Journal of Organometallic Chemistry, 390 (1990) 371–378
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20796

Carbene derivatives of areneruthenium(II) complexes in one step from terminal alkynes

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(Received January 22nd, 1990)

Abstract

The complexes $[(\eta^6\text{-arene})Ru{=}C(OMe)CH_2R')Cl(PR_3)]PF_6$ ($R' = Ph$; arene = $Me_4C_6H_2$, $^iPr_3C_6H_3$, $Et_3C_6H_3$; $PR_3 = PMe_3$, PPh_3, $P(OMe)_3$) have been made from $RuCl_2(PR_3)$(arene) precursors by activation at room temperature of phenylacetylene in methanol containing $NaPF_6$. The complex with $R' = {}^nBu$, arene = $Me_4C_6H_2$, and $PR_3 = PMe_3$ is similarly formed from hex-1-yne but much more slowly, and a complex of the type $[(p\text{-cymene})Ru{=}C(OMe)CH_2R')Cl(PR_3)]^+PF_6^-$ could be obtained only when the phosphine was the bulky PPh_3 (**10b**). It has been shown that the steric hindrance by both arene and phosphine ligands contributes to the stabilization of the carbeneruthenium complexes.

Introduction

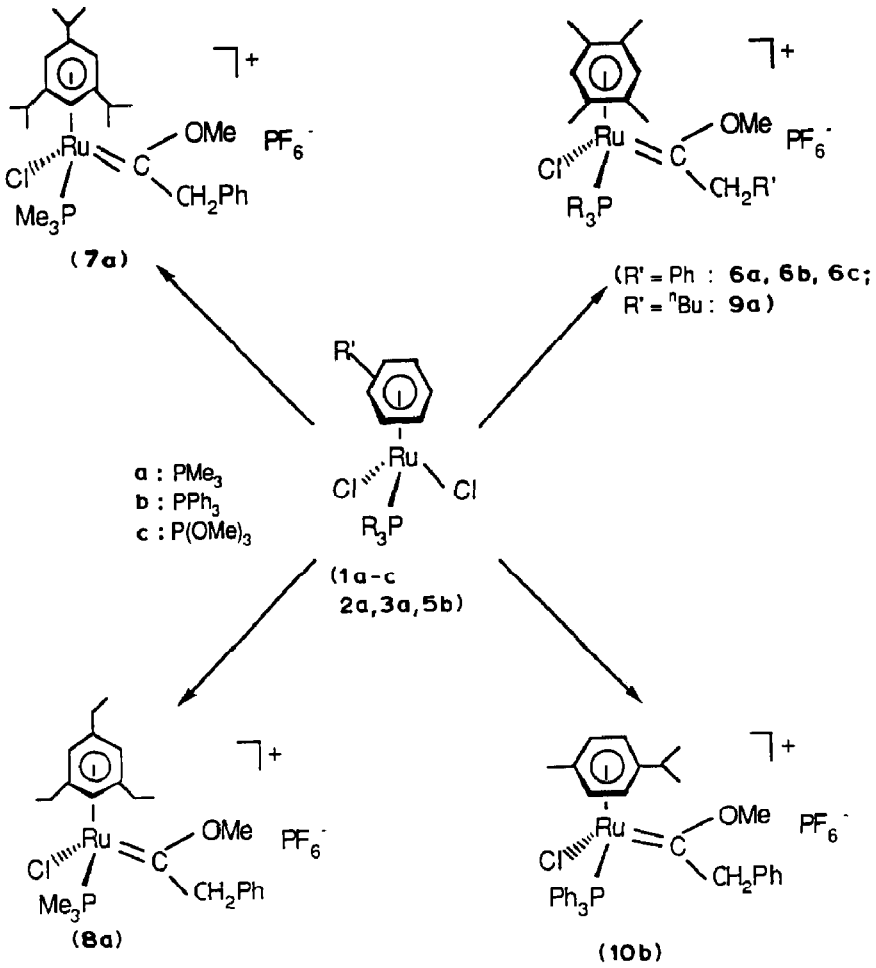
Activation of terminal alkynes by $RuCl_2(PR_3)(\eta^6\text{-arene})$ complexes has been shown to provide a catalytic and regioselective synthesis of vinylcarbamates, whereas the isoelectronic complexes $RuCl(R_3P)_2(C_5H_5)$ are inactive [1]. A study of the stoichiometric interactions of terminal alkynes with $RuCl_2(PR_3)(\eta^6\text{-}C_6Me_6)$, one of the most efficient catalyst precursors, led to the discovery of a direct route to the first arene–ruthenium–carbene complexes $[(C_6Me_6)Ru(=C(OR)CH_2R')Cl(PMe_3)]^+PF_6^-$ [2,3]. (The only earlier such species was $[(C_6Me_6)Ru(=CH_2)(Me)(PMe_3)]^+$, which was suggested to be formed as an intermediate by hydride elimination from $(C_6Me_6)RuMe_2(PMe_3)$ [4].) The formation of carbeneruthenium complexes has been shown to proceed via the vinylidene intermediates $[(C_6Me_6)Ru(=C{=}CHR)Cl(PMe_3)]^+$, which are much more easily produced and much more reactive toward nucleophiles such as alcohols [5] than the isoelectronic cations $[(C_5H_5)(R_3P)_2Ru]^+{=}C{=}CHR$ [6,7].

