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Organometallic cumulenes: allenylidene- and alkenyl allenylidene-ruthenium complexes

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Abstract

The complex $\{N(CH_2CH_2PPh_2)_3\}RuCl_2$ reacts with the diphenyl propargyl alcohol ($HC\equiv CCPh_2OH$) to give a ruthenium-allenylidene compound stable in methanol. Reaction of the same complex with the diyne 5,5-diphenyl-penta-1,3-diyn-5-ol in methanol gives an alkenyl allenylidene compound containing the ($Ru=C=C=C(OMe)CH=CPh_2$ moiety. An X-ray diffraction study has revealed an almost linear arrangement Ru-C(1)-C(2)-C(3) with bond lengths of 1.921(5), 1.254(7) and 1.369(7) Å, respectively.

Introduction

Organometallic compounds containing delocalized π-systems are receiving attention as intermediates for the synthesis of new polyunsaturated organic substrates [1] or as precursors of metal-containing polymers [2]. This potential is stimulating the search for new polyunsaturated organometallics such as cumullenyl-metal [3] or allenylidene-metal [4] derivatives. The dehydration of propargyl alcohol derivatives to give an allenylidene-metal moiety has been achieved with a cyclopentadienylruthenium(II) complex [5], and we have shown that the less electron rich arene-ruthenium(II) complexes are especially effective in giving reactive allenylidene [6], alkenylcarbene [6], or pentatrienylidene-ruthenium complexes [7]. We have now investigated the influence of a sterically hindered and electron rich L_4RuCl^+ organometallic fragment on the activation of propargyl alcohol and diyne derivatives. We report below the first allenylidene- and alkenyl allenylidene-Ru(NP_3) complexes [NP_3: $N(CH_2CH_2PPh_2)_3$], and the X-ray characterization of a complex containing the $M=C=C=C(OMe)CH=CR_2$ arrangement.

