. The solvent was removed in vacuo and the residue redissolved in 1 mL of CH_2Cl_2. On addition of Et_2O (3 mL) a bright yellow precipitate formed, which was collected on a glass frit, washed with Et_2O (3 × 1 mL), and dried in vacuo. Yield: 208 mg (95%). Anal. Calcd for $C_{26}H_{43}BrF_6P_2Ru$: C, 43.83; H, 6.08. Found: C, 44.06; H, 6.41. ^{1}H NMR (δ, $CDCl_3$, 20 °C): 5.94 (s, 5H, Cp), 4.66 (m, 1H, CH_2), 4.50 (dd, $^3J_{HHtrans}$ = 11.2 Hz, *J* = 2.6 Hz, 1H, CH_2), 4.23 (m, 1H, C*H*), 3.92 (m, 1H, CH_2), 3.23 (d, $^3J_{HHtrans}$ = 10.9 Hz, 1H, CH_2), 2.55−1.21 (m, 33H, Cy). ^{13}C{^{1}H} NMR (δ, $CDCl_3$, 20 °C): 93.2 (CH_2CHCH_2), 92.9 (5C, Cp), 69.3 (d, $^2J_{CP}$ = 3.3 Hz, CH_2CHCH_2), 53.9 (d, $^2J_{CP}$ = 4.2 Hz, CH_2CHCH_2), 37.0 (bd, $^1J_{CP}$ = 18.2 Hz, 3C, Cy^1), 30.7 (bs, 6C, $Cy^{3,5}$), 28.2 (bd, $^2J_{CP}$ = 10.4 Hz, 6C, $Cy^{2,6}$), 26.5 (bs, 3C, Cy^4). ^{31}P{^{1}H} NMR (δ, $CDCl_3$, 20 °C): 31.9 (*P*Cy_3), −143.5 ($^1J_{PF}$ = 713.3 Hz, *P*F_6).

[RuCp(η^2-CH_2═$CHCH_2NEt_3$)(PPh_3)Br]PF_6 (9). To a suspension of **8a** (208 mg, 0.299 mmol) in acetone (8 mL) was added NEt_3 (50 μL, 1.2 equiv). Stirring for 2 h led to precipitation of an orange microcrystalline solid, which was collected on a glass frit, washed with 5 mL of Et_2O/acetone (1:1), and dried in vacuo. Yield: 197 mg (83%). Anal. Calcd for $C_{32}H_{40}BrF_6NP_2Ru$: C, 48.31; H, 5.07; N, 1.76. Found: C, 48.62; H, 5.04; N, 1.71. ^{1}H NMR (δ, CD_3NO_2, 20 °C): 7.61−7.27 (m, 15H, Ph), 5.06 (s, 5H, Cp), 4.43 (dd, $^3J_{HHtrans}$ = 12.8 Hz, $^2J_{HH}$ = 2.0 Hz, 1H, H_2C═CH), 3.54−3.09 (m, 8H, H_2C═$CHCH_2$, $N(CH_2CH_3)_3$), 2.83−2.51 (m, 2H, H_2C═$CHCH_2$), 1.34 (t, 9H, $N(CH_2CH_3)_3$). ^{13}C{^{1}H} NMR (δ, $CDCl_3$, 20 °C): 136.0−133.0 (m, 9C, $Ph^{1,2,6}$), 131.8−131.6 (m, 3C, Ph^4), 129.7−129.2 (m, 6C, $Ph^{3,5}$), 87.8 (d, $^2J_{CP}$ = 2.8 Hz, 5C, Cp), 65.8 (bs, 1C, H_2C═*C*H), 54.7 (1C, H_2C═$CHCH_2$), 53.0−52.9 (m, 3C, $N(CH_2CH_3)_3$), 44.1 (d, $^2J_{CP}$ = 2.8 Hz, 1C, CH_2═CH), 7.9 (s, 3C, $N(CH_2CH_3)_3$). ^{31}P{^{1}H} NMR (δ, CD_3NO_2, 20 °C): 52.1 (*P*Ph_3), −143.5 ($^1J_{PF}$ = 707.0 Hz, *P*F_6).