The corresponding carbeneruthenium complexes could not be isolated from the reaction of the related $(p\text{-cymene})RuCl_2(PMe_3)$ precursor, and it was thought that

this could be due to the lower stability of the Ru–(η^6-*p*-cymene) than of the Ru–(η^6-C_6Me_6) bond. This is not, in fact, the main reason, since we now report that (i) the isolation of new arene–ruthenium–carbene complexes [(arene)Ru(=C(OMe)-CH_2R')Cl(PR_3)]$^+PF_6^-$ which do not contain the stable hexamethylbenzene–ruthenium bond but instead a variety of other arene along with other phosphine ligands, and (ii) the stability of the complexes markedly depends on the steric influence of the ligands rather than on the electron donating ability of the {(arene)(PR_3)ClRu} moiety.

Results and discussion

The $RuCl_2(PMe_3)$(arene) complexes **1a** (1,2,4,5-$Me_4C_6H_2$), **2a** (1,3,5-$^i Pr_3C_6H_3$) and **3a** (1,3,5-$Et_3C_6H_3$) were treated with a slight excess (1.5 equivalent) of phenylacetylene in the presence of one equivalent of $NaPF_6$, in a methanol/dichloromethane (1/1) mixture. After 45 to 60 min stirring at room temperature the orange carbeneruthenium complexes **6a** (75%), **7a** (65%) and **8a** (73%) respectively, were isolated (Scheme 1).



Scheme 1

The complexes **6a–8a** show in $^{13}C\{^1H\}$ NMR a typical low field doublet for the carbene carbon nucleus [5] (δ ppm (^2J(PC)): **6a**: 392.92 (20.6 Hz); **7a**: 325.76 (19.5 Hz); **8a**: 324.80 (20.6 Hz)). Evidence that the ruthenium centre is chiral is provided by the ^1H NMR spectrum, which shows the non-equivalence of the Ru=C(OMe)–CH_2 methylene protons (δ ppm (^2J(AB)): **6a**: 5.28–4.29 (11.8 Hz); **7a**: 5.32–4.88 (14.2 Hz); **8a**: 5.17–4.39 (12.4 Hz)) and the non-equivalence of the arene-methyl groups in **6a** and the isopropyl-methyl groups in **7a**.

The $RuCl_2(PR_3)(1,2,4,5\text{-}Me_4C_6H_2)$ complexes **1b** ($PR_3 = PPh_3$) and **1c** ($PR_3 = P(OMe)_3$) reacted with phenylacetylene under similar conditions to give the corresponding carbene complexes **6b** (70%) and **6c** (72%) after 1 and 4 h, respectively ($^{13}C\{^1H\}$ NMR, δ ppm (^2J(PC)); **6b**: 323.60 (18.65 Hz); **6c**: 323.15 (26.70 Hz)). Comparison of the reactivities of complexes **1** shows that the presence of the less electron-releasing phosphite ligand significantly lowers the reaction rate but does not the stability of the carbene complex.