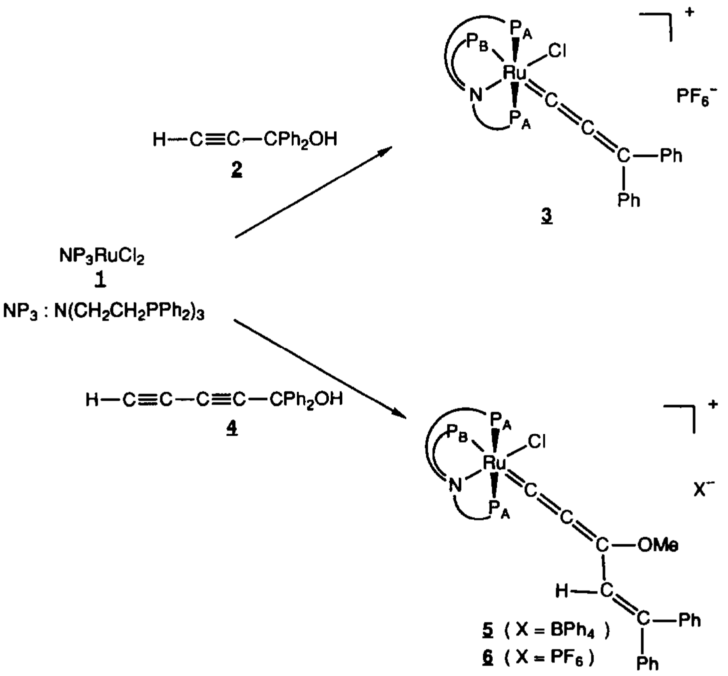
Results and discussion

Preparation of complex 3

Complex $(NP_3)RuCl_2$ (**1**) [8] reacts slowly with one equivalent of 1,1-diphenylprop-2-yn-1-ol (**2**) in dichloromethane in the presence of $NaPF_6$ during 6 h at 25 °C to give the violet allenylidene–ruthenium complex **3** (55%) (Scheme 1). The identification of **3** ($\surd$(C=C=C) 1933 cm^{-1}) is based on the ^{31}P NMR spectrum, which shows an A_2B system (^{31}P NMR (CD_2Cl_2), δ (ppm): 17.70 (d, 2P_A), 10.77 (t, P_B)), and the ^{13}C NMR spectrum (205.94 (d, Ru=C=*C*, $^3J(P_B, C)$ 26.3 Hz), 167.82 (s, *C*Ph_2)), which shows a very low-field signal at δ 323.8 ppm (dt) ($^2J(P_B, C)$ 96.7, $^2J(P_A,C)$ 17.8 Hz), for the ^{13}C (Ru=C) nucleus compared with δ 288.3 ppm (^2J(P,C) 29 Hz) in $[Ru{=}C{=}C{=}CPh_2(Cl)(PPh_3)(C_6Me_6)]PF_6$ [9]. Whereas the latter reacts very readily with methanol to give the $Ru{=}C(OMe)CH{=}CPh_2$ moiety [9], complex **3** is inert towards this alcohol. This is attributed to steric hindrance by the $N(CH_2CH_2PPh_2)_3$ ligand and to the electron-releasing properties of the $[(NP_3)RuCl]^+$ fragment. The reversible oxidation potential, determined by cyclic voltammetry, of NP_3RuCl_2 is $E^0 = +0.60$ V (SCE), compared with that of +0.87 V for $RuCl_2(PPh_3)(C_6Me_6)$ [9], and so the allenylidene ligand in **3** is expected to be less electrophilic toward alcohol.

Preparation of complexes 5 and 6

The evidence for a marked stabilization of the allenylidene ligand by NP_3RuCl^+ led us to study the activation of the diynol **4**, a possible precursor of the $Ru{=}(C{=})_4CPh_2$ intermediate.



Scheme 1

Complex **1** was treated with an excess of the diyne derivative **4** in methanol at room temperature for 3 h. Addition of $NaBPh_4$ led to the isolation of the deep red complex **5** (66%). Similarly, addition of $NaPF_6$ to the reaction mixture gave complex **6** (46%). Complex **6** was obtained in the same yield from **1**, $HC{\equiv}CC{\equiv}CCPh_2OSiMe_3$, and $NaPF_6$. The alkenyl allenylidene structure of complexes **5** and **6** was established on the basis of infrared (ν(C=C=C), ν(C–OMe) 1955, 1234 (**5**); 1995, 1230 (**6**) cm^{-1} in KBr) and NMR spectroscopy, which show that the NP_3Ru moiety is retained (**6**: $^{31}P\{^1H\}$ NMR δ(ppm): 24.25 (d, $2P_A$), 11.64 (t, P_B), $^2J(PP)$ 30.0 Hz) and a Ru=C=C=C(OMe) $CH=CPh_2$ group is present: $^{13}C\{^1H\}$ NMR (**6**: δ (ppm): 253.08 (dt, Ru=*C*, $^2J(P_B,C)$ 95.5, $^2J(P_A,C)$ 18.5 Hz), 159.04 (s, Ru=C=C=*C*) 157.53 (s, =*C*Ph_2), 143.90 (dt, Ru=C=*C*, $^3J(P_B,C)$ 25, $^3J(P_A,C)$ 1 Hz), 123.33 (s, *C*H=), 66.12 (s, O*Me*)) with a high field ^{13}C (Ru=C^1) nucleus resonance.

The sequence δ (C^1) > δ (C^3) > δ (C^2) was observed previously only in the first allenylidene-metal derivative $(OC)_5W{=}C^1{=}C^2{=}C^3(NMe_2)Ph$ [10], and seems to be due to the presence of a heteroatom group linked to C^3.