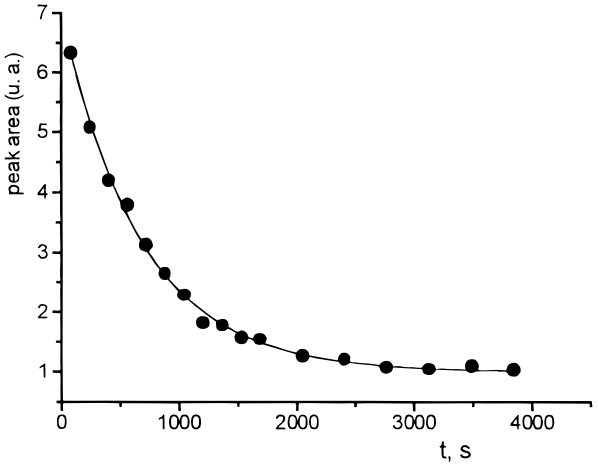


Figure 1. Peak area, as a function of time, of the ^{1}H NMR signal of coordinated CH_3CN after addition of CD_3CN (8.1 μL, 30.81 mM) to a solution of $[RuCp(PMe_3)(CH_3CN)_2]^+$ (**2b**; 25 mM) in CD_3NO_2 at 295 K.

Acetonitrile Exchange Kinetics. The method of investigation depended on the rate of reaction. In the case of **2a** and **2b**, the rate constants are small (<0.1 s^{-1}), and the exchange according to eq 1

$$[RuCp(PR_3)(CH_3CN)_2]PF_6 + 2CD_3CN \rightarrow [RuCp(PR_3)(CD_3CN)_2]PF_6 + 2CH_3CN \quad (1)$$

was studied as a function of temperature and CD_3CN concentration by monitoring the increase in intensity of the proton NMR signal of free CH_3CN (at 1.97 ppm) and the decrease of the bound CH_3CN (a doublet in the range of 2.12−2.42 ppm) after fast injection of CD_3CN into solutions of **2a**,**b** in CD_3NO_2. Figure 1 shows a typical example of a kinetic run. The time dependence of the mole fraction $x = [CH_3CN]_c/([CH_3CN]_c + [CH_3CN]_f)$ of coordinated nondeuterated acetonitrile, obtained by integration of the signals (the peak area is proportional to *x*), was fitted to eq 2[13]

$$x = x_\infty + (x_0 - x_\infty)\exp[-kt/(1 - x_\infty)] \quad (2)$$

where x_0 and x_∞ are the values of *x* at $t = 0$ and ∞, and *k* is the observed first-order rate constant for the exchange of a particular solvent molecule. The adjustable parameters were x_0, x_∞, and *k*. In the case of **2c**, the CH_3CN exchange is faster and can be followed by NMR line broadening. From the variable-temperature NMR studies, exchange rate constants were determined by visual comparison of the observed and computer-simulated spectra using the DNMR3 program.[14]

(13) Helm, L.; Elding, L. I.; Merbach, A. E. *Inorg. Chem.* **1985**, *24*, 1719.

