Metallacumulenes: Preparation of Novel Alkenyl–Allenylidene– and Diynyl–Ruthenium Complexes. Crystal Structure of a Ru–C≡C–C≡C–C(OSiMe$_3$)Ph$_2$ Derivative

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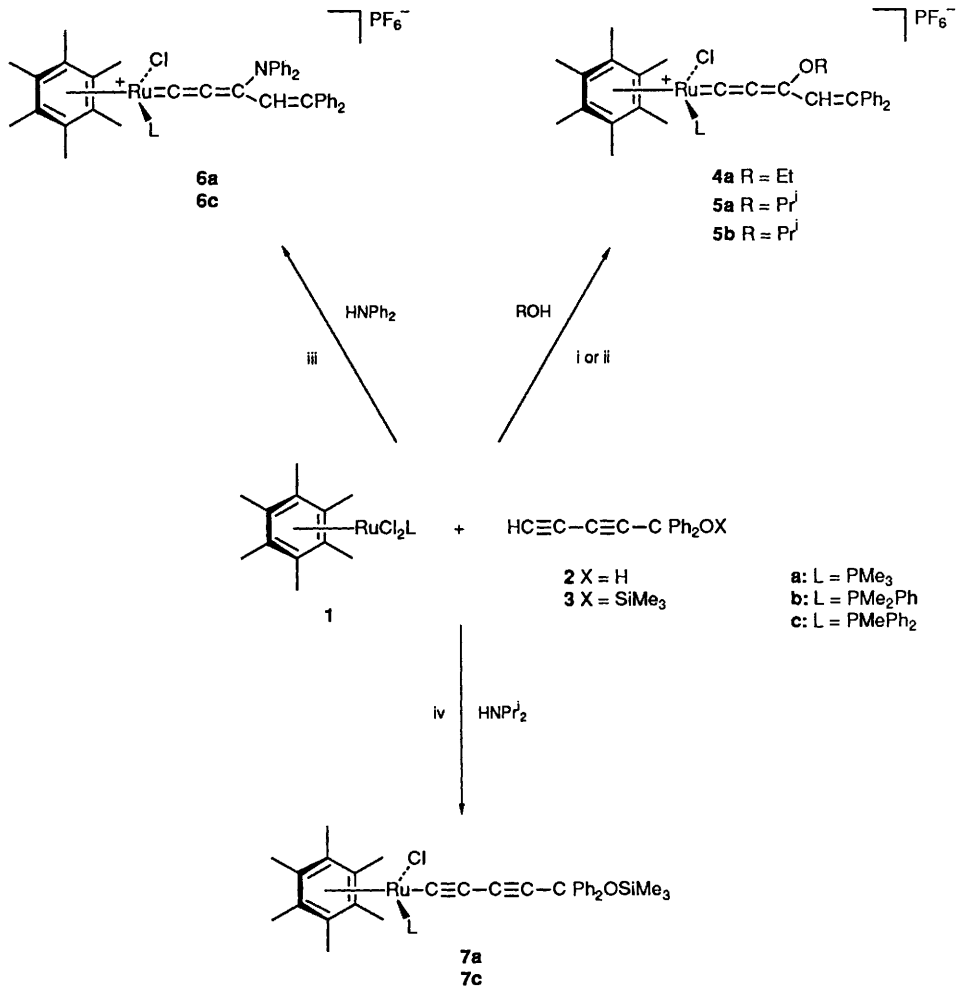
Complexes (η^6-arene)(PR_3)$RuCl_2$ **1** react with HC≡C–C≡C–CPh_2OX derivatives (X = H, $SiMe_3$) to afford, in alcohol or in the presence of $HNPh_2$, 3-alkenyl allenylidene complexes [(η^6-arene)(PR_3)ClRu=C=C=C(Y)CH=CPh_2]$^+$ (Y = OEt **4a**, OPr^i **5a**, NPh_2 **6**) and diynyl–ruthenium derivatives in the presence of $HNPr^i_2$.