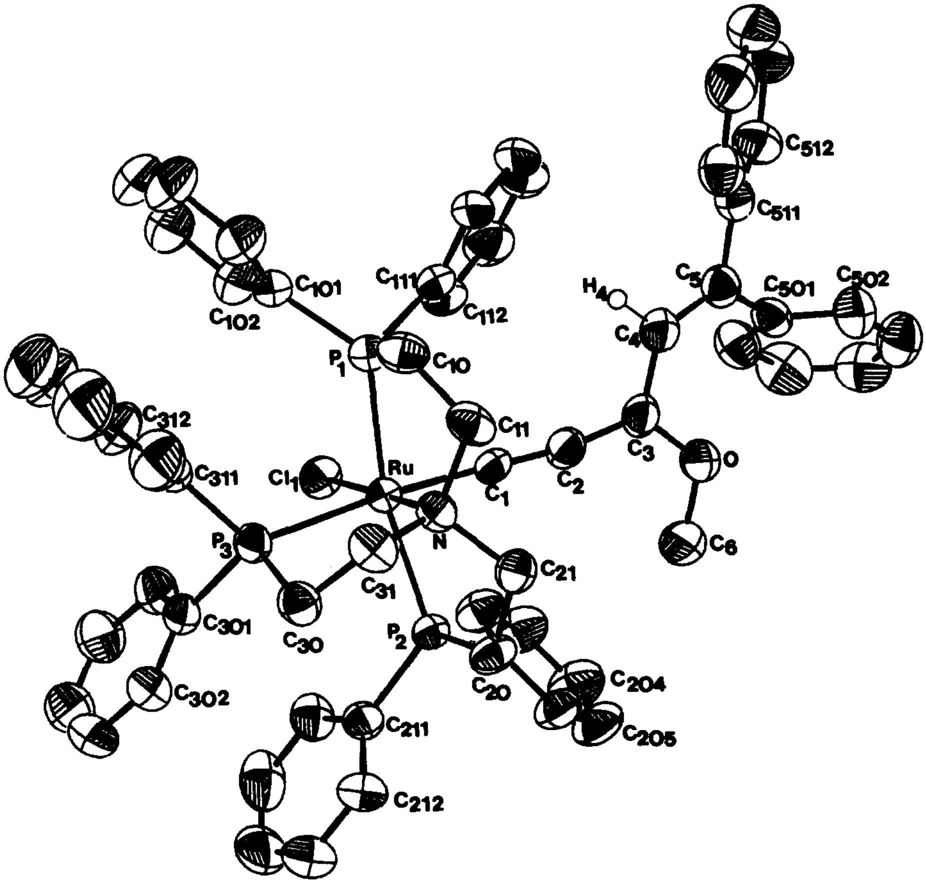


Fig. 1. ORTEP view of compound **6**.

Table 1

Crystal analysis parameters of compound **6**

Crystal data	
Formula	$C_{60}H_{56}NOF_6ClP_4Ru \cdot 1/2CH_2Cl_2$
Crystal size (mm)	$0.18 \times 0.25 \times 0.80$
Symmetry	Triclinic, $P\bar{1}$
Unit cell dimensions	13.515(1), 12.909(1), 19.411(3) Å 108.55(1), 95.18(1), 102.79(1) °
Packing: V (Å^3), Z	3083.2(6), 2
D_c (g cm^{-3}), M, F(000)	1.3119, 1223.98, 1254
μ (cm^{-1})	43.896
Experimental data	
technique	Four-circle diffractometer Philips PW 1100 monochromated Cu-K_α, $\theta_{max} = 58$ °
No. of reflexions:	
measured	7889
observed	7506 [$I \geqslant 3\sigma(I)$ criterion]
standard reflections	232 and $\bar{2}\bar{3}\bar{2}$ reflections every 90 min no variation
Solution and refinement	
solution	Patterson and Fourier Synthesis
refinement	least squares on F_o with 3 blocks
absorption correction [12]	yes; max and min, 1.261 and 0.803
no. of variables	679
H atoms	Difference Fourier Synthesis
Final R and R_w	0.057, 0.055
computer and programs	VAX 6410, XRAY 80 System [13], DIRDIF [15], PESOS [16]
scattering factors	Int. Tables for X-Ray crystallography [14]
anomalous dispersion	Int. Tables for X-Ray crystallography [14]