The complex $RuCl_2(CO)(1,2,4,5\text{-}Me_4C_6H_2)$ **1d** was recovered unchanged after 24 h in contact with phenylacetylene and no formation of the corresponding carbene complex was observed. Complex **1a** reacted with an excess of hex-1-yne in a (1/1) $MeOH/CH_2Cl_2$ mixture in the presence of $NaPF_6$, but complex **9a** was formed very slowly; after 20 h of reaction at 25°C it was isolated in 82% yield (δ ppm Ru=C: 330.26 (^2J(PC) 20.36 Hz)).

The formation of carbeneruthenium complexes **6–9** can result from the initial dissociation of one Ru–Cl bond of $Ru\text{–}Cl_2(L)$(arene) precursors in polar solvent, η^2-coordination of the alkyne, rearrangement to η^1-vinylidene complex, and addition of methanol to the electrophilic carbon of the heteroallene moiety (Ru=C=CHR) (eq. 1). The dissociation step is favored by basic phosphines capable of stabilizing the 16 electron cationic intermediate. Thus the rate was markedly lower for a complex containing the weak electron donating $L = P(OMe)_3$ in place of the basic PMe_3 or even the bulky PPh_3 ligand, and no reaction was observed for L = CO. The low rate observed for hex-1-yne is probably due to the fact that this alkyne is less acidic than phenylacetylene. Theoretical studies have indicated that a decrease in the acidity of the terminal alkyne should disfavor the η^2-alkyne–metal to η^1-vinylidene–metal rearrangement [8].

$$\{Ru\text{—}Cl \xrightarrow[Cl^-]{H\text{—}C\equiv C\text{—}R} \{Ru^+ \leftarrow \overset{CH}{\underset{CR}{\|}} \longrightarrow \{Ru^+ = C = CHR \xrightarrow{MeOH} \{Ru^+ = C\begin{matrix}\nearrow OMe \\ \searrow CH_2R\end{matrix} \quad (1)$$

It is noteworthy that these reactions occur under very mild conditions, whereas the isoelectronic carbeneruthenium complexes $(C_5H_5)(Ph_3P)_2Ru^+=C(OMe)CH_2R$ were isolated only after a 24 h reflux of a solution of $RuCl(Ph_3P)_2(C_5H_5)$ and phenylacetylene in methanol [6,9].

The precursors $RuCl_2(PMe_3)$(arene) **4a** ($1,3,5\text{-}Me_3C_6H_3$) and **5a** (p-Me-C_6H_4-^{i}Pr), analogues of complexes **1a–3a**, were also treated with phenylacetylene. Although a reaction occurred no stable product could be isolated even at −10°C. From **5a** an unstable product was isolated at −10°C, but could not be char-

Table 1

Cyclic voltammetry of $RuCl_2$(L)arene complexes in acetonitrile containing Bu_4NPF_6 (0.1 *M*) at 0.2 V s^{-1}

Complex		$E_{1/2}$ (V_{SCE})	Complex		$E_{1/2}$ (V_{SCE})
1a	$Me_4C_6H_2/PMe_3$	0.89	**2a**	$^iPr_3C_6H_3/PMe_3$	0.96
1b	$Me_4C_6H_2/PPh_3$	1.02	**3a**	$Et_3C_6H_3/PMe_3$	0.92
1c	$Me_4C_6H_2/P(OMe)_3$	1.00	**4a**	$Me_3C_6H_3/PMe_3$	0.94
1d	$Me_4C_6H_2/CO$	1.49(E_{pa})	**5a**	$MeC_6H_4{}^iPr/PMe_3$	0.98
			5b	$MeC_6H_4{}^iPr/PPh_3$	1.09

acterized; however its IR and ^1H NMR spectra are consistent with the compound $Ru(C(OMe)CH_2Ph)(Cl)(PMe_3)(MeC_6H_4{}^iPr)^+PF_6^-$ (**11a**).

Electronic and steric effects of the ancillary arene and phosphine ligands could be evoked to account for the instability of the carbene derivatives of **4a** and **5a** with respect to complexes **6–9**. A cyclic voltammetry study of the precursors $RuCl_2(PR_3)$(arene) was thus undertaken (Table 1), and showed that the oxidation of all complexes containing a PR_3 group is quasi reversible, occurs at a potential of 0.89 to 1.09 V(SCE), and corresponds to a Ru^{II}/Ru^{III} redox system [5]. The oxidation potentials of **4a** and **5a**, which do not afford stable complexes, are quite similar to those of **1a** and **2a**. Assuming that the sequence of electron-releasing ability of the $[(arene)(PR_3)ClRu]^+$ moieties correlates with that of the $[(arene)(PR_3)ClRu]$–Cl complexes, the values of the potentials indicate that the stability of the $[(arene)(PR_3)ClRu]^+$-carbene complexes cannot be controlled by the electronic influence of the ligands.

