Isocyanide Arene–Ruthenium(II) Complexes and Activation of Alkenylacetylenes: Synthesis and Characterization of Isocyanide Carbene– and Mixed Carbene–Ruthenium Compounds

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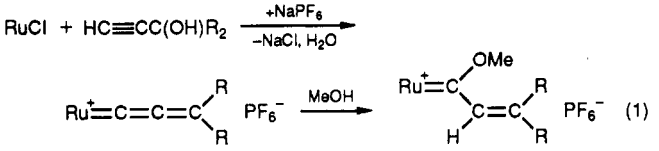
$[RuCl_2(\eta^6\text{-arene})]_2$ complexes **1** (η^6-$MeC_6H_4{}^iPr$), **2** (η^6-$C_6H_2Me_4$), and **3** (η^6-C_6Me_6) react with isocyanide CNR [R = ^{t}Bu (**a**), C_6H_{11} (**b**), $CH_2CO_2C_6H_4Me$ (**c**), CH_2CO_2Et (**d**), $(CH_2)_4Cl$ (**e**), and $(CH_2)_2OSiMe_3$ (**f**)] to produce a variety of $RuCl_2(CNR)(\eta^6\text{-arene})$ derivatives **4–6**, which give a C≡N absorption in the infrared at high wavenumbers between 2165 and 2206 cm^{-1}. $(C_6Me_6)Cl_2RuCN(CH_2)_2OSiMe_3$ (**6f**) on reaction with KF in methanol affords the carbene complex $(C_6Me_6)Cl_2Ru{:}CNHCH_2CH_2O$ (**8**). Cyclic voltammetry of complexes **4–6** shows that only with the most electron-releasing arene C_6Me_6 a reversible oxidation occurs, at 1.06–1.15 V_{SCE} for complexes **6a–f** and at 0.80 V_{SCE} for **8**. Complexes **6a**, **6e**, and **8** activate isopropenylacetylene, via an allenylidene intermediate, and in the presence of methanol give access to alkenylcarbene complexes containing the $Ru{=}C(OMe)CH{=}CMe_2$ moiety **7a,e** and the mixed carbene complex **9**.

Introduction

Arene–ruthenium(II) complexes $RuCl_2(L)(\eta^6\text{-arene})$ have recently been shown to be efficient catalyst precursors, when L is a phosphine ligand, for the activation of terminal alkynes and the regioselective synthesis of vinylcarbamates.[1] They also are able to promote the dehydration of propargyl alcohol derivatives under mild conditions in the stoichiometric synthesis of alkenylcarbene–ruthenium derivatives via allenylidene–ruthenium intermediates[2] (eq 1).



(1)

The stability of carbene–ruthenium (arene) derivatives largely depends on the steric hindrance of ancillary ligands protecting the ruthenium site,[3] and it was established that optimal conditions for the activation of terminal alkynes were reached with labile Ru–Cl bonds and electron-rich ruthenium(II) centers.[4] For instance, whereas the formation of carbene complexes is fast when L is PMe_3 or PMe_2Ph, no reaction is observed with $RuCl_2(CO)(C_6Me_6)$.[4]

Isocyanide metal complexes[5] have recently attracted interest as reactive functional ligands in cycloaddition reactions to give cyclic carbene complexes[6] or as precursors for carbyne complexes.[7] Isocyanides are stronger electron-donating ligands than carbon monoxide and weaker ones than phosphines.[5] To our knowledge only one isocyanide ruthenium(II) arene derivative has been reported to date, namely, $RuCl_2(CNC_6H_{11})(C_6H_6)$,[8] and the reaction of CNPh or CNC_6H_4Me with $[RuCl_2(C_6H_6)]_2$ has led to $RuCl_2(CNR)_4$ derivatives.[8]

We now report (i) a general method of preparation and the characterization of a variety of $RuCl_2(CNR)(\eta^6\text{-arene})$ complexes containing *p*-cymene, 1,2,4,5-tetramethylbenzene, or hexamethylbenzene ligands, (ii) an electrochemical study of $RuCl_2(CNR)(\eta^6\text{-arene})$ complexes and the electronic influence of isocyanide ligands CNR [R = ^{t}Bu, C_6H_{11}, CH_2CO_2Et, $CH_2SO_2C_6H_4Me$, $(CH_2)_4Cl$, and $CH_2CH_2OSiMe_3$] on the ruthenium(II) center, and (iii) the activation of alkenylacetylene by $RuCl_2(CNR)(C_6Me_6)$ complexes to afford new alkenylcarbene ruthenium derivatives and by a carbene–$RuCl_2(C_6Me_6)$ derivative to give rise to a mixed carbene ruthenium complex.

Experimental Section

General Procedures. Standard techniques, with Schlenk-type equipment for the manipulation of air-sensitive compounds under a blanket of nitrogen, were employed. All solvents were dried (sodium benzophenone ketyl for ether, CaH_2 for pentane and acetonitrile, $Mg(OMe)_2$ for methanol, and P_2O_5 for CH_2Cl_2) and nitrogen-saturated prior to use. Isocyanides CNR were purchased from Aldrich (R = ^{t}Bu, C_6H_{11}, $CH_2SO_2C_6H_4Me$, CH_2CO_2Et) or prepared according to previously published procedures (R = $(CH_2)_4Cl$,[9] $(CH_2)_2OSiMe_3$[10]). Isopropenylacetylene[11] and arene–ruthenium complexes $[RuCl_2(arene)]_2$[12] of *p*-cymene 1[13] and

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hexamethylbenzene 3[13a,14] were prepared as reported in the literature; $[RuCl_2(1,2,4,5\text{-}Me_4C_6H_2)]_2$ (2) was prepared as $[RuCl_2(1,2,3,4\text{-}Me_4C_6H_2)]_2$.[15]

Instrumentation. *Infrared spectra* were recorded on FT-IR Nicolet 20 C spectrometer with KBr diks containing 1–5% of complex. *^1H and ^{13}C NMR spectra* were measured at the CRMPO Center of the University of Rennes on Bruker AC 300 and RM 300 WB spectrometers operating at 300.133 MHz for ^1H and at 75.496 MHz for ^{13}C and on a Bruker 250 spectrometer operating at 250.133 MHz for ^1H and at 62.896 MHz for ^{13}C. ^1H and ^{13}C shifts are relative to Me_4Si. *Cyclic voltammetry*: Conventional electrochemical equipment was used, EGG PAR Model 362 scanning potentiostat with an *X–Y* recorder BD90. The working electrode was a stationary platinum disk electrode of 1-mm diameter. The auxiliary electrode was a platinum electrode and the reference electrode was an aqueous saturated calomel electrode (SCE). In a typical experiment, 4×10^{-5} mol of complex was dissolved under an argon atmosphere in 15 mL of distilled and deoxygenated acetonitrile containing 0.4 g of pure NBu_4PF_6 (0.1 M) as electrolyte. Mass spectra were obtained with a Varian MAT 711 apparatus. *Microanalyses* were obtained from the CNRS laboratory, Villeurbanne, and at the Institut für Anorganische und Analytische Chemie der FU, Berlin.