Structure of complex 6

As very few metallacumulenes have previously been structurally characterized [4,5,10,11], an X-ray diffraction study of the first alkenyl allenylidene–ruthenium complex **6** was undertaken. The ORTEP view of the molecule is shown in Fig. 1, and the main data are listed in Tables 1, 2 and 3. The structure shows that the addition of the methoxy group of methanol has taken place at C(3) and that of the proton at C(4). There is an almost planar Ru–C(1)–C(2)–C(3)(OMe)–C(4)–C(5) arrangement, with a long Ru–C(1) distance (1.921(5) Å) for the bond *trans* to a Ph_2P_B group, a short C=C double bond (1.254(7) Å), and a slight distortion from linearity of the Ru–C(1)–C(2)–C(3) moiety.

Formation of complexes 5 and 6

The formation of complexes **5** and **6** suggests that activation of the diynol **4** by the NP_3RuCl^+ moiety involves dehydration to give the intermediate $NP_3Ru{=}(C{=})_4CPh_2^+$ which is very reactive compared with the analogous $NP_3Ru{=}(C{=})_2CPh_2^+$ (**3**)) and that nucleophilic addition of methanol occurs at carbon C(3) whereas addition at the most electrophilic carbon C(1) was observed when in a similar reaction with $RuCl_2(PMe_3)(C_6Me_6)$ [7]. This protection of the

Table 2

Selected bond lengths (Å) and angles (°) for compound **6**

Ru-P1	2.339(1)	P2-C20	1.844(4)	C10-C11	1.514(8)
Ru-P2	2.356(1)	P2-C201	1.828(5)	C20-C21	1.516(7)
Ru-P3	2.430(1)	P2-C211	1.830(5)	C30-C31	1.514(6)
Ru-N	2.170(3)	P3-C30	1.831(5)	C1-C2	1.254(7)
Ru-Cl1	2.422(1)	P3-C301	1.831(4)	C2-C3	1.369(7)
Ru-C1	1.921(5)	P3-C311	1.840(6)	C3-C4	1.443(8)
P1-C10	1.826(4)	N-C11	1.524(6)	C3-O	1.332(8)
P1-C101	1.831(6)	N-C21	1.515(7)	O-C6	1.435(11)
P1-C111	1.825(5)	N-C31	1.523(6)	C4-C5	1.358(7)
				C4-H4	1.04

P1-Ru-P2	165.28(4)	P1-C10-C11	109.7(3)
P1-Ru-P3	95.62(4)	N-C11-C10	111.5(4)
P1-Ru-N	85.2(1)	P2-C20-C21	110.2(3)
P1-Ru-Cl1	93.78(4)	N-C21-C20	111.8(3)
P1-Ru-C1	86.3(1)	P3-C30-C31	109.0(3)
P2-Ru-P3	92.02(4)	N-C31-C30	114.5(3)
P2-Ru-N	83.3(1)	Ru-C1-C2	174.1(3)
P2-Ru-Cl1	98.29(4)	C1-C2-C3	170.2(6)
P2-Ru-C1	84.2(2)	C2-C3-O	122.3(5)
P3-Ru-N	82.8(1)	C2-C3-C4	121.4(5)
P3-Ru-Cl1	93.55(4)	C4-C3-O	116.3(5)
P3-Ru-C1	170.3(1)	C3-O-C6	118.1(5)
N-Ru-Cl1	176.1(1)	C3-C4-C5	127.8(5)
N-Ru-C1	87.8(1)	C3-C4-H4	114.0
Cl1-Ru-C1	95.8(1)	C5-C4-H4	118.0
C11-N-C21	105.8(3)	C4-C5-C501	124.2(5)
C11-N-C31	107.3(3)	C4-C5-C511	118.8(5)
C21-N-C31	108.9(4)	C501-C5-C511	116.9(4)

C(1) site is thought to be due, as in the case of **3**, to the electron richness of the NP_3RuCl^+ moiety and to the steric hindrance by the phenyl groups of the NP_3 ligand.