Scheme 1

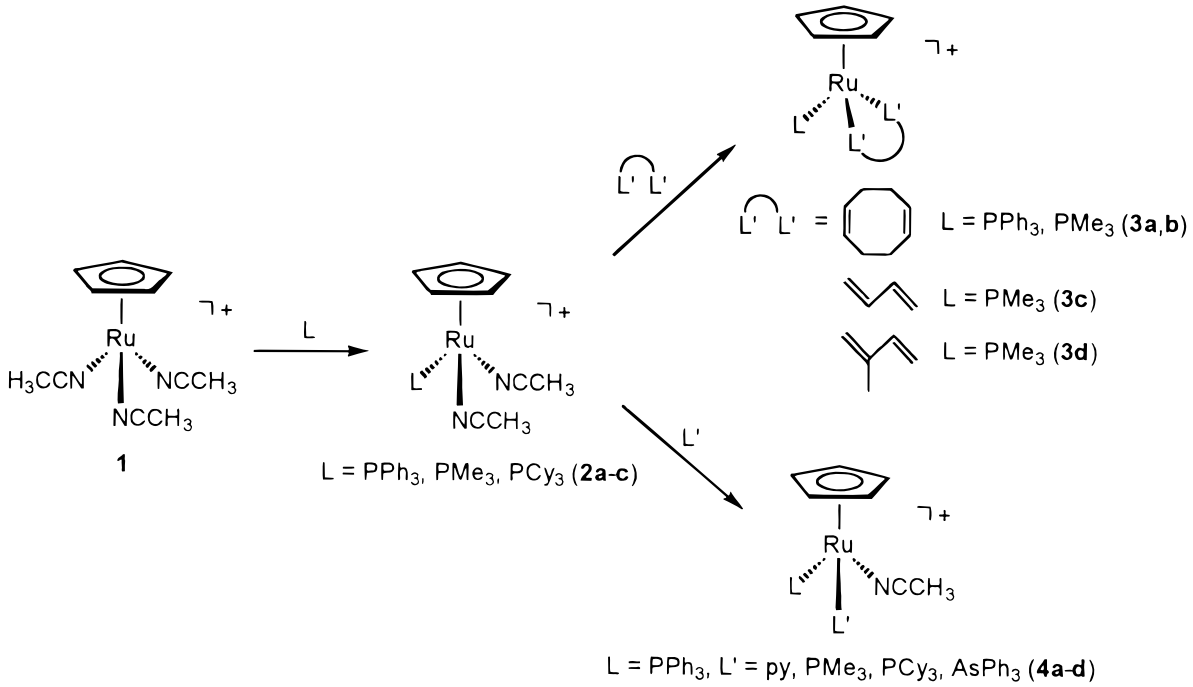


Table 1. Structure and Reactivity of $[RuCp(CH_3CN)_3]^+$ (1), $[RuCp(PPh_3)(CH_3CN)_2]^+$ (2a), $[RuCp(PMe_3)(CH_3CN)_2]^+$ (2b), $[RuCp(PCy_3)(CH_3CN)_2]^+$ (2c), and $[RuCp(Me_2NCH_2CH_2NMe_2)(CH_3CN)]^+$ (5b)

	1[a]	2a	2b	2c	5b
Ru−N(av), Å	2.083(1)		2.056(3)	2.053(2)	
Ru−P, Å			2.294(1)	2.359(1)	
Ru−C_5(av), Å	2.135(3)		2.177(5)	2.185(3)	
C≡N(av), Å	1.131(3)		1.136(4)	1.135(4)	
$\Delta H^{\ddagger}$, kcal mol^{-1}	20.7 ± 0.5	25.9 ± 0.5	25.0 ± 0.3	21.3 ± 1.0	15.4 ± 0.6
$\Delta S^{\ddagger}$, cal K^{-1} mol^{-1}	14.2 ± 1.7	16.8 ± 1.8	14.3 ± 0.8	12.7 ± 2.3	3.2 ± 2.2
k^{298}, s^{-1}	5.6	$2.9\cdot10^{-3}$	$2.7\cdot10^{-3}$	0.38	167
mechanism	D	D	D	D	D (I_d)

[a] Reference 18.

Temperature readings were calibrated by using the method of Raiford et al.,[15] corrected to 250.13 MHz, by adding a capillary of methanol to the experimental sample. The temperature dependence of the rate constants is given by the Eyring equation (eq 3).

$$k = (k_B T/h)(\exp(-(\Delta H^{\ddagger} - T\Delta S^{\ddagger})/RT) \quad (3)$$

X-ray Structure Determination for 2b, 2c, and 9·CH_2Cl_2. Crystals of **2b**, **2c**, and **9**·CH_2Cl_2 were obtained by diffusion of Et_2O into CH_2Cl_2 solutions. Crystal data and experimental details are given in Table 2. X-ray data for **2b** and **2c** were collected on a Siemens Smart CCD area detector diffractometer (graphite-monochromated Mo Kα radiation, $\lambda = 0.710\ 73$ Å, a nominal crystal-to-detector distance of 4.45 cm, 0.3° ω-scan frames). For **9**·CH_2Cl_2 X-ray data were collected on a Philips PW 1100 four-circle diffractometer using graphite-monochromated Mo Kα radiation and the $\theta-2\theta$ scan technique. Corrections for Lorentz and polarization effects, for crystal decay, and for absorption were applied. All structures were solved by direct methods using the program SHELXS97.[16] Structure refinement on F^2 was carried out with the program SHELXL97.[17] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were inserted in idealized positions and were refined riding with the atoms to which they were bonded.

Results and Discussion

Synthesis and Substitution Reactions of $[RuCp(PR_3)(CH_3CN)_2]PF_6$. Treatment of **1** with 1 equiv of the monodentate ligands PR_3 (R = Ph, Me, Cy) at room temperature affords the cationic complexes $[RuCp(PR_3)(CH_3CN)_2]PF_6$ (**2a**−**c**) in essentially quantitative yields as monitored by ^{1}H NMR spectroscopy (Scheme 1). The complexes are stable to air in the solid state but decompose slowly in solutions exposed to air. Characterization was by ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR and IR spectroscopy as well as elemental analysis. The ^{1}H NMR spectra of **2a**−**c** bear no unusual features. Thus, the Cp ligand exhibits a singlet at about 4.5 ppm and the proton resonance of the CH_3CN ligand gives a doublet in the range of 2.1−2.4 ppm. In the ^{31}P{^{1}H} NMR spectra of **2a**−**c** the phosphine ligand exhibits respectively a singlet at 51.7, 5.4, and 47.8 ppm.