Since complexes **4a** and **5a** are the least sterically hindered in the series, it is likely that the stability of the carbene derivatives depends on the steric hindrance of the ligands. To check this hypothesis, the complex **5b**, which is less easily oxidized than **5a** but contains a phosphine bulkier than PMe_3, was treated with an excess of phenylacetylene. A stable carbeneruthenium complex **10b** (59%) was isolated after 45 min at room temperature. Its ^1H NMR spectrum revealed the non-equivalence of the isopropyl methyl groups (δ ppm (Me_2CH–): 1.03 and 1.04 (^3J(HH) 7.0 Hz)) and a low field doublet in $^{13}C\{^1H\}$ NMR (δ ppm Ru=C: 325.4 (^2J(PC) 21.2 Hz)) characteristic of the carbene carbon nucleus coupled with a ^{31}P nucleus.

The above results show that although the formation of the carbene ruthenium arene complexes requires the presence of an electron-donating PR_3 group on the metal centre, their stabilities are largely controlled by the steric hindrance of both the arene and phosphine ligands.

Experimental

General data

The complexes $RuCl_2(PR_3)$(arene) and $RuCl_2(CO)$(arene) were prepared from the corresponding $[RuCl_2(arene)]_2$ complexes by the procedures previously described for the preparation of $RuCl_2(PR_3)$(arene) [10,13] and $RuCl_2(CO)(C_6H_6)$ [14]. All solvents were dried by standard methods, and all manipulations were conducted under nitrogen by standard Schlenk techniques. Elemental analyses were performed by the CNRS analysis laboratory, Villeurbanne (France). NMR spectra

were recorded at the CRMPO Center of the University of Rennes on a Bruker WP80DF operating at 80 MHz for ^{1}H and at 32.38 MHz for ^{31}P nuclei, and on a Bruker AMWB300 operating at 300.134 MHz for ^{1}H and at 75.469 MHz for ^{13}C nuclei. ^{31}P chemical shifts are relative to external H_3PO_4 (85%).

Cyclic voltammetry

Conventional electrochemical equipment was used for cyclic voltammetry: EGG PAR Model 362 scanning potentiostat with an *X–Y* recorder BD90. The working electrode was a stationary platinum disc electrode of 1 mm of diameter. The auxiliary electrode was also 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.

Synthesis of complexes $Ru{=}C(OR)CH_2R'(Cl)(PR_3)(arene)^+PF_6^-$

General procedure

To a mixture of 1 mmol of complex $RuCl_2(PR_3)$(arene) and 1 mmol of $NaPF_6$ (0.168 g). Under argon atmosphere in a Schlenk tube were successively added 10 ml of dichloromethane, 10 ml of dry methanol and 1.5 mmol of alkyne. The red solution was stirred at room temperature for 45–60 min, during which it progressively turned orange. The volume of solvents was reduced to one-third by evaporation under vacuum, and this led to precipitation of the carbene complex, which was completed by addition of 10 ml of ether. The orange solid was filtered off on a frit and dissolved in 10 ml of dichloromethane. The solution was freed from NaCl by filtration through a frit and the recovered yellow-orange complex was recrystallized from a dichloromethane/ether (1/5) mixture.

Complex $[Ru(=C(OMe)CH_2Ph)Cl(PMe_3)(1,2,4,5\text{-}Me_4C_6H_2)]PF_6$ (6a)