Conclusion

The combination of the activation of terminal 1,3-diynes by ruthenium(II) complexes with steric protection of the electrophilic carbon C(1) should demonstrate the wide scope of these reactions and provide a route access to new metallacumulenes by modification of the environment of the ruthenium site.

Experimental

Synthesis

All reactions were carried out under nitrogen by Schlenk techniques. NMR spectra were recorded on a Bruker WP 80 (FT) (^1H, ^{31}P, ^{13}C) or Bruker AM 300 WB(FT) (^1H, ^{31}P, ^{13}C) spectrometer at the "Centre de Mesures Physiques de l'Ouest" University of Rennes. Infrared spectra were obtained with a Nicolet FT

Table 3

Atomic parameters for $C_{60}H_{56}NOF_6ClP_4Ru\cdot 1/2CH_2Cl_2$. Coordinates and thermal parameters as $U_{eq} = 1/3\Sigma[U_{ij}a_i^*a_j^*\mathbf{a}_i\mathbf{a}_j \cos(a_i, a_j)]\cdot 10^4$

Atom	x	y	z	U_{eq}
Ru	0.23281(2)	0.23289(2)	0.76554(2)	333(1)
P1	0.26337(8)	0.39813(9)	0.73621(6)	426(4)
P2	0.24688(8)	0.08521(9)	0.80928(5)	378(4)
P3	0.09705(8)	0.27374(9)	0.83540(6)	409(4)
Cl1	0.11325(8)	0.12059(9)	0.65185(6)	491(54)
N	0.3319(2)	0.3389(3)	0.8700(2)	398(13)
C1	0.3548(3)	0.2094(3)	0.7263(2)	393(16)
C2	0.4396(4)	0.2006(4)	0.7071(2)	482(19)
C3	0.5330(4)	0.2080(5)	0.6843(3)	515(20)
C4	0.5816(4)	0.3022(4)	0.6634(3)	528(20)
C5	0.6590(3)	0.3088(4)	0.6237(2)	472(18)
O	0.5852(3)	0.1309(4)	0.6816(2)	720(19)
C6	0.5375(6)	0.0329(7)	0.6984(5)	938(39)
C501	0.6990(3)	0.2109(4)	0.5851(2)	466(18)
C502	0.8033(4)	0.2198(5)	0.5963(3)	608(22)
C503	0.8411(5)	0.1292(6)	0.5601(4)	737(27)
C504	0.7766(6)	0.0317(5)	0.5111(4)	791(30)
C505	0.6738(6)	0.0236(5)	0.4971(4)	799(28)
C506	0.6339(4)	0.1124(5)	0.5339(3)	658(23)
C511	0.7035(3)	0.4180(4)	0.6137(3)	490(18)
C512	0.7355(4)	0.4183(5)	0.5471(3)	610(22)
C513	0.7718(5)	0.5202(6)	0.5359(4)	762(29)
C514	0.7794(5)	0.6212(6)	0.5906(4)	792(30)
C515	0.7500(5)	0.6224(5)	0.6569(4)	761(27)
C516	0.7126(4)	0.5214(5)	0.6686(3)	602(22)
C10	0.3398(4)	0.5005(4)	0.8233(3)	515(18)
C11	0.4011(3)	0.4426(4)	0.8610(2)	487(17)
C101	0.1695(4)	0.4666(4)	0.7086(3)	555(22)
C102	0.0991(4)	0.4047(6)	0.6434(4)	719(27)
C103	0.0331(5)	0.4572(8)	0.6157(5)	987(43)
C104	0.0373(7)	0.5677(9)	0.6522(7)	1154(57)
C105	0.1059(7)	0.6286(7)	0.7168(7)	1112(51)
C106	0.1731(5)	0.5787(5)	0.7459(4)	807(30)
C111	0.3401(3)	0.4010(4)	0.6638(2)	455(18)
C112	0.3195(4)	0.3051(4)	0.6010(3)	553(21)
C113	0.3723(5)	0.3059(5)	0.5421(3)	697(26)
C114	0.4439(5)	0.4022(6)	0.5468(3)	733(31)
C115	0.4646(4)	0.4984(6)	0.6080(4)	668(27)
C116	0.4132(4)	0.4999(4)	0.6682(3)	552(21)
C20	0.3450(4)	0.1615(4)	0.8934(2)	473(17)
C21	0.4037(3)	0.2748(4)	0.8913(2)	453(17)
C201	0.2913(4)	−0.0321(4)	0.7520(2)	458(17)
C202	0.2558(4)	−0.0737(4)	0.6762(3)	585(21)
C203	0.2765(6)	−0.1713(5)	0.6319(3)	767(27)
C204	0.3345(6)	−0.2259(5)	0.6618(4)	822(30)
C205	0.3723(5)	−0.1849(5)	0.7359(4)	750(29)
C206	0.3493(4)	−0.0890(4)	0.7821(3)	583(21)
C211	0.1420(3)	0.0010(3)	0.8381(3)	450(17)
C212	0.1446(4)	−0.0040(5)	0.9089(3)	635(23)
C213	0.0611(6)	−0.0720(6)	0.9248(4)	831(33)
C214	−0.0223(5)	−0.1356(5)	0.8721(5)	845(35)
C215	−0.0252(5)	−0.1323(5)	0.8017(5)	824(30)