The solid-state structures of **2b** and **2c** were determined by single-crystal X-ray diffraction. ORTEP diagrams of **2b** and **2c** are depicted in Figures 2 and 3 with important bond distances and angles reported in the captions. Both complexes adopt typically a three-legged piano-stool conformation. It is interesting to note that in **2b** the Ru−C(1) bond *trans* to the PMe_3 ligand is significantly longer (2.217(3) Å) than the other Ru−C bonds that range from 2.153(4) to 2.179(4) Å. Similarly

(14) (a) Binsch, G.; Kleier, D. DNMR3; QCPE; Indiana University, Bloomington, IN, 1970; Program 165. (b) Binsch, G.; Kessler, H. *Angew. Chem.* **1980**, *92*, 445.

(15) Raiford, D. S.; Fisk, C. L.; Becker, E. D. *Anal. Chem.* **1979**, *51*, 2050.

(16) Sheldrick, G. M. SHELXS97: Program for the Solution of Crystal Structures; University of Göttingen, Göttingen, Germany, 1997.

(17) Sheldrick, G. M. SHELXL97: Program for Crystal Structure Refinement; University of Göttingen, Göttingen, Germany, 1997.

Table 2. Crystallographic Data for 2b, 2c, and 9·CH_2Cl_2

	2b	**2c**	**9**·CH_2Cl_2
formula	$C_{12}H_{20}F_6N_2P_2Ru$	$C_{27}H_{44}F_6N_2P_2Ru$	$C_{33}H_{42}BrCl_2F_6NP_2Ru$
fw	469.31	637.65	880.50
cryst size, mm	0.60 × 0.50 × 0.28	0.30 × 0.10 × 0.03	0.66 × 0.55 × 0.41
space group	$P2_12_12_1$ (No. 19)	*Cc* (No. 9)	$P\bar{1}$ (No. 2)
a, Å	8.307(2)	14.224(3)	9.394(2)
b, Å	12.383(3)	14.906(4)	13.560(4)
c, Å	18.014(4)	15.011(4)	15.551(3)
α, deg			89.75(2)
β, deg		106.44(1)	75.97(2)
γ, deg			73.07(2)
V, Å^3	1853.0(8)	3053(1)	1833.9(8)
Z	4	4	2
ρ_{calcd}, g cm^{-3}	1.682	1.466	1.595
T, K	295(2)	295(2)	298(2)
μ(Mo Kα), mm^{-1}	1.070	0.674	1.805
abs cor	multiscan	multiscan	empirical
F(000)	936	1392	748
min/max transmissn factors	0.75/0.58	0.80/0.72	0.75/0.65
θ_{max}, deg	30	30	25
index ranges	$-8 \le h \le 11$	$-20 \le h \le 19$	$-10 \le h \le 11$
	$-14 \le k \le 17$	$-20 \le k \le 20$	$-16 \le k \le 16$
	$-24 \le l \le 20$	$-20 \le l \le 20$	$0 \le l \le 18$
no. of rflns measd	13 153	21 969	6405
no. of unique rflns	5223	8697	6405
no. of rflns, $I > 2\sigma(I)$	4960	8213	5665
no. of params	236	348	476
R1 ($I > 2\sigma(I)$)[a]	0.031	0.030	0.029
R1 (all data)[a]	0.034	0.033	0.035
wR2 (all data)[a]	0.085	0.081	0.073
min/max diff Fourier peaks, e Å^{-3}	−0.30/0.36	−0.44/0.61	−0.32/0.36