In spite of their interest as polyunsaturated organometallic complexes,[1] for polymerization of alkynes[2] or synthesis of cumulene derivatives,[3,4] allenylidene–metal complexes are still unusual. Such compounds have been made by alkoxide elimination from alkoxy and alkenylcarbene complexes,[5] treatment of (η^2-HC≡C–CO_2Me)–manganese derivatives with alkyllithium,[6] reaction of LiC≡C–CR_2OLi with metal carbonyls[7] or by activation of disubstituted propargyl alcohol derivatives by ruthenium(II) complexes.[8,9] Recently, we have shown that (arene)$RuCl_2(PR_3)$ complexes **1**[10] react with propargyl alcohol derivatives in methanol to provide methoxy, alkenylidene–metal complexes *via* ruthenium–allenylidene intermediates.[9] We now report that the activation of the diyne derivatives HC≡C–C≡C–CPh_2OX (**2**: X = H; **3**: X = $SiMe_3$) by complexes **1a–c**, in the presence of bulky alcohols or amines, allows access either to novel 1,2,4-pentatrienylidene– or 1,3-pentadiynyl–ruthenium complexes.

The reaction of the arene–ruthenium(II) complex **1a** with



Scheme 1 *Reagents and conditions*: (with one equiv. of $NaPF_6$ at room temp.): i, **2** or **3** and **1a** in alcohol (EtOH or Pr^{i}OH), 3 h; ii, **3** and **1a** or **1b** in CH_2Cl_2 (1 h) and an excess (0.2 cm^3) of EtOH or Pr^{i}OH, 1–2 h; iii, **3** and **1a** in CH_2Cl_2 (1 h) and one equiv. of $HNPh_2$ (1 h); **3** and **1c** in CH_2Cl_2 (2 h) and one equiv. of $HNPh_2$ (2 h); iv, **1a** or **1c** and **3** in CH_2Cl_2 (30 min) and $HNPr^i_2$ (30 min)

one equivalent of $NaPF_6$ and the diyne derivative **2** in ethanol results after 3 h at room temperature, in a violet complex **4a** isolated in 45% yield† (Scheme 1). From a similar reaction of **1a** with **3** in CH_2Cl_2, followed by addition of alcohol, complex **4a** was isolated in the same yield. When the reaction of **1a** and **1b** with **3** was performed in propan-2-ol, complexes **5a** and **5b** were obtained in 57 and 48% yield, respectively.†

The allenylidene–ruthenium structure of compounds **4–5** is based on a very strong IR absorption at *ca.* ν 2000 cm^{-1} (KBr) assigned to a C=C=C group. A ^{13}C NMR doublet for the Ru=*C* carbon nucleus [δ_C 231.20 ($^2J_{PC}$ 28.6 Hz) **4a**; 229.0 ($^2J_{PC}$ 30.5 Hz) **5a**; 228.0 ($^2J_{PC}$ 28.8 Hz) **5b**] is consistent with a Ru=*C*=C=C(OR) arrangement as the Ru=C ^{13}C NMR peak for the related alkenylcarbene–ruthenium moiety Ru=*C*(OMe)CH=CPh_2 is at much lower field [δ 304.2 ($^2J_{PC}$ 18.7 Hz)].[9]

The treatment of **1a** with **3** in dichloromethane leads to a green–blue solution. After 1 h one equivalent of the weak basic amine $HNPh_2$ (pK_a 0.79) was added, which produced red–brown crystals of **6a** (53%).† Under similar conditions complex **1c**, which contains the bulky $PMePh_2$ ligand, reacts with **3** and leads to the slow formation of **6c** (81%)† (Scheme 1). The assignment of the Ru=C(1)=C(2)=C(3) resonances is based on that of the complex $(OC)_5W$=C(1)=C(2)=C(3)(N-Me_2)Ph for which δ [C(1)] 198.9 < δ [C(3)] 157.5 < δ [C(2)] 121.3 as indicated by the J_{WC} values.[5]

A closely related reaction was attempted but using a more basic secondary amine $HNPr^i_2$ (pK_a 10.96): **1a** and **3** in dichloromethane afforded a green–blue solution after 30 min when $HNPr^i_2$ was added to the solution it immediately turned brown. The white salt $H_2N^+Pr^i_2 \cdot PF_6^-$ and the orange complex **7a**† (36%) were isolated. Complex **7c**† was also obtained in 42% yield from **1c**, **3** and $HNPr^i_2$. IR and ^{13}C NMR spectroscopy show the presence of two C≡C bonds [ν(C≡C) 2215, 2060 cm^{-1} **7a**] and that the $OSiMe_3$ group is retained. A single crystal X-ray structural analysis was carried out on complex **7a**.‡ The ORTEP plot (Fig. 1) shows the first structural characterization of a diynyl–ruthenium complex, with a slight lengthening of the C≡C bond [C(1)–C(2) 1.26(4) Å] close to the chiral ruthenium atom with respect to the C(3)–C(4) bond [1.16(6) Å]. However, the lengthening cannot be considered significant within the accuracy attained (*R* 7.6%).‡

Complex **7a** was inert to treatment with propan-2-ol or diphenylamine. This suggests that the diyne **3** reacts with complex **1** to afford, by displacement of one chloride, a blue intermediate assumed to be a [Ru(η²-HC≡C–C≡C–C($OSiMe_3$)-Ph_2]$^+$ cation; the latter is either deprotonated to **7** by a basic amine $HNPr^i_2$ or affords, by slow elimination of $HOSiMe_3$, the metallacumulene Ru^+=(C=)$_4CR_2$, which is the site of a nucleophilic addition at carbon C(3) in the presence of EtOH,

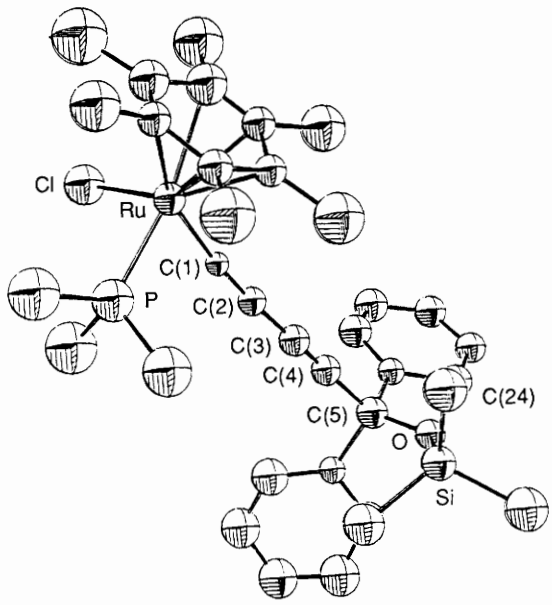


Fig. 1 Molecular structure of $(C_6Me_6)(PMe_3)(Cl)Ru$–C≡C–C≡C–$C(OSiMe_3)Ph_2$ **7a** (ORTEP view). Selected bond distances (Å) and angles (°): Ru–C(1) 1.93(3), C(1)–C(2) 1.26(4), C(2)–C(3) 1.40(5), C(3)–C(4) 1.16(6), C(4)–C(5) 1.53(6), C(5)–O 1.43(5), Ru–P 2.26(1); P–Ru–C(1) 82(1), Ru–C(1)–C(2) 174(3), C(1)–C(2)–C(3) 175(4), C(2)–C(3)–C(4) 176(4), C(3)–C(4)–C(5) 171(4), C(4)–C(5)–O 111(4)

† Satisfactory elemental analyses were obtained for derivatives **4a–7b**. *Selected spectroscopic data* for: **4a**: IR (KBr) 2000 cm^{-1} (vs, ν C=C=C); ^1H NMR (300.13 MHz) δ 6.74 (s, CH=), 4.33 (q, OCH_2), 2.14 (s, C_6Me_6), 0.94 (t, Me); ^{31}P (^1H) NMR (121.49 MHz) δ 12.39 (s, PMe_3), −143.49 (sept, PF_6^-); ^{13}C NMR (75.47 MHz) δ 231.20 (d, Ru=C, $^2J_{PC}$ 28.6 Hz), 162.12 (s), 161.13 (s) {Ru=C=C=*C*, =*C*Ph_2}, 133.55 (s, Ru=C=*C*=C), 123.12 ppm (s, =CH, $^1J_{PC}$ 162.3 Hz).

For **5a**: IR (KBr) 2000 cm^{-1} (vs, ν C=C=C); ^1H NMR (300.13 MHz) δ 6.77 (s, CH=), 5.21 (sept, OC*H*Me_2), 1.04 (d, CH*Me*$_2$, $^3J_{HH}$ 6.2 Hz); ^{13}C NMR (75.47 MHz) δ 229.0 (d, Ru=C, $^2J_{PC}$ 30.5 Hz), 161.60, 161.12 (s, Ru=C=C=*C*, =*C*Ph_2}, 131.88 (s, Ru=C=*C*=C), 123.67 ppm (s, =CH, $^1J_{CH}$ 162.6 Hz).

For **5b**: IR (KBr) 1975 cm^{-1} (vs, ν C=C=C); ^1H NMR (300.13 MHz) δ 6.85 (s, CH=), 5.25 (sept, OC*H*Me_2), 1.06 and 0.95 (dd, CH*Me*$_2$, $^3J_{HH}$ 5.7 Hz); ^{31}P (^1H) NMR (121.49 MHz) δ 20.