Table 3 (continued)

Atom	x	y	z	U_{eq}
C216	0.0566(4)	−0.0637(4)	0.7844(3)	593(20)
C30	0.1700(4)	0.3062(4)	0.9272(2)	480(18)
C31	0.2764(4)	0.3814(4)	0.9339(2)	503(18)
C301	−0.0228(3)	0.1665(4)	0.8251(3)	468(18)
C302	−0.0596(4)	0.1457(5)	0.8857(3)	620(23)
C303	−0.1544(5)	0.0673(6)	0.8742(4)	796(32)
C304	−0.2124(5)	0.0136(6)	0.8050(5)	873(35)
C305	−0.1770(5)	0.0353(6)	0.7453(4)	813(29)
C306	−0.0814(4)	0.1107(5)	0.7553(3)	611(22)
C311	0.0438(4)	0.3959(4)	0.8445(3)	518(19)
C312	−0.0277(5)	0.3877(5)	0.7857(4)	735(27)
C313	−0.0766(6)	0.4727(7)	0.7908(6)	979(40)
C314	−0.0540(7)	0.5656(7)	0.8531(7)	1088(49)
C315	0.0180(7)	0.5778(6)	0.9104(6)	1039(40)
C316	0.0684(5)	0.4915(5)	0.9066(4)	800(28)
P4	0.3566(1)	0.2736(1)	0.1253(1)	709(6)
F1	0.4236(4)	0.3048(5)	0.0681(2)	1217(24)
F2	0.3934(5)	0.4017(4)	0.1744(3)	1394(27)
F3	0.2816(5)	0.2500(6)	0.1781(3)	1602(33)
F4	0.3230(6)	0.1461(4)	0.0764(3)	1566(32)
F5	0.2644(5)	0.2805(9)	0.0731(4)	1794(51)
F6	0.4509(7)	0.2646(8)	0.1703(5)	1936(48)
Cl2	0.6803(12)	0.2836(13)	0.9592(8)	2490(49)
Cl3	0.6905(10)	0.4035(12)	0.8514(7)	2279(42)
C7	0.7193(26)	0.3119(29)	0.8906(18)	1703(96)

205 and elemental analyses were performed by the CNRS laboratory, Vernaison (France).

Materials

Solvents were dried by refluxing over appropriate drying agents and stored under an inert atmosphere. Tetrahydrofuran and diethyl ether were distilled over benzophenone ketyl, pentane and hexane over calcium hydride, dichloromethane first over phosphorous pentoxide and then over calcium hydride, and methanol over magnesium. The starting complex NP_3RuCl_2 (**1**) was prepared by Bianchini's method [8].