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

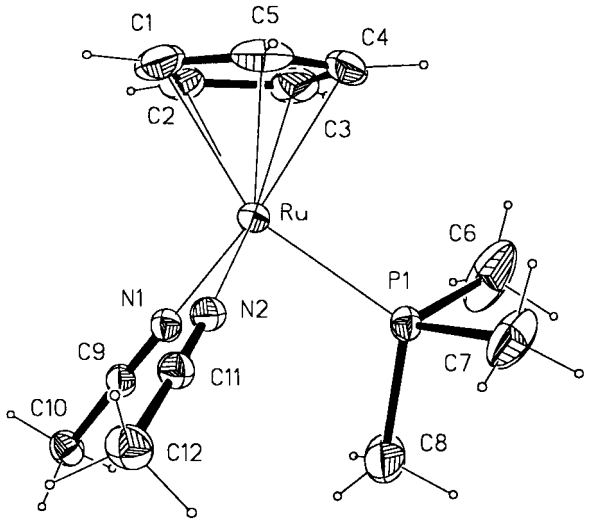


Figure 2. Structural view of $[RuCp(PMe_3)(CH_3CN)_2]PF_6$ (**2b**) showing 20% thermal ellipsoids (PF_6^- omitted for clarity). Selected bond lengths (Å) and angles (deg): Ru(1)−C(1−5)$_{av}$ = 2.177(5), Ru−P(1) = 2.294(1), Ru−N(1) = 2.054(3), Ru−N(2) = 2.059(3), C(1)−C(2) = 1.359(9), C(2)−C(3) = 1.430(9), C(3)−C(4) = 1.442(9), C(4)−C(5) = 1.381(9), C(1)−C(5) = 1.370(9), N(1)−C(9) = 1.135(4); N(2)−Ru−C(11) = 1.137(4), C(9)−N(1)−Ru = 179.5(3), C(11)−N(2)−Ru = 177.2(3), N(1)−Ru−N(2) = 85.9(1), N(1)−Ru−P(1) = 93.5(1), N(2)−Ru−P(1) = 90.7(1).

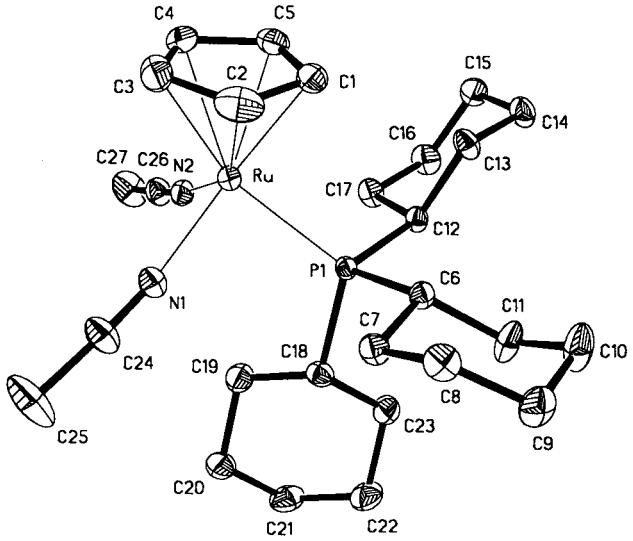


Figure 3. Structural view of $[RuCp(PCy_3)(CH_3CN)_2]PF_6$ (**2c**) showing 20% thermal ellipsoids (PF_6^- omitted for clarity). Selected bond lengths (Å) and angles (deg): Ru(1)−C(1−5)$_{av}$ = 2.185(3), Ru−P(1) = 2.359(1), Ru−N(1) = 2.050(2), Ru−N(2) = 2.056(2), C(1)−C(2) = 1.443(3), C(2)−C(3) = 1.465(7), C(3)−C(4) = 1.365(7), C(4)−C(5) = 1.396(5), C(1)−C(5) = 1.407(5), N(1)−C(24) = 1.142(4), N(2)−C(26) = 1.128(4); C(24)−N(1)−Ru = 171.2(3), C(26)−N(2)−Ru = 172.9(3), N(1)−Ru−N(2) = 89.5(1), N(1)−Ru−P(1) = 89.1(1), N(2)−Ru−P(1) = 89.7(1).

in **2c**, the Ru−C(3) and Ru−C(4) bonds are long (2.203 and 2.205 Å, respectively) and the Ru−C(1), Ru−C(2), and Ru−C(5) bonds are short (2.169, 2.169, and 2.180 Å, respectively). Whereas the Ru−N distances are practically invariant in **2b** and **2c**, the Ru−P(1) bond lengths are significantly different (see Table 1). Note further the angles between the central axis and the Ru−N and Ru−P bonds: while in **2b** these angles are 52.0 (cf. 52.8° in **1**) and 56.3°, respectively, in **2c** they are 56.3 and 54.1°.