Preparation of $RuCl_2(CNR)(\eta^6\text{-arene})$ Complexes 4–6. In a Schlenk tube were successively introduced $[RuCl_2(arene)]_2$ 1, 2, or 3 (1 mmol), 20 mL of dry dichloromethane, and an excess of isocyanide CNR (5–10 mmol). On stirring at room temperature the initial slurry converted into a deep-red solution. After 20 h of stirring, pentane (20–60 mL) was added and an orange-red product precipitated. It was isolated via filtration on a frit, washed with 20–40 mL of pentane, and dried under vacuum. When purification of the product was necessary it was dissolved in the minimum of dichloromethane, and the resulting solution was poured on a short column (2–3 cm) of Merck silica gel 60 on a frit and eluted with ethyl acetate. The complex was recrystallized from dichloromethane–ether (1:5).

$RuCl_2(CN^tBu)(MeC_6H_4{}^iPr)$ (4a). Orange powder, 0.16 g (44%), was obtained from 0.29 g of 1 (0.48 mmol), 10 mL of CH_2Cl_2, and 0.27 mL (2.4 mmol) of CN^tBu. Mp = 145 °C; ^1H NMR (300.133 MHz, $CDCl_3$, 297 K) δ (ppm) 1.32 (d, 6 H, $CHMe_2$, $^3J_{HH}$ = 7 Hz), 1.56 (s, 9 H, CMe_3), 2.30 (s, 3 H, C_6H_4Me), 2.84 (sept, 1 H, $CHMe_2$), 5.42 (d, 2 H), 5.58 (d, 2 H) (C_6H_4, $^3J_{HH}$ = 6.1 Hz); $^{13}C\{^1H\}$ NMR (75.496 MHz, $CDCl_3$, 297 K) δ (ppm) 18.82 (s, MeC_6H_4), 22.55 (s, $CHMe_2$), 30.66 (s, CMe_3), 31.88 (s, $CHMe_2$), 58.55 (s, CMe_3), 87.32, 87.56, 106.44, 107.64 (s, C_6H_4), 138.02 (t, CNR, $^1J(^{13}C\text{–}^{14}N)$ = 18 Hz); IR (KBr) ν (cm^{-1}) 2195 (s, C≡N), 1467 (m). Anal. Found (calcd for $C_{15}H_{23}Cl_2NRu$): C, 45.92 (46.28); H, 6.01 (5.95); Cl, 18.06 (18.21); N, 3.45 (3.60).

$RuCl_2(CNC_6H_{11})(MeC_6H_4{}^iPr)$ (4b). Orange powder, 0.52 g (83%), was obtained from 1 (0.92 g, 1.5 mmol), 50 mL of CH_2Cl_2, and 7.5 mmol (0.92 mL) of CNC_6CH_{11}. Mp = 129 °C; ^1H NMR (300.133 MHz, $CDCl_3$, 297 K) δ (ppm) 1.23 (d, 6 H, $CHMe_2$, $^3J_{HH}$ = 6.8 Hz), 1.30–1.93 (m, 10 H, $(CH_2)_5$), 2.22 (s, 3 H, MeC_6H_4), 2.78 (m, 1 H, $CH(CH_2)_5$, $^3J_{HH}$ = 4 Hz), 3.96 (sept, 1 H, $CHMe_2$, $^3J_{HH}$ = 6.9 Hz), 5.36 (d) and 5.53 (d) (4 H, C_6H_4, $^3J_{HH}$ = 6.0 Hz); $^{13}C\{^1H\}$ NMR (75.496 MHz, $CDCl_3$, 297 K) δ (ppm) 18.8 (s, MeC_6H_4), 22.5 (s, $CHMe_2$), 22.7, 24.8, 32.6, 55.2 (s, *cyclohexyl*), 31.3 (s, $CHMe_2$), 87.4, 87.7, 106.7, 107.1 (s, C_6H_4), 138.6 (t, CNR, $^1J(^{13}C\text{–}^{14}N)$ = 16 Hz); IR (KBr) ν (cm^{-1}) 2187 (s, C≡N), 1450 (m). Anal. Found (calcd for $C_{17}H_{25}Cl_2NRu$): C, 49.32 (49.16); H, 6.05 (6.07); Cl, 17.37 (17.07); N, 3.35 (3.37).

$RuCl_2(CNCH_2SO_2C_6H_4Me)(MeC_6H_4{}^iPr)$ (4c). Orange powder, 0.22 g (46%), was obtained from 0.47 g (2.4 mmol) of $CNSO_2C_6H_4Me$ (TosMIC) in 15 mL of CH_2Cl_2 and 0.29 g (0.48 mmol) of 1, after washing of the product with ether to eliminate the residual TosMIC. Mp = 168 °C; IR (KBr) ν (cm^{-1}) 2161 (s, C≡N), 1596 (m). Anal. Found (calcd for $C_{16}H_{23}Cl_2NO_2RuS$): C, 45.14 (45.51); H, 4.57 (4.62); N, 2.86 (2.79); S, 7.11 (6.39); Cl, 14.60 (14.14). The product proved to be insoluble and did not allow the recording of NMR spectra.