Synthesis of $[Ru(=C=C=CPh_2)(Cl)N(CH_2CH_2PPh_2)_3]PF_6$ *(3)*

To a solution of 0.412 g (0.5 mmol) of **1** and 0.104 g (0.5 mmol) of **2** in 50 ml of dry dichloromethane was added 0.083 g (0.5 mmol) of $NaPF_6$. The solution was stirred at room temperature for 6 h, during which the color of the solution changed slowly from yellow to violet. The solution was filtered and the solvent distilled off. The residue was washed with diethyl ether and recrystallised from a dichloromethane/hexane mixture to give 0.315 g (55%) of **3** was obtained.

3: violet, 55% yield. IR (KBr): 1933 (C=C=C), 838 (PF_6) cm^{-1}. ^{31}P NMR (CD_2Cl_2, 297 K, 121.496 MHz) δ (ppm): 17.70 (d, P_A), 10.77 (t, P_B) ($^2J(PP)$ 32.5 Hz), −143.2 (sept.). ($J(PF)$ 710 Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 297 K, 75.469 MHz) δ(ppm): 323.81 (dt, Ru=*C*, $^2J(P_B,C)$ 96.6, $^2J(P_A,C)$ 17.8 Hz), 205.94 (d, Ru=C=*C*,

$^3J(P_B,C)$ 26.3 Hz), 167.82 (s, CPh_2), 144.04 (s, C_{ipso}). Anal. Found: C, 59.63; H, 4.78; N, 1.24; Cl, 3.08; P, 11.05. $C_{57}H_{52}NClF_6P_4Ru$ calc.: C, 60.83; H, 4.65; N, 1.24; Cl, 3.15; P, 11.01%.

Synthesis of [Ru(=C=C=C(OMe)CH=CPh$_2$)(Cl)N(CH$_2$CH$_2$PPh$_2$)$_3$]BPh$_4$ (5) and [Ru(=C=C=C(OMe)CH=CPh$_2$)(Cl)N(CH$_2$CH$_2$PPh$_2$)$_3$]PF$_6$ (6)

Complex **4** (0.348 g, 1 mmol) was added to a suspension of 0.412 g (0.5 mmol) of **1** in 30 ml of dry methanol. The mixture was stirred at room temperature for 3 d, giving red solution, which was concentrated to half its volume and treated with 0.171 g of $NaBPh_4$. The precipitate was filtered off, washed with methanol, and dried. The residue was purified by crystallisation from a dichloromethane/hexane mixture to give 0.44 g of **5** (66%).

When 0.168 g of $NaPF_6$ was added to the solution instead of $NaBPh_4$, 0.270 g of **6** (46%) was obtained after work up and recrystallisation.

5: red, IR(KBr): 1955 (C=C=C), 1234 (C–OMe) cm^{-1}. ^1H NMR (CD_2Cl_2, 297 K, 300.134 MHz) δ(ppm): 2.91 (s, OCH_3). ^{31}P NMR (CD_2Cl_2, 297 K, 121.496 MHz) δ (ppm): 24.64 (d, P_A), 12.07 (t, P_B)($^2J(PP)$ 29.8 Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 297 K, 75.469 MHz) δ ppm: 252.90 (dt, Ru=*C*, $^2J(P_B,C)$ 95.7, $^2J(P_A,C)$ 16.2 Hz), 159.19 (s, Ru=C=C=*C*), 141.51 (s, C_{ipso}) 139.56 (s, C_{ipso}), 123.31 (s, CH), 66.40 (s, OCH_3), 166.82 (dd, BPh_4). ^{13}C NMR (CD_2Cl_2, 297 K, 300.134 MHz) δ (ppm): 123.31 (d, CH, $^1J(CH)$ 163.9 Hz). Anal. Found: C, 75.08; H, 6.03; N, 1.10; Cl, 2.73; P, 6.51. $C_{84}H_{76}NBClOP_3Ru$ calc.: C, 74.41; H, 5.64; N, 1.03; Cl, 2.61; P, 6.85%.