6a was obtained from 0.382 g (1 mmol) of complex **1a** as orange crystals in 75% yield (0.47 g). ^{1}H NMR (300.134 MHz, CD_2Cl_2, 309 K) δ ppm: 7.43 (m, 5H, Ph), 5.36 (s, 2H, $C_6H_2Me_4$), 5.28–4.29 (AB, 2H, CH_2Ph, ^{2}J(HH) 11.8 Hz), 4.71 (s, 3H, O–CH_3), 1.93 (s, 6H, $C_6H_2Me_2$), 1.71 (s, 6H, $C_6H_2Me_2$), 1.50 (d, 9H, PMe_3, ^{2}J(PH) 10.9 Hz). $^{13}C\{^{1}H\}$ NMR (75.469 MHz, CD_2Cl_2, 309 K) δ ppm: 326.92 (d, Ru=C, ^{2}J(PC) 20.6 Hz), 131.9, 131.4, 129.6, 128.6 (s, C_6H_5), 108.4, 107.9, 99.4 (s, $C_6Me_4H_2$), 67.78 (s, Me–O), 55.1 (s, CH_2), 17.2 (d, PMe_3, ^{1}J(PC) 41.3 Hz), 17.0, 16.2 (s, $C_6H_2Me_4$). $^{31}P\{^{1}H\}$ NMR (32.80 MHz, CD_2Cl_2, 309 K) δ ppm: 10.71 (s, PMe_3), −144.41 (sept., PF_6^-). IR (KBr) ν cm^{-1}: 1290 (C–O), 970 (PMe_3), 860 (P–F). Anal. Found: C, 42.09; H, 5.04; P, 10.13. $C_{22}H_{33}ClF_6OP_2Ru$ calcd.: C, 42.20; H, 5.27; P, 9.92%.

Complex $[Ru(=C(OMe)CH_2Ph)Cl(PMe_3)(1,3,5\text{-}{}^{i}Pr_3C_6H_3)]PF_6$ (7a)

7a was obtained from 0.452 g (1 mmol) of complex **2a** as orange crystals in 65% yield (0.45 g). ^{1}H NMR (300.134 MHz, CD_2Cl_2, 309 K) δ ppm: 7.33 (m, 5H, Ph), 5.60 (s, 3H, $C_6H_3{}^{i}Pr_3$), 5.32–4.88 (AB, 2H, CH_2Ph, ^{2}J(HH) 14.2 Hz), 4.47 (s, 3H, Me–O), 2.78 (sept., $CHMe_2$, ^{3}J(HH) 6.80 Hz), 1.55 (d, 9H, PMe_3, ^{2}J(PH) 10.8 Hz), 1.25 (d, 9H, $CHMe_2$, ^{3}J(HH) 6.8 Hz), 1.21 (d, 9H, $CHMe_2$, ^{3}J(HH) 6.8 Hz). $^{13}C\{^{1}H\}$ NMR (75.469 MHz, CD_2Cl_2, 309 K) δ ppm: 325.76 (d, Ru=C, ^{2}J(PC) 19.5

Hz); 132.5, 130.3, 129.2, 127.8 (s, C_6H_5); 121.4, 91.3 (s, $C_6H_3{}^iPr_3$), 68.7 (s, *Me*–O), 59.3 (s, CH_2), 34.3 (s, $CHMe_2$); 23.9, 21.1 (s, $CHMe_2$), 17.6 (d, PMe_3, ^1J(PC) 36.20 Hz). $^{31}P\{^1H\}$ NMR (32.80 MHz, CD_2Cl_2, 309 K) δ ppm: 9.88 (s, PMe_3), −144.409 (sept., PF_6^-). IR (KBr) ν cm^{-1}: 1290 (C–O), 975 (PMe_3), 870 (P–F). Anal. Found: C, 49.61; H, 5.69; P, 8.60. $C_{30}H_{40}ClF_6OP_2Ru$ calcd.: C, 49.41; H, 5.49; P, 8.51%.

*Complex [Ru(=C(OMe)CH$_2$Ph)Cl(PMe$_3$)(1,3,5-Et$_3$C$_6$H$_3$)]PF$_6$ (**8a**)*