The kinetic results of the exchange of CH_3CN are included in Table 1. It is seen that CH_3CN is much less labile in **2a** and **2b** compared to **1**,[18] mainly due to higher activation enthalpies. In contrast, the lability of CH_3CN in **2c** approaches that in **1**. Nevertheless, the

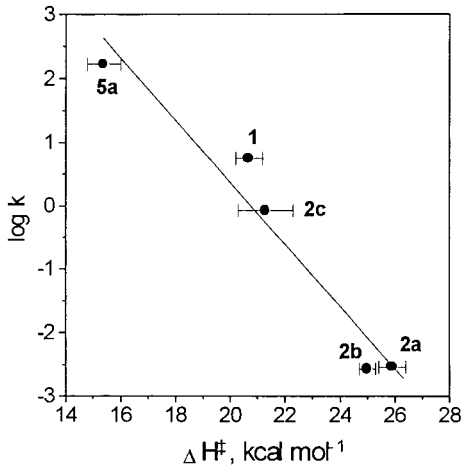


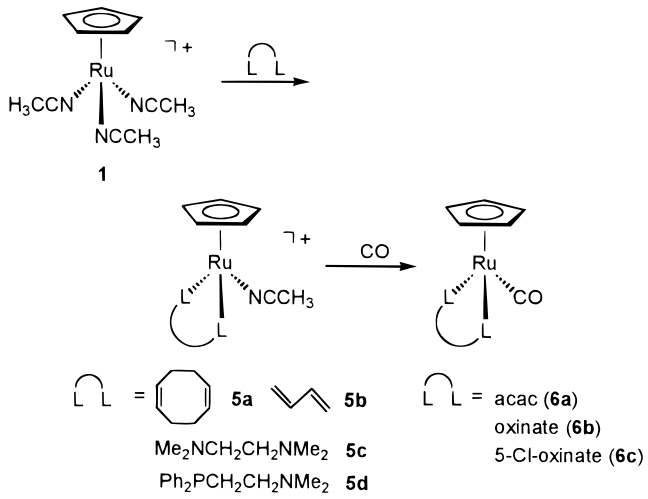
Figure 4. Linear free energy relationship for the CH_3CN exchange in $[RuCp(CH_3CN)_3]^+$ (**1**), $[RuCp(PPh_3)(CH_3CN)_2]^+$ (**2a**), $[RuCp(PMe_3)(CH_3CN)_2]^+$ (**2b**), $[RuCp(PCy_3)(CH_3CN)_2]^+$ (**2c**), and $[RuCp(Me_2NCH_2CH_2NMe_2)(CH_3CN)]^+$ (**5c**).

linear trend seen between values of log k and $\Delta H^{\ddagger}$ (Figure 4) points to the operation of a common exchange mechanism. Since the reaction rate is unaffected by the free CH_3CN concentration, a unimolecular process (dissociative mechanism, D) is indicated. This is further reflected by positive entropies of activation along with large activation enthalpies.

The role of the phosphine ligands may be discussed in terms of either nucleophilicity increasing in the order of pK_a values,[19] PPh_3 (2.73) < PMe_3 (8.65) < PCy_3 (9.70), or bulkiness, as expressed by the cone angles,[20] PMe_3 (118°) < PPh_3 (145°) < PCy_3 (170°). A comparison of these orders with the order of the rate constants of Table 1 suggests that the present phosphine ligand effect is predominantly steric in origin. van der Waals repulsive interactions between PCy_3 and the nitrile ligands are also reflected by the bond angles described above. Thus, in **2c**, the angle between the central axis and the Ru−N and Ru−P bond is larger and smaller, respectively, in comparison to those in **2b**. Ligand repulsive energies E_R calculated for some $Cr(CO)_5PR_3$ complexes have been found to be extremely high for R = Cy.[21] It is the value of E_R that may explain why in a series of $Cp^*Ru(PR_3)X$ complexes, with X being some σ-donor ligand, only that with R = Cy forms (planar) stable 16e complexes.[22,23] In these terms the rapid CH_3CN exchange in **2c** is obvious.

The reactivity of complexes **2** has been further investigated as follows. Treatment of **2a**,**b** with COD yields the cationic complexes $[RuCp(PR_3)(\eta^2{:}\eta^2\text{-COD})]^+$ (R = Ph (**3a**), Me (**3b**)), whereas with **2c** no reaction takes place. Conjugated dienes, e.g., butadiene and isoprene,

Scheme 2



react with **2b** to give $[RuCp(PMe_3)(\eta^4\text{-}CH_2{=}CHCH{=}CH_2)]^+$ (**3d**) and $[RuCp(PMe_3)(\eta^4\text{-}CH_2{=}C(Me)CH{=}CH_2)]^+$ (**3e**), respectively (Scheme 1). Further, **2a** has been reacted with the monodentate ligands py, PMe_3, PCy_3, and $AsPh_3$, giving the chiral complexes $[RuCp(PPh_3)(L)(CH_3CN)]^+$ (**4a**−**d**) in high yields. The products have been characterized by NMR spectroscopy and elemental analyses.