6: red, IR(KBr): 1955 (C=C=C), 1230 (C–OMe), 860 (PF_6) cm^{-1}. ^1H NMR (CD_2Cl_2, 297 K, 300.134 MHz) δ (ppm): 2.94 (s, OCH_3). ^{31}P NMR (CD_2Cl_2, 297 K, 121.496 MHz) δ (ppm): 24.25 (d, P_A), 11.64 (t, P_B), ($^2J(PP)$ 30.0 Hz), -143.70 (sept., $J(PF)$ 711 Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 297 K, 75.469 MHz) δ (ppm): 253.08 (dt, Ru=*C*, $^2J(P_B,C)$ 95.5, $^2J(P_A,C)$ 18.5 Hz), 159.04 (s, Ru=C=C=*C*), 157.53 (s, CPh_2), 143.90 (dt, Ru=C=*C*, $^3J(P_B,C)$ 25.0, $^3J(P_A,C)$ 1 Hz), 141.51 (s, C_{ipso}), 139.47 (s, C_{ipso}), 123.33 (s, CH), 66.12 (s, O*C*H_3). ^{13}C NMR (CD_2Cl_2, 297 K, 75.469 MHz) δ (ppm): 123.33 (d, *C*H, $^1J(CH)$ 163.9 Hz). Anal. Found: C, 60.45; H, 4.87; N, 1.14; Cl, 3.94; P, 10.51. $C_{60}H_{56}NClF_6OP_4Ru$ calc.: C, 60.99; H, 4.77; N, 1.18; Cl, 3.00; P, 10.48%.

X-Ray diffraction of complex 6

Single crystals of complex **6** suitable for X-ray diffraction study were obtained by recrystallization from CH_2Cl_2/Et_2O at room temperature. A single crystal of dimensions 0.18 × 0.25 × 0.80 mm was mounted on the end of a glass fiber. The X-ray diffraction intensity data of 7889 independent reflections, of which 7506 with $I \geqslant 3\sigma(I)$ were regarded as observed, was collected on a PW1100 four-circle diffractometer with graphite-monochromated Cu-K_α radiation, in the $\omega/2\theta$ scan mode, the range $2° < \theta < 58°$. Unit-cell parameters were obtained from least-squares refinement of 2θ values of 37 reflections. The observation of systematic absences led to the space group $P1$ or $P\bar{1}$, and the latter was shown to be correct during the refinement. Instrumental and compound stability were monitored by measuring two standard reflections (232 and $\bar{2}\bar{3}\bar{2}$) every 90 min; no variation was observed.

The structure was solved by heavy-atom methods, the ruthenium atom being located in the Patterson map and light atoms in subsequent Fourier syntheses. Least-squares refinement of positions and isotropical thermal parameters for non-hydrogen atoms gave an R value $[R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|]$ of 0.125. After isotropic refinement, an empirical absorption correction was applied [12], with maximum and minimum absorption corrections of 1.261 and 0.803, respectively. Conversion to anisotropic temperature factors and further cycles of refinement followed by a difference Fourier syntheses allowed the location of all the hydrogen atoms and of a CH_2Cl_2 molecule of crystallization that was revealed by further refinement to be present in a 1/2 ratio to the complex, so the actual formula of the crystal is $C_{60}H_{56}NOF_6ClP_4Ru \cdot 1/2CH_2Cl_2$. The final cycle of anisotropic treatment of the non-hydrogen atoms (non H-atoms of CH_2Cl_2 molecule as isotropic, all H-atoms as isotropic fixed) included 679 variable parameters and converged to the unweighted and weighted agreement factors of $R = 0.057$ and $R_w = 0.055$.

All calculations were by the full matrix method and were carried out on a VAX 6410 computer with the XRAY 80 system [13]. Scattering factors were taken from International Tables of X-ray Crystallography [14]. The final positional and thermal parameters are listed in Table 1. Selected bond lengths and angles are listed in Table 2. A complete table of bond lengths and angles, and lists of thermal parameters and structure factors are available from the authors.

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