8a was obtained from 0.410 g of **3a** as orange crystals in 73% yield (0.47 g). ^1H NMR (300.134 MHz, CD_2Cl_2, 309 K) δ ppm: 7.40 (m, 5H, Ph), 5.17–4.39 (AB, 2H, CH_2Ph, ^2J(HH) 12.4 Hz), 5.09 (s, 3H, $C_6Et_3H_3$), 4.66 (s, 3H, Me–O), 2.26 (q, 6H, CH_2Me, ^3J(HH) 6.2 Hz), 1.51 (d, 9H, PMe_3, ^2J(PH) 10.8 Hz), 1.15 (t, 9H, CH_2CH_3, ^3J(HH) 6.2 Hz). $^{13}C\{^1H\}$ NMR 975.469 MHz, CD_2Cl_2, 309 K) δ ppm: 324.80 (d, Ru=C, ^2J(PC) 20.6 Hz), 132.3, 131.2, 129.6, 128.52 (s, C_6H_5), 122.9, 89.6 (s, $C_6Et_3H_3$), 68.2 (s, *Me*–O), 56.6 (s, CH_2Ph), 27.7 (s, CH_2–Me), 17.7 (d, PMe_3, ^1J(PC) 35.6 Hz), 15.3 (s, CH_2–*Me*). $^{31}P\{^1H\}$ NMR (32.80 MHz, CD_2Cl_2, 309 K) δ ppm: 8.22 (s, PMe_3), −144.41 (sept., PF_6^-). IR (KBr) ν cm^{-1}: 1290 (C–O), 965 (PMe_3), 860 (P–F). Anal. Found: C, 43.84; H, 5.49; P, 9.33. $C_{24}H_{37}ClF_6OP_2Ru$ calcd.: C, 44.07; H, 5.41; P, 9.48%.

*Complex [Ru(=C(OMe)CH$_2$Ph)Cl(PPh$_3$)(1,2,4,5-Me$_4$C$_6$H$_2$)]PF$_6$ (**6b**)*

6b was obtained from 0.57 g (1 mmol) of complex **1b** as orange crystals in 70% yield (0.57 g). ^1H NMR (300.134 MHz, $CDCl_3$, 309 K) δ ppm: 7.45 (s, 15H, PPh_3), 7.36 (s, 5H, *Ph*–CH_2), 5.29–3.28 (AB, 2H, CH_2Ph, ^2J(HH) 12.2 Hz), 4.94 (s, 2H, $C_6H_2Me_4$), 4.33 (s, 3H, *Me*–O), 1.75 (s, 6H, $C_6H_2Me_2$), 1.64 (s, 6H, $C_6H_2Me_2$). $^{13}C\{^1H\}$ NMR (75.469 MHz, $CDCl_3$, 309 K) δ ppm: 323.6 (d, Ru=C, ^2J(PC) 18.6 Hz), 134.3, 132.1, 131.3 (s, PPh_3), 129.1 (s, CH_2Ph), 111.9, 108.5, 100.8 (s, $C_6H_2Me_4$), 68.0 (s, *Me*–O), 51.7 (s, CH_2), 17.3, 16.5 (s, $C_6H_2Me_4$). $^{31}P\{^1H\}$ NMR 932.80 MHz, $CDCl_3$, 309 K) δ ppm: 35.04 (s, PPh_3), −144.3 (sept., PF_6^-). IR (KBr) ν cm^{-1}: 1290 (C–O), 850 (P–F). Anal. Found: C, 53.88; H, 4.85; P, 7.82. $C_{37}H_{39}ClF_6OP_2Ru$ calcd.: C, 54.03; H, 4.87; P, 7.75%.

*Complex [Ru(=C(OMe)CH$_2$Ph)Cl(P(OMe)$_3$)(1,2,4,5-Me$_4$C$_6$H$_2$)]PF$_6$ (**6c**)*

6c was obtained from 0.43 g (1 mmol) of complex **1c**, but after 4 h of reaction, as orange-yellow crystals in 72% yield (0.48 g). ^1H NMR (300.134 MHz, CD_2Cl_2, 309 K) δ ppm: 7.35 (m, 5H, Ph), 5.56 (s, 2H, $C_6H_2Me_4$), 5.23–4.30 (AB, 2H, CH_2Ph, ^2J(HH) 13.6 Hz), 4.62 (s, 3H, Me–O), 3.73 (d, 9H, $P(OMe)_3$, ^3J(PH) 11.4 Hz), 1.98 (s, 6H, $C_6H_2Me_2$), 1.92 (s, 6H, $C_6H_2Me_2$). $^{13}C\{^1H\}$ NMR (75.469 MHz, CD_2Cl_2, 309 K) δ ppm: 323.15 (d, Ru=C, ^2J(PC) 26.7 Hz), 133.2, 130.5, 129.5, 128.0 (s, C_6H_5), 111.1, 109.9, 92.1 (s, $C_6Me_4H_2$), 68.9 (s, Me–O), 59.3 (d, $P(OMe)_3$, ^2J(PC) 8.2 Hz), 17.9, 17.3 (s, $C_6Me_4H_2$). $^{31}P\{^1H\}$ NMR (32.80 MHz, CD_2Cl_2, 309 K) δ ppm: 124.14 (s, $P(OMe)_3$), −145.11 (sept., PF_6^-). IR (KBr) ν cm^{-1}: 1280 (C–O), 860 (P–F). Anal. Found: C, 39.49; H, 4.84; P, 9.33. $C_{22}H_{33}ClF_6O_4P_2Ru$ calcd.: C, 39.29; H, 4.90; P, 9.21%.