$RuCl_2(CNCH_2CO_2Et)(MeC_6H_4{}^iPr)$ (4d). Red crystals, 0.12 g (28%), were obtained from 0.29 g (0.48 mmol) of 1, 10 mL of CH_2Cl_2, and 2.4 mmol (0.26 mL) of $CNCH_2CO_2Et$ and after filtration on silica gel and crystallization from dichloromethane (1:5). Mp = 140 °C; ^1H NMR (300.133 MHz, $CDCl_3$, 297 K) δ (ppm) 1.31 (d, 6 H, $CHMe_2$, $^3J_{HH}$ = 7 Hz), 1.35 (t, 3 H, CH_2CH_3, $^3J_{HH}$ = 7.3 Hz), 2.32 (s, 3 H, MeC_6H_4), 2.96 (sept, 1 H, *CH*-cyclohexyl, $^3J_{HH}$ = 7 Hz), 4.32 (q, 2 H, CH_2CH_3), 4.66 (s, 2 H, $CNCH_2$), 5.50 (d), 5.70 (d) (4 H, C_6H_4, $^3J_{HH}$ = 6 Hz); $^{13}C\{^1H\}$ NMR (75.496 MHz, $CDCl_3$, 297 K) δ (ppm) 14.1 (s, CH_2CH_3), 18.86 (s, MeC_6H_4), 22.48 (s, $CHMe_2$), 31.12 (s, $CHMe_2$), 46.48 (s, $CNCH_2$), 63.16 (s, OCH_2CH_3), 88.15, 88.65, 107.52, 108.89 (s, C_6H_4), 146.27 (s, CNR), 164.2 (s, COOR); IR (KBr) ν (cm^{-1}) 2202 (s, C≡N), 1754 (s, C=O). Anal. Found (calcd for $C_{15}H_{21}Cl_2NO_2Ru$): C, 42.50 (42.96); H, 4.96 (5.04); Cl, 16.77 (16.91); N, 3.24 (3.33).

$RuCl_2(CN^tBu)(C_6H_2Me_4)$ (5a). Red crystals, 0.4 g (64%), were obtained from 0.5 g (0.8 mmol) of 2, 20 mL of CH_2Cl_2, and 0.67 g (8 mmol) of CN^tBu. Mp = 155 °C; ^1H NMR (300.133 MHz, $CDCl_3$, 297 K) δ (ppm) 1.56 (s, 9 H, CMe_3), 2.13 (s, 12 H, C_6Me_4), 5.28 (s, 2 H, C_6H_2); $^{13}C\{^1H\}$ NMR (75.496 MHz, $CDCl_3$, 297 K) δ (ppm) 16.79 (s, C_6Me_4), 30.87 (s, CMe_3), 58.26 (s, CMe_3), 90.98, 99.22 (s, $C_6Me_4H_2$), 140.38 (m, CNR); IR (KBr) ν (cm^{-1}) 2161 (s, C≡N), 1449 (m). Anal. Found (calcd for $C_{15}H_{23}Cl_2NRu$): C, 46.28 (46.27); H, 5.69 (5.95); N, 3.72 (3.59); Cl, 18.05 (18.24).

$RuCl_2(CNC_6H_{11})(C_6H_2Me_4)$ (5b). Orange complex, 0.39 g (59%), was obtained from 0.5 g (0.8 mmol) of 2, 20 mL of CH_2Cl_2, and 0.87 g (8 mmol) of CNC_6H_{11}, and after filtration on silica gel. Mp = 170 °C; ^1H NMR (300.133 MHz, $CDCl_3$, 297 K) δ (ppm) 1.40–2.05 (m, 10 H, $CH(CH_2)_5$), 2.14 (s, 12 H, $C_6H_2Me_4$), 4.02 (m, 1 H, $CH(CH_2)_5$), 5.30 (s, 2 H, C_6H_2); $^{13}C\{^1H\}$ NMR (75.496 MHz, $CDCl_3$, 297 K) δ (ppm) 16.87 (s, $C_6Me_4H_2$), 22.88, 24.88, 32.93, 55.17 (s, C_6H_{11}), 91.02, 99.32 (s, $C_6H_2Me_4$), 140.88 (m, CNR); IR (KBr) ν (cm^{-1}) 2194 (s, C≡N), 1623 (m). Anal. Found (calcd for $C_{17}H_{25}Cl_2NRu$): N, 3.56 (3.37); Cl, 16.94 (17.07).

$RuCl_2(CNCH_2SO_2C_6H_4Me)(C_6H_2Me_4)$ (5c). Orange crystals, 0.47 g (59%) were obtained from 0.5 g (0.8 mmol) of 2, 20 mL of CH_2Cl_2, and 1.56 g (8 mmol) of TosMIC in 5 mL of CH_2Cl_2, after elimination of the residual TosMIC with ether, filtration on silica gel, and crystallization from dichloromethane–ether (1:5). Mp = 180 °C; ^1H NMR (300.133 MHz, $CDCl_3/CD_2Cl_2$, 297 K) δ (ppm) 2.13 (s, 12 H, $C_6H_2Me_4$), 2.46 (s, 3 H, C_6H_4Me), 5.14 (s, 2 H, $CNCH_2SO_2R$), 5.51 (s, 2 H, $C_6H_2Me_4$), 7.44 (d), 7.88 (d): (4 H, C_6H_4Me, $^3J_{HH}$ = 8 Hz); $^{13}C\{^1H\}$ NMR (75.496 MHz, $CDCl_3$, 297 K) δ (ppm) 16.97 (s, $C_6Me_4H_2$), 21.98 (s, C_6H_4Me), 64.28 (s, NCH_2S), 93.05, 101.94 (s, $C_6Me_4H_2$), 125.47, 130.80, 132.78, 147.02 (C_6H_4Me), 154.48 (s, CNR); IR (KBr) ν (cm^{-1}) 2186 (s, C≡N), 1596 (m). Anal. Found (calcd for $C_{19}H_{23}Cl_2NO_2RuS$): C, 45.41 (45.61) H, 4.59 (4.62); N, 3.07 (2.75); Cl, 13.50 (14.10).

$RuCl_2(CNCH_2CO_2Et)(C_6H_2Me_4)$ (5d). Orange powder, 0.38 g (57%), was obtained from 0.5 g (0.8 mmol) of 2, 20 mL of CH_2Cl_2, and 0.9 g (8 mmol) of $CNCH_2CO_2Et$, after filtration on silica gel, dissolution in CH_2Cl_2, and precipitation with pentane. Mp = 125 °C; ^1H NMR (300.133 MHz, $CDCl_3$, 297 K) δ (ppm) 1.28 (t, 3 H, CH_2CH_3, $^3J_{HH}$ = 7.2 Hz), 2.11 (s, 12 H, $C_6Me_4H_2$), 4.25 (q, 2 H, CH_2CH_3), 4.60 (s, 2 H, CH_2COOEt), 5.35 (s, 2 H, $C_6Me_4H_2$); $^{13}C\{^1H\}$ NMR (75.496 MHz, $CDCl_3$, 297 K) δ (ppm) 14.14 (s, CH_2CH_3), 16.85 (s, $C_6Me_4H_2$), 46.49 (s, $CNCH_2R$), 63.10 (s, OCH_2CH_3), 91.81, 100.64 (s, $C_6Me_4H_2$), 148.08 (s, CNR), 164.55 (s, COOR); IR (KBr) ν (cm^{-1}) 2175 (s, C≡N), 2037 (s), 1763 (s, C=O), 1744 (s, C=O). Anal. Found (calcd for $C_{15}H_{21}Cl_2NO_2Ru$): C, 42.97 (42.98); H, 5.05 (5.02); N, 3.31 (3.34); Cl, 17.28 (16.91).