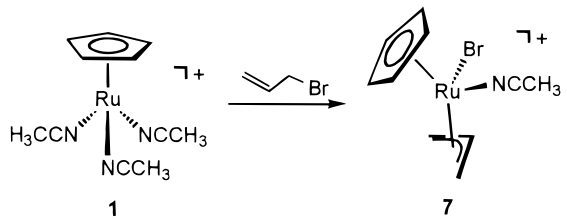
As anticipated, complex **1** also reacts readily with the bidendate ligands L−L = 1,5-COD, 1,3-butadiene, $Me_2NCH_2CH_2NMe_2$, and $Ph_2PCH_2CH_2NMe_2$ to give the cationic complexes $[RuCp(L{-}L)(CH_3CN)]^+$ (**5a**−**d**) in good yields (Scheme 2). In the case of L−L = acac, oxinate, 5-Cl-oxinate, the intermediates $[RuCp(L{-}L)(CH_3CN)]$ could not be isolated but were trapped as the stable CO complexes [RuCp(acac)(CO)] (**6a**), [RuCp(oxinate)(CO)] (**6b**), and RuCp(5-Cl-oxinate)(CO) (**6c**) (Scheme 2). Characterization of all complexes was again accomplished by a combination of elemental analysis and ^1H, $^{13}C\{^1H\}$, and, where possible, $^{31}P\{^1H\}$ NMR spectroscopy. Complexes **6b** and **6c** have also been characterized by IR spectroscopy.

The CH_3CN ligand in $[RuCp(Me_2NCH_2CH_2NMe_2)(CH_3CN)]^+$ (**5c**) is extremely labile and is readily replaced by CD_3CN in a solution of CD_3NO_2 at room temperature. The kinetics of this process has been studied in detail by ^1H NMR spectroscopy as a function of temperature, with results given in Table 1. Despite the low activation entropy, the reaction rate is independent of the free CH_3CN concentration, again pointing to a dissociative exchange mechanism (D or I_d).

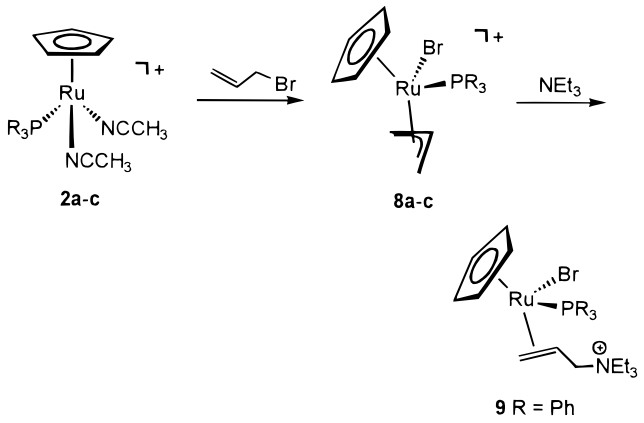
Oxidative Addition Reactions. In addition to substitution, **1** also undergoes oxidative addition reactions with allyl halides. Thus, with allyl bromide, the Ru(IV) η^3-allyl complex $[RuCp(\eta^3\text{-}CH_2CHCH_2)(CH_3CN)Br]PF_6$ (**7**) is obtained in 91% isolated yield (Scheme 3). Similarly, **2a**−**c** give the corresponding Ru(IV) η^3-allyl complexes $[RuCp(\eta^3\text{-}CH_2CHCH_2)(PR_3)Br]PF_6$ (**8a**−**c**) in high isolated yields (Scheme 4). All of these complexes are air stable both in solution and in the solid state. The ^1H NMR spectra show the expected singlet resonances appearing in the ranges 5.87−6.07 ppm and the characteristic doublet and multiplet resonances assignable to the allyl ligands. In the $^{13}C\{^1H\}$ NMR spectra,

(18) Luginbühl, W.; Zbinden, P.; Pittet, P. A.; Armbruster, T.; Bürgi, H.-B., Merbach, A. E.; Ludi, A. *Inorg. Chem.* **1991**, *30*, 2350.
(19) (a) Golovin, M. N.; Rahman, M. M.; Belemonte, J. E. Giering, W. P. *Organometallics* **1985**, *4*, 1981. (b) Bush, R. C.; Angelici, R. J. *Inorg. Chem.* **1988**, *27*, 681. (c) Chenm, L.; Poë, A. J. *Coord. Chem. Rev.* **1995**, *143*, 265.
(20) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.
(21) Brown, T. L. *Inorg. Chem.* **1992**, *31*, 1286.
(22) Luo, L.; Nolan, S. P. *Organometallics* **1993**, *12*, 4305.
(23) Johnson, T. J.; Folting, K.; Streib, W. E.; Martin, J. D.; Huffman, J. C.; Jackson, S. A.; Eisenstein, O.; Caulton, K. G. *Inorg. Chem.* **1995**, *34*, 488.

Scheme 3



Scheme 4



the Cp carbon atoms give rise to doublets between 94.5 and 92.9 ppm (cf 77.1, 76.0, and 75.6 ppm in **2a**−**c**). The downfield chemical shifts are indicative of the higher oxidation state of the Ru center.

As concerns the reactivity toward nucleophiles, **8a** has been treated with stoichiometric amounts of NEt_3, giving the olefin complex $[RuCp(\eta^2\text{-}CH_2{=}CHCH_2NEt_3)(PPh_3)Br]PF_6$ (**9**) in 83% yield (Scheme 4). Apart from a full NMR spectroscopic and analytical characterization, the solid-state structure of **9**·CH_2Cl_2 has been determined by single-crystal X-ray diffraction. A structural view is depicted in Figure 5 with selected bond distances and angles reported in the captions. Thus, **9**·CH_2Cl_2 adopts a three-legged piano-stool conformation with P(1), Br, and the olefin C(24)−C(25) moiety as the legs. The olefin moiety of the $CH_2{=}CHCH_2NEt_3$ ligand is bonded slightly asymmetrically to the metal center with the Ru bonds to the terminal and internal carbon atoms C(24) and C(25) being 2.172(3) and 2.193(3) Å, respectively. The C(24)−C(25) distance is 1.392(4) Å. The Ru−P(1) and Ru−Br distances are 2.315(1) and 2.565(1) Å, respectively.

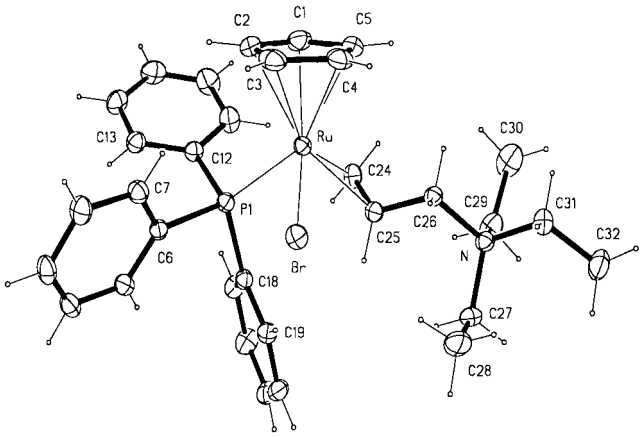


Figure 5. Structural view of $[RuCp(\eta^2\text{-}CH_2{=}CHCH_2NEt_3)(PPh_3)Br]PF_6{\cdot}CH_2Cl_2$ (**9**·CH_2Cl_2) showing 20% thermal ellipsoids (PF_6^- and CH_2Cl_2 omitted for clarity). Selected bond lengths (Å) and angles (deg): $Ru(1)-C(1-5)_{av}$ = 2.216(3), Ru−P(1) = 2.315(1), Ru−Br = 2.565(1), Ru−C(24) = 2.172(3), Ru−C(25) = 2.193(3), C(1)−C(2) = 1.403(5), C(2)−C(3) = 1.380(6), C(3)−C(4) = 1.425(5), C(4)−C(5) = 1.385(5), C(1)−C(5) = 1.403(5), C(24)−C(25) = 1.392(4); C(24)−Ru−C(25) = 37.2(1), C(24)−Ru−P(1) = 98.5(1), C(25)−Ru−P(1) = 85.2(1).

Conclusions

The complexes $[RuCp(PR_3)(CH_3CN)_2]PF_6$ are intriguing compounds because of versatile reactivity patterns under mild conditions with respect to substitution and oxidative addition reactions. Furthermore, preliminary studies reveal that (i) these complexes promote C−C coupling of acetylenes to give allyl carbene complexes capable of C−H activation of alkyl groups and (ii) they are able to efficiently catalyze the redox isomerization of allyl alcohols. These studies will be described in future contributions.

Acknowledgment. Financial support by the "Fonds zur Förderung der wissenschaftlichen Forschung" is gratefully acknowledged (Project No. 11896).

Supporting Information Available: Listings of atomic coordinates, anisotropic temperature factors, bond lengths and angles, and least-squares planes for **2b**, **2c**, and **9**·CH_2Cl_2 (Tables S1−S15) and kinetic data (Tables S16-S20), including the conditions and all of the measured rate constants. This material is available free of charge via the Internet at http://pubs.acs.org.

OM990245O