*Complex [Ru(=C(OMe)CH$_2$(CH$_2$)$_3$CH$_3$)Cl(PMe$_3$)(C$_6$H$_2$Me$_4$)]PF$_6$ (**9a**)*

9a was obtained from 0.38 g (1 mmol) of complex **1a**, but after 20 h of reaction, as orange crystals in 82% yield (0.50 g). ^1H NMR (300.134 MHz, CD_2Cl_2, 309 K) δ ppm: 5.74 (s, 2H, $C_6H_2Me_4$), 4.51 (s, 3H, Me–O), 3.77–3.08 (tq, 2H, CH_2–$(CH_2)_3$,

^2J(HH) 4.09 Hz, ^3J(HH) 11.4 Hz), 2.01 (s, 6H, $C_6H_2Me_2$), 1.96 (s, 6H, $C_6H_2Me_2$), 1.68 (m, 6H, $(CH_2)_3$), 1.44 (d, 9H, PMe_3, ^2J(PH) 10.9 Hz), 0.91 (t, 3H, $(CH_2)_3$–*Me*, ^3J(HH) 7.0 Hz). $^{13}C\{^1H\}$ NMR (75.469 MHz, CD_2Cl_2 309 K) δ ppm: 330.26 (d, Ru=C, ^2J(PC) 20.36 Hz), 109.1, 98.6, 107.6 (s, $C_6Me_4H_2$), 66.3 (s, *Me*–O), 51.9 (s, CH_2–C=Ru), 32.2, 25.3, 22.5 (s, $(CH_2)_3$), 17.5, 17.3 (s, $C_6Me_4H_2$), 17.0 (d, PMe_3, ^1J(PC) 38.3 Hz), 14.0 (s, *Me*–$(CH_2)_3$). $^{31}P\{^1H\}$ NMR (32.80 MHz, CD_2Cl_2, 309 K) δ ppm: 12.75 (s, PMe_3, −144.4 (sept., PF_6^-). IR (KBr) ν cm^{-1}: 1290 (C–O), 980 (PMe_3), 860 (P–F). Anal. Found: C, 39.69; H, 6.12; P, 10.11. $C_{20}H_{37}ClF_6OP_2Ru$ calcd.: C, 39.64; H, 6.15; P, 10.22%.

*Complex [Ru(=C(OMe)CH_2Ph)Cl(PPh_3)(p-Me-$C_6H_4^iPr$)]PF_6 (**10b**)*

10b was obtained from 0.57 g (1 mmol) of complex **5b** [12] as orange crystals in 59% yield (0.48 g). ^1H NMR (300.134 MHz, $CDCl_3$, 309 K) δ ppm: 7.73 (s, 15H, PPh_3), 7.46 (s, 5H, *Ph*–CH_2), 5.34–3.84 (AB, 2H, CH_2Ph, ^2J(HaHb) 11.50 Hz), 5.32–4.96 (AB, 2H, C_6H_4Me(^{i}Pr), ^3J(HH) 6.5 Hz), 5.20–4.79 (AB, 2H, $MeC_6H_4^iPr$, ^3J(HH) 6.5 Hz), 4.27 (s, 3H, Me–O), 2.58 (sept., 1H, C*H*Me_2, ^3J(HH) 6.8 Hz), 1.77 (s, 3H, MeC_6), 1.13 (d, 3H, CH*Me*$_2$, ^3J(HH) 7.0 Hz), 1.04 (s, 3H, CH*Me*$_2$, ^3J(HH) 6.85 Hz). $^{13}C\{^1H\}$ NM R(75.469 MHz, $CDCl_3$, 309 K) δ ppm: 325.4 (d, Ru=C, ^2J(PC) 21.2 hz), 134.0, 133.2, 132.7 (s, PPh_3), 129.1 (s, CH_2Ph), 96.9, 94.9, 94.3 (s, $MeC_6H_4^iPr$), 67.8 (s, Me–O), 54.5 (s, CH_2), 33.7 (s, *C*HMe_2), 21.4 (s, *Me*$C_6H_4^iPr$), 17.6 (s, CH*Me*$_2$). $^{31}P\{^1H\}$ NMR (32.80 MHz, $CDCl_3$, 309 K) δ ppm: 35.87 (s, PPh_3), −144.3 (sept., PF_6^-). IR (KBr) ν cm^{-1}: 1290 (C–O), 850 (P–F). Anal. Found: C, 54.88; H, 4.87; P, 7.72. $C_{36}H_{39}ClF_6OP_2Ru$ calcd.: C, 54.71; H, 4.80; P, 7.64%.