$RuCl_2(CN^tBu)(C_6Me_6)$ (6a). Red crystals, 0.63 g (75%), were obtained from 0.67 g (1 mmol) of 3, 15 mL of CH_2Cl_2, and 10 mmol (11 mL) of CN^tBu, after filtration on silica gel and evaporation of the solvents. Mp = 190 °C; ^1H NMR (300.133 MHz, $CDCl_3$, 297 K) δ (ppm) 1.53 (s, 9 H, CMe_3), 2.10 (s, 18 H, C_6Me_6); $^{13}C\{^1H\}$ NMR (75.496 MHz, $CDCl_3$, 297 K) δ (ppm) 15.9 (s, C_6Me_6), 31.04 (s, CMe_3), 58.0 (s, CMe_3), 97.7 (s, C_6Me_6), 142.66 (t, CNR, $^1J_{^{13}C\text{–}^{14}N}$ = 18.5 Hz); IR (KBr) ν (cm^{-1}) 2174 (s, C≡N), 1455 (m). Anal. Found (calcd for $C_{17}H_{27}Cl_2NRu$): N, 3.11 (3.35).

$RuCl_2(CNC_6H_{11})(C_6Me_6)$ (6b). Red crystals, 0.77 g (87%), were obtained from 0.67 g (1 mmol) of 3, 15 mL of CH_2Cl_2, and 10 mmol (1.3 mL) of CNC_6H_{11}. Mp = 192 °C; ^1H NMR (300.133 MHz, $CDCl_3$, 297 K) δ (ppm) 1.30–2.01 (m, 10 H, $CH(CH_2)_5$), 2.05 (s, 18 H, C_6Me_6), 3.88 (m, 1 H, $CH(CH_2)_5$, $^3J_{HH} \sim 4$ Hz); $^{13}C\{^1H\}$

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NMR (75.496 MHz, $CDCl_3$, 297 K) δ (ppm) 15.9 (s, C_6Me_6), 23.1, 24.8, 33.2, 55.1 (s, *cyclohexyl*), 97.8 (s, C_6Me_6), 143.47 (m, *C*NR); IR (KBr) ν (cm^{-1}) 2167 (s, C≡N), 1453 (s). Anal. Found (calcd for $C_{19}H_{29}Cl_2NRu$): C, 50.89 (51.46); H, 6.69 (6.59); N, 3.24 (3.16); Cl, 15.79 (15.99).

$RuCl_2(CNCH_2SO_2C_6H_4Me)(C_6Me_6)$ (6c). An orange powder, 0.97 g (92%), was obtained from 0.67 g (1 mmol) of **3**, 20 mL of CH_2Cl_2, and 2 g (10 mmol) of $CNCH_2SO_2C_6H_4Me$ (TosMIC) in 5 mL of CH_2Cl_2, after evaporation of half of the solvent, filtration, and washing with ether to eliminate traces of TosMIC. Mp = 188 °C; ^1H NMR (300.133 MHz, $CDCl_3$, 297 K) δ (ppm) 2.15 (s, C_6Me_6), 2.42 (s, C_6H_4Me), 4.97 (s, $CNCH_2$), 7.40 (d), 7.83 (d) (4 H, C_6H_4Me, $^3J_{HH}$ = 8 Hz); $^{13}C\{^1H\}$ NMR (75.496 MHz, $CDCl_3$, 297 K) δ (ppm) 16.04 (s, C_6Me_6), 21.86 (s, C_6H_4Me), 63.77 (s, $CNCH_2$), 100.45 (s, C_6Me_6), 129.17, 130.78, 132.534, 146.93 (s, C_6H_4Me), 157.27 (s, *C*NR); IR (KBr) ν (cm^{-1}) 2157 (s, C≡N), 2045 (m), 1595 (m). Anal. Found (calcd for $C_{21}H_{27}Cl_2NO_2RuS$): C, 46.97 (47.64); H, 5.37 (5.14); N, 2.94 (2.65); S, 6.90 (6.05); Cl, 12.69 (13.39).

$RuCl_2(CNCH_2CO_2Et)(C_6Me_6)$ (6d). Orange crystals, 0.55 g (62%), were obtained from 0.67 g (1 mmol) of **3**, 15 mL of CH_2Cl_2, and 1.13 g (10 mmol) of $CNCH_2CO_2Et$, after filtration on silica gel and crystallization from CH_2Cl_2–ether (1:5). Mp = 173 °C; ^1H NMR (300.133 MHz, $CDCl_3$, 297 K) δ (ppm) 1.34 (t, 3 H, CH_2CH_3; $^3J_{HH}$ = 7.1 Hz), 2.18 (s, 18 H, C_6Me_6), 4.32 (q, 2 H, CH_2CH_3), 4.2 (s, $CNCH_2$); $^{13}C\{^1H\}$ NMR (75.496 MHz, $CDCl_3$, 297 K) δ (ppm) 12.61 (s, CH_2CH_3), 14.37 (s, C_6Me_6), 44.85 (s, $CNCH_2$), 61.55 (s, OCH_2CH_3), 57.55 (s, C_6Me_6), 149.01 (s, *C*NR), 163.15 (s, *C*OOEt); IR (KBr) ν (cm^{-1}) 2194 (s, C≡N), 1754 (s, C=O). Anal. Found (calcd for $C_{17}H_{25}NCl_2O_2Ru$): C, 45.63 (45.64); H, 5.25 (5.63); N, 2.91 (3.13); Cl, 15.86 (15.85).

$RuCl_2(CN(CH_2)_4Cl)(C_6Me_6)$ (6e). An orange powder, 0.6 g (66%), was obtained from 0.67 g (1 mmol) of **3**, 15 mL of CH_2Cl_2, and 0.4 g (3.5 mmol) of $CN(CH_2)_4Cl$. Mp = 176 °C; ^1H NMR (300.133 MHz, $CDCl_3$, 297 K) δ (ppm) 1.98 (t, 4 H, $CH_2(CH_2)_2CH_2$, $^3J_{HH}$ = 3 Hz), 2.14 (s, 18 H, C_6Me_6), 3.61 (t, 2 H, $CNCH_2$, $^3J_{HH}$ = 5.6 Hz), 3.88 (t, 2 H, CH_2Cl, $^3J_{HH}$ = 5.6 Hz); $^{13}C\{^1H\}$ NMR (75.496 MHz, $CDCl_3$, 297 K) δ (ppm) 15.95 (s, C_6Me_6), 27.05 (s, $CNCH_2CH_2$), 29.01 (s, CH_2CH_2Cl), 44.13 (s, $CNCH_2$), 44.50 (s, CH_2Cl), 98.08 (s, C_6Me_6), 145.8 (t, *C*NR, $^1J_{^{13}C-^{14}N}$ = 18 Hz); IR (KBr) ν (cm^{-1}) 2177 (s, C≡N), 1454 (m). Anal. Found (calcd for $C_{17}H_{26}Cl_3NRu$): C, 44.85 (45.19); H, 5.79 (5.80); N, 3.29 (3.10); Cl, 23.95 (23.54).

Preparation of $[RuCl_2\{CN(CH_2)_2OSiMe_3\}(C_6Me_6)]$ (6f). Complex **3** (2 g) and 1.2 mL of $CNCH_2CH_2OSiMe_3$[10] were stirred at room temperature for 1 h to give a red solution. The solvent and the residual isocyanide were removed under vacuum and the product was crystallized from dichloromethane–ether (1:5) to give **6f** as red crystals (2 g, 71%). MS (EI, 100 °C), *m/e* 477 (M^+, 10%), 403 [$(M - SiMe_3)^+$, 10%], 371 [$(M - CNCH_2CH_2OSiMe_3)^+$, 15%), 298 [$(M - CNR - Cl)^+$, 5%], 262 ($M - CNR - 2Cl)^+$; ^1H NMR (250.133 MHz $CDCl_3$, 297 K) δ (ppm) 3.92–400 (m, 4 H, CH_2CH_2), 2.20 (s, 18 H, C_6Me_6), 0.20 (s, $SiMe_3$); $^{13}C\{^1H\}$ NMR (62.896 MHz, $CDCl_3$, 297 K) δ (ppm) −0.77 (s, $SiMe_3$), 15.61 (s, C_6Me_6), 47.48 (s, OCH_2), 60.6 (s, NCH_2), 97.9 (s, C_6Me_6), 145.0 (s, *C*NR); IR (KBr) ν (cm^{-1}) 2196 (s, C≡N), 1258 (s, $SiMe_3$), 1102 (s, O—Si). Anal. Found (calcd for $C_{15}H_{31}Cl_2NORuSi$): C, 44.68 (45.28); H, 6.35 (6.54); N, 2.64 (2.93).

Preparation of $[RuCl(C\{OMe\}CH{=}CMe_2)(CN^tBu)(C_6Me_6)]PF_6$ (7a). In a throughly dried Schlenk tube were successively introduced 0.41 g (1 mmol) of **6a**, 15 mL of dry CH_2Cl_2 with a syringe, 0.168 g (1 mmol) of $NaPF_6$, and 15 mL of MeOH. Isopropylenylacetylene,[11] 2.5 mmol (0.24 mL), was then added and the mixture was stirred for 2.5 h at room temperature. The solvents were separated from the orange solid by transfer with a cannula. The solid was dissolved in 5 mL of CH_2Cl_2 and the solution filtered on a frit to eliminate the insoluble salts. Ether, 20 mL was slowly added to the dichloromethane solution so as not to mix the two phases. After 24 h at 25 °C orange crystals precipitated, which were dried under vacuum. **7a**, 0.2 g (32%), was isolated. Mp = 121 °C; MS (FAB), *m/e* 480 (M^+, 48%), 382 ($M - (C(OMe)CH{=}CMe_2)^+$, 77%), 326 ([RuCl(CNH)$(C_6Me_6)]^+$, 70%), 299 ([RuCl$(C_6Me_6)]^+$, 100%); ^1H NMR (300.133 Hz, $CDCl_3$, 297 K) δ (ppm) 1.53 (s, 9 H, CMe_3), 1.95 (d, 3 H, C=C*Me*, $^4J_{HH}$ = 0.55 Hz), 2.02 (d, 3 H, C=C*Me*, $^4J_{HH}$ = 0.55 Hz), 2.13 (s, 18 H, C_6Me_6), 4.65 (s, 3 H, O*Me*), 6.96 (s, 1 H, $CH{=}CMe_2$); $^{13}C\{^1H\}$ NMR (75.496 MHz, $CDCl_3$, 297 K) δ (ppm) 16.04 (s, C_6Me_6), 23.44 (s, =C*Me*), 28.6 (s, =C*Me*), 30.61 (s, CMe_3), 59.4 (s, CMe_3), 68.2 (s, O*Me*), 107.63 (s, C_6Me_6), 138.11 (s, $CH{=}CMe_2$), 153.68 (s, $CH{=}CMe_2$), 301.25 (s, Ru=*C*(OMe)), the (RuCNR)^{13}C signal was not observed; IR (KBr) ν (cm^{-1}) 2178 (s, C≡N), 1587 (s, C=C), 1283 (s, C—O), 850 (s, PF_6^-). Anal. Found (calcd for $C_{23}H_{37}ClNOPRu$): C, 44.58 (44.20); H, 6.11 (5.97); N, 2.19 (2.24).

Preparation of $[RuCl(C\{OMe\}CH{=}CMe_2)(CN\{CH_2\}_4Cl)(C_6Me_6)]PF_6$ (7e). Complex **7e**, 0.15 g (34%), was obtained in a way analogous to **7a** from 0.3 g (0.66 mmol) of **6e**, 0.11 g (0.66 mmol) of $NaPF_6$, and 1.98 mmol (0.18 mL) of isopropenylacetylene.[11] Mp = 130 °C dec; MS (FAB) *m/e* 514 (M^+, 11%), 416 ($(M - (C(OMe)CH{=}CMe_2)^+$, 3%), 299 ([RuCl$(C_6Me_6)]^+$, 10%); ^1H NMR (270.133 MHz, $CDCl_3$, 297 K) δ (ppm) 1.91 (m, 4 H, $CH_2(CH_2)_2CH_2$), 2.0 (s, 3 H, =C*Me*), 2.06 (s, 3 H, =C*Me*), 2.17 (s, 18 H, C_6Me_6), 3.58 (t, 2 H, CH_2Cl, $^3J_{HH}$ = 6 Hz), 3.94 (ABX_2, 2 H, $CNCH_2$, $^2J_{AB}$ = 17, $^3J_{HH}$ = 6.5 Hz), 4.68 (s, 3 H, O*Me*), 7.04 (s, 1 H, $CH{=}CMe_2$); $^{13}C\{^1H\}$ NMR (67.925 MHz, $CDCl_3$, 297 K) δ (ppm) 15.84 (s, C_6Me_6), 23.10 (s, CH=C*Me*), 26.76 (s, $(CH_2)_2$), 28.17 (s, CH=C*Me*), 28.95 (s, $(CH_2)_2$), 43.77 (s, $CNCH_2$), 44.60 (s, CH_2Cl), 67.90 (s, O*Me*), 107.40 (C_6Me_6), 138.0 (s, $CH{=}CMe_2$), 142.7 (s, *C*NR), 153.5 (s, $CH{=}CMe_2$), 310.35 (s, Ru=*C*); IR (KBr) ν (cm^{-1}) 2181 (s, C≡N), 1582 (s, C=C), 1284 (s, C—O), 850 (s, PF_6^-); complex **7e** is not very stable and correct analyses could not be obtained. Anal. Found (calcd for $C_{23}H_{36}Cl_2F_6NOPRu$): C, 39.8 (41.9); H, 5.2 (5.5); N, 2.1 (2.1).

Preparation of $[RuCl_2(\overline{CNHCH_2CH_2O})(C_6Me_6)]$ (8). 6f, 0.95 g (2 mmol), and 0.3 mmol of KF in 20 mL of undistilled methanol were stirred at room temperature for 2 h. The solvent was evaporated and the brown-orange powder was washed with acetone and then dissolved in dichloromethane. After filtration the orange powder was recrystallized from methanol to afford 0.45 g of complex **8** (45%). MS (EI, 200 °C), *m/e* 405 [$(M)^+$, 0.5), 396 [$(M - Cl)^+$, 0.5], 299 [$(M - Cl - (CNHCH_2CH_2O))^+$, 0.45]; ^1H NMR (270.133 MHz, $CDCl_3$, 297 K) δ (ppm) 8.50 (s, 1 H, NH), 4.72 (t, 2 H, CH_2O), 3.72 (m, 2 H, NCH_2), 2.08 (s, 16 H, C_6Me_6); ^{13}C NMR (67.925 MHz, $CDCl_3$, 297 K) δ (ppm) 15.62 (s, C_6Me_6), 43.6 (s, NCH_2), 71.5 (s, OCH_2), 96.2 (s, C_6Me_6), 217.7 (s, Ru=*C*); IR (KBr) ν (cm^{-1}) 3260 (br, NH), 1530 (s, NCO), 1145 (s, NCO). Anal. Found (calcd for $C_{15}H_{23}Cl_2NORu$): C, 44.08 (44.45); H, 5.77 (5.72); N, 3.40 (3.46).

$[RuCl(C\{OMe\}CH{=}CMe_2)(\overline{CNHCH_2CH_2O})(C_6Me_6)]PF_6$ (9). In a Schlenk tube were introduced 0.3 g (0.74 mmol) of **8**, 0.12 g (0.74 mmol) of $NaPF_6$, and 15 mL of CH_2Cl_2/MeOH (1:1). Then an excess (0.21 mL, 2.2 mmol) of isopropenylacetylene[11] was added and the mixture stirred for 2 h at room temperature. After evaporation of the solvents under vacuum, the product was extracted with dichloromethane and the solution filtered on a frit. The solvent was evaporated and complex **9** recovered as an orange powder (0.35 g, 77%). MS (FAB), *m/e* 468 (M^+, 19%), 432 ($(M - Cl)^+$, 74%), 370 ($(M - (C(OMe)CH{=}CMe_2)^+$, 9%); ^1H NMR (270.133 MHz, CD_2Cl_2, 270 K) δ (ppm) 8.62 (s, 1 H, NH), 6.65 (s, 1 H, $CH{=}CMe_2$), 4.70 (m, 2 H, CH_2O), 4.55 (s, 3 H, OMe), 3.64 (m, 2 H, NCH_2), 2.02 (s, 21 H, C_6Me_6, CH=C*Me*), 1.95 (s, 3 H, CH=C*Me*); ^{13}C NMR (62.896 MHz, CD_2Cl_2, 270 K) δ (ppm) 16.25 (s, C_6Me_6), 22.78 (s, CH=*C*Me), 27.85 (s, CH=C*Me*), 44.5 (s, CH_2N), 66.9 (s, O*Me*), 72.93 (s CH_2O), 107.65 (s, C_6Me_6), 137.55 (s, $CH{=}CMe_2$), 148.0 (s, $CH{=}CMe_2$), 216.41 (s, Ru=*C*(NH(C$H_2)_2O$), 305.29 (s, Ru=*C*(OMe)); IR (KBr) ν (cm^{-1}) 3260 (br, NH), 1540 (s, NCO), 1620 (s, C=C), 1280 (s, COMe), 1140 (s, NCO), 850 (s, PF_6^-). Anal. Found (calcd for $C_{21}H_{33}ClF_6NO_2PRu$): C, 40.68 (41.15); H, 6.23 (5.43); N, 2.16 (2.28).

Results and Discussion

The precursors $[RuCl_2(\eta^6\text{-arene})]_2$ **1**, **2**, and **3** react with an excess of the isocyanides **a–f** (5–10 equiv) in dichloromethane at room temperature to afford isocyanide–ruthenium complexes of *p*-cymene **4a–d**, 1,2,4,5-tetramethylbenzene **5a–d**, and hexamethylbenzene **6a–f** (Scheme I). The reaction proceeds by a cleavage of the chloride bridges of the binuclear compounds **1–3** by the two-electron isocyanide ligand and is very slow compared to the formation of the isoelectronic phosphine derivatives.[12-15] No displacement of the arene ligand was ob-

Scheme I

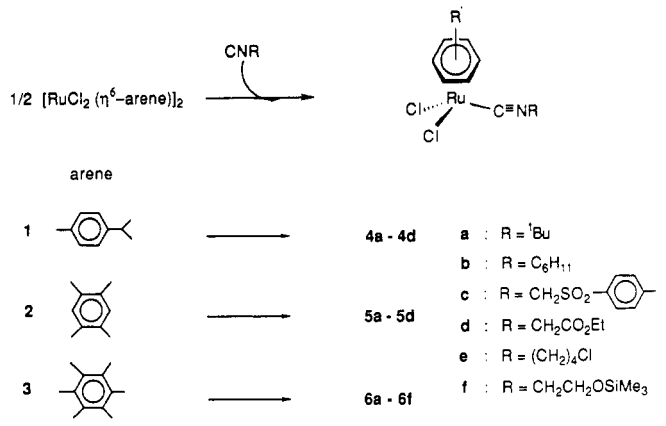


Table I. Spectroscopic Data of $RuCl_2(CNR)(arene)$ Complexes 4–7

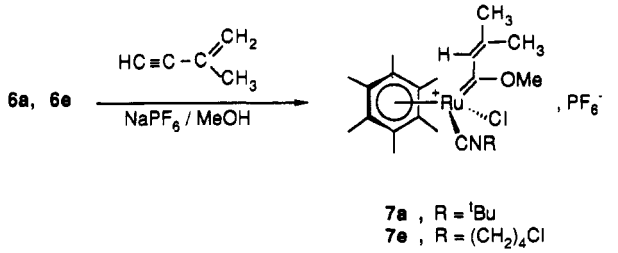
	^{13}C NMR[a]		IR (KBr), cm^{-1}	
complex	RuCNR, δ (ppm)	$^1J(^{13}C-^{14}N)$	ν(CN)	$\Delta\nu$[b]
4a	138.02 (t)	18	2195	+59
4b	138.60 (t)	16	2186	+46
4c	145.60 (t)	28	2161	+7
4d	146.27 (s)		2202	+37
5a	140.38 (m)		2161	+25
5b	140.88 (m)		2194	+54
5c	154.48 (s)		2184	+30
5d	148.08 (s)		2175	+10
6a	142.66 (t)	18.5	2174	+38
6b	143.47 (m)		2165	+25
6c	157.27 (s)		2158	+4
6d	149.01 (s)		2194	+29
6e	145.8 (t)	18	2177	+26
6f	145.0 (s)		2196	+47
7e	142.7 (s)		2181	+30

[a] In $CDCl_3$ at 297 K. [b] $\Delta\nu$ = [ν(RuC≡**NR**) - ν(**C≡NR** free)] cm^{-1}.

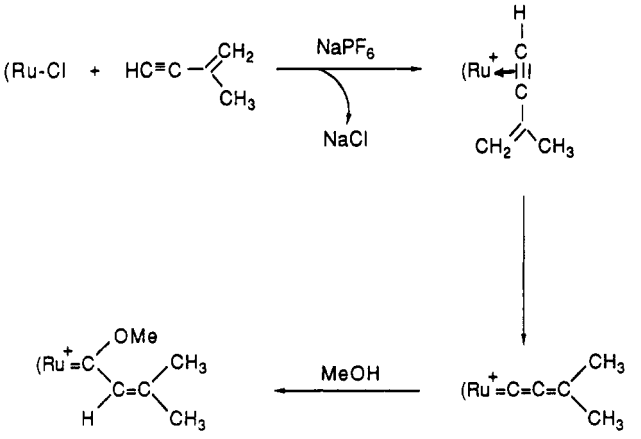
served in contrast to the formation of $RuCl_2(CNR)_4$ derivatives from $[RuCl_2(C_6H_6)]_2$.[8] Both the stability and the yields of the isocyanide complexes tend to be higher when the bulkier and more electron rich hexamethylbenzene ligand is used (**6**). Complexes **4–6** give in the infrared a characteristic absorption for the C≡N bond between 2165 and 2202 cm^{-1} (Table I). In all ruthenium complexes, this absorption occurs at higher wavenumbers than in the uncoordinated CNR molecule [$\Delta\nu = \nu_{CNR}$ (**4–6**) - ν_{CNR} (free) = 60–25 cm^{-1}]. This effect probably reflects the relatively weak back-donation to the CNR ligand in these complexes. In the ^{13}C NMR spectra the resonance due to the (Ru*C*NR) carbon nucleus appears at higher field (δ = 157–138 ppm) than in the uncoordinated ligand (δ = 154–165 ppm). The $^1J(^{13}C-^{14}N)$ coupling constant can clearly be observed for complexes **4a–c**, **6a**, and **6e** (Table I).

Attempts to activate phenylacetylene with complexes **4–6**, under similar conditions to those used with $RuCl_2(PR_3)$(arene) derivatives,[3,4] failed. We have therefore undertaken comparative electrochemical studies of complexes **4–6** in acetonitrile using cyclic voltammetry (Table II). The data show that the Ru(II)/Ru(III) oxidation is irreversible for compounds **4** and **5**, whereas that of complexes of the better electron donor arene C_6Me_6 **6** appears reversible. For a given CNR ligand the oxidation peak potential E^p_{ox} decreases in the sequence $MeC_6H_4{}^iPr$ > $C_6H_2Me_4$ > C_6Me_6, i.e., with the increasing electron-donating capability of the arene ligand. For a given arene it appears that the strongest electron-donating CNR ligands are CN^tBu (**a**), CNC_6H_{11} (**b**), $CN(CH_2)_4Cl$ (**e**), and

Scheme II



Scheme III



$CNCH_2CH_2OSiMe_3$ (**f**). The observed reversible oxidation of complexes **6** occurs at much higher potentials [$E^{1/2}{}_{ox}$ = 1.06–1.15 V_{SCE}] than that of the corresponding $RuCl_2(PR_3)$(arene) complexes [$E^{1/2}{}_{ox}$ = 0.73–1.0 V_{SCE}][4b] (Table II). Thus, the electron density in all isocyanide ruthenium complexes **4–6** is much lower than that in the $RuCl_2(PR_3)$(arene) derivatives, and this observation supports the hypothesis that the activation of terminal alkynes is affected by the lability of the Ru–Cl bond and by an increase of the electron density at the ruthenium site,[4b] both phenomena being assisted by electron-releasing ligands L.

We have therefore studied the activation of two of the more electron-rich complexes, **6a** and **6e**, toward isopropenylacetylene. Complexes **6a** and **6e** were reacted with an excess of isopropenylacetylene in a mixture of dichloromethane and methanol in the presence of $NaPF_6$. Carbene complexes **7a** and **7e**, although not very stable, were isolated in 32% and 34% yield, respectively (Scheme II). The $CNCH_2$ protons of **7e** appear diastereotopic in ^1H NMR due to the chirality of the ruthenium atom. Complexes **7** probably result from the displacement of one chloride ligand, coordination of the alkyne, 1,4-shift of the alkyne hydrogen atom,[16] and addition of methanol to the electrophilic carbon C_1 of the allenylidene ligand (Scheme III). Experiments with deuteriated isopropenylacetylene and methanol, but involving another type of ruthenium complex $RuCl_2(PR_3)$(arene),[16] were consistent with this mechanism rather than the expected formation of the vinylidene intermediate Ru=C=CHC(Me)=CH_2 followed by addition of methanol. $NaPF_6$ is *essential* in these reactions to remove the leaving chloride from the coordination sphere of ruthenium and to avoid its reversible coordination, which would prevent the activation of alkynes.

The synthesis of **6f** was designed to introduce on the ruthenium atom, before activation of isopropenyl acetylene, a stronger electron-donating group than the iso-

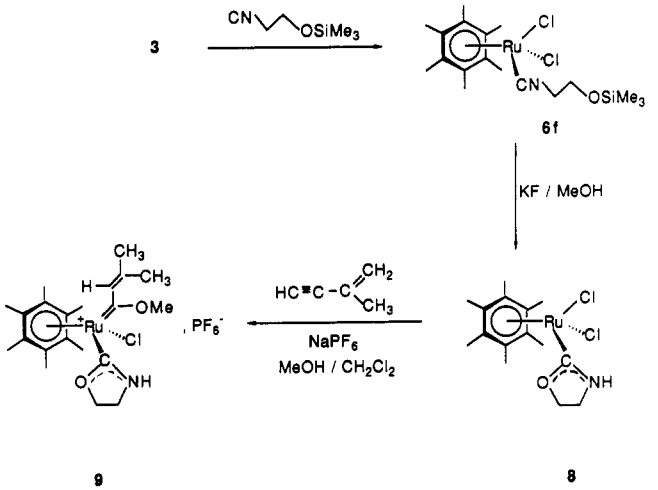
(16) Devanne, D.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1990**, 641–643.

Table II. Cyclic Voltammetric Data of $RuCl_2(CNR)(arene)$ Complexes[a]

arene		R	E^p_{ox}, V	$E^{1/2}_{ox}$, V	ΔE_p, mV
$MeC_6H_4{}^iPr$	**4a**	^{t}Bu	1.22		
	4b	C_6H_{11}	1.21		
	4c	$CH_2SO_2C_6H_4CH_3$	1.33		
	4d	CH_2COOEt	1.29		
$C_6H_2Me_4$	**5a**	^{t}Bu	1.17		
	5b	C_6H_{11}	1.15		
	5c	$CH_2SO_2C_6H_4CH_3$	1.25		
	5d	CH_2COOEt	1.24		
C_6Me_6	**6a**	^{t}Bu		1.06	70
	6b	C_6H_{11}		1.06	90
	6c	$CH_2SO_2C_6H_4CH_3$		1.15	100
	6d	CH_2COOEt		1.10	80
	6e	$(CH_2)_4Cl$		1.07	80
	6f	$(CH_2)_2OSiMe_3$		1.06	70
	8	$:\overline{CNHCH_2CH_2O}$		0.80	60
$RuCl_2(PMe_3)(C_6H_2Me_4)$[3]				0.89	70
$RuCl_2(PMe_3)$(p-cymene)[3]				0.98	90
$RuCl_2(PR_3)(C_6Me_6)$[4]		PMe_3		0.77	80
		PMe_2Ph		0.83	70
		PPh_3		0.92	80

[a] E versus SCE, Pt working electrode, 200 mV/s. Recorded in CH_3CN solution with 0.1 M Bu_4NPF_6 as supporting electrolyte.

Scheme IV



cyanide ligand. It has previously been shown that coordination of the $CNCH_2CH_2OH$ ligand can activate the C≡N bond toward an intramolecular addition of the hydroxyl group to afford a cyclic *N,O*-carbene ligand.[17] However, when the same ligand $CNCH_2CH_2OH$ was coordinated to chromium(0), no cyclization occurred.[18] Complex **6f** has been prepared (71%) by coordination of the isocyanide $CNCH_2CH_2OSiMe_3$ (**f**). On reaction of **6f** with KF in dry methanol, carbene complex **8** was formed and isolated in 45% yield showing that, when the oxygen atom of **6f** was desilylated, intraligand cycloaddition of the alkoxide group occurred. The arene ruthenium(II) moiety is able to activate the C≡N bond toward the nucleophilic addition of the alkoxide and the transformation **3** → **6f** → **8** illustrates a stepwise procedure for the elaboration of a cyclic carbene complex (Scheme IV).

Complex **8** ($E^{1/2}_{ox}$ = 0.80 V_{SCE}) appears to be oxidized much more easily than its precursor **6f** ($E^{1/2}_{ox}$ = 1.06 V_{SCE}) (Table II). Consequently, the electron-rich complex **8** was used for the activation of isopropenylacetylene in dichloromethane–methanol in the presence of $NaPF_6$.

Table III. ^{13}C NMR Data of Complexes 6f, 7a, 7e, 8, and 9

		$Ru^+=C(OMe)CH=CMe_2$ δ, ppm		
complex	CNR δ, ppm	Ru=C	$=CMe_2$	HC=
6f[a]	145.0			
7a[b]		301.2	153.7	138.1
7e[a]	142.7	301.3	153.5	138.0
8[a]	217.7			
9[b]	216.4	305.3	148.0	137.5
I[d,3]		308.0	134.5	131.8
II[d,3]		302.2	153.3	139.4

[a] In $CDCl_3$, 297 K, 62.896 MHz. [b] In CD_2Cl_2, 297 K, 75.496 MHz. [c] In CD_2Cl_2, 270 K, 62.896 MHz. [d] $[Ru=C(OMe)CH=CMe_2]Cl(L)(C_6H_2Me_4)$: L = PMe_3 (I); L = $P(OMe_3)$ (II) (ref 3).

Complex **9** was isolated (77%) and identified as an arene–ruthenium(II) complex containing two different carbene ligands.

In the ^{13}C NMR, complexes **7a**, **7e**, and **9** show low-field [Ru=*C*(OMe)] carbon resonances at δ = 301–305 ppm, consistent with a very electrophilic carbene carbon nucleus[3,4] (Table III). It is noteworthy that the alkenyl carbene ligand does not appear in the ^{13}C NMR to be influenced by the ancillary ligands: CNR (**7a,e**), L^1 = $:\overline{CNHCH_2CH_2O}$ (**9**) or PR_3.[3] By contrast, the $Ru=\overline{CNHCH_2CH_2O}$ carbon resonance is at a much higher field (**8**, δ = 217.7, and **9**, δ = 216.4 ppm). This high-field signal parallels the strong σ-donor properties and the absence of π-accepting capability of the ligand L^1 = $:\overline{CNHCH_2CH_2O}$ and suggests a Ru–C(sp^2) single bond in Ru^{II}–$\overline{CNHCH_2CH_2O}$ derivatives as already demonstrated by the X-ray structure of Pd(II)←(L^1)[19] and Co(III)←(L^1)[20] complexes.

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