*Complex [Ru(=C(OMe)CH_2Ph)Cl(PMe_3)(p-Me-C_6H_4-^{i}Pr)]PF_6 (**11a**)*

11a was obtained from 0.382 g (1 mmol) of complex **5a** [12] but at a temperature of −10°C–0°C as a dark-yellow powder 0.30 g (48% yield). ^1H NMR (80 MHz, CD_2Cl_2, 309 K) δ ppm: 7.20 (s, 5H, Ph), 5.38 (m, 4H, *p*-Me–C_6H_4–^{i}Pr), 5.10–4.15 (AB, 2H, CH_2Ph, ^2J(HH) 12.0 Hz), 2.90 (m, 1H, C*H*Me_2), 1.52 (d, 9H, PMe_3, ^2J(PH) 11.2 Hz), 1.20 (d, 3H, CH*Me*, ^3J(HH) 8.0 Hz), 1.10 (d, 3H, CH*Me*, ^3J(HH) 8.0 Hz). IR (KBr) ν cm^{-1}: 1290 (C–O), 985 (PMe_3), 860 (P–F). The instability of this complex did not allow elemental analysis and the recording of ^{31}P or ^{13}C NMR spectra.

Acknowledgement

We are grateful to Dr. H. Le Bozec for helpful discussions, to MRT for a doctorate grant to D.D., and to Johnson Matthey Chemicals Limited for a loan of ruthenium trichloride.

References

1 (a) R. Mahé, P.H. Dixneuf and S. Lecolier, Tetrahedron Lett., 27 (1986) 6333. (b) R. Mahé, Y. Sasaki, C. Bruneau, P.H. Dixneuf and S. Lecolier, J. Org. Chem., 54 (1989) 1518.
2 K. Ouzzine, H. Le Bozec and P.H. Dixneuf, J. Organomet. Chem., 317 (1986) C25.
3 H. Le Bozec, D. Touchard and P.H. Dixneuf, Adv. Organomet. Chem., 29 (1989) 163.
4 (a) H. Werner and H. Kletzin, Angew. Chem. Int. Ed. Eng., 22 (1983) 46; (b) H. Werner, H. Kletzin, A. Höhn, W. Paul and W. Knaup, J. Organomet. Chem., 306 (1986) 227.

5 K. Ouzzine, Thèse Université de Rennes, I, 1988; H. Le Bozec, K. Ouzzine and P.H. Dixneuf, unpublished results.
6 M.I. Bruce and A.G. Swincer, Aust. J. Chem., 33 (1980) 1471.
7 R.M. Bullock, J. Chem. Soc., Chem. Commun., (1989) 165.
8 J. Sylvestre and R. Hoffmann, Helv. Chim. Acta, 68 (1985) 1461.
9 M.I. Bruce and A.G. Swincer, Adv. Organomet. Chem., 22 (1983) 59.
10 R.A. Zelonka and M.C. Baird, Can. J. Chem., 50 (1972) 3063.
11 M.A. Bennett and K.A. Smith, J. Chem. Soc., Dalton Trans., (1974) 233.
12 M.A. Bennett, T.W. Matheson, G.B. Robertson, K.A. Smith and P.A. Tucker, Inorg. Chem., 19 (1980) 1014.
13 J.W. Hull, Jr and W.L. Gladfelter, Organometallics, 3 (1984) 605.
14 H. Werner and R. Werner, J. Organomet. Chem., 174 (1979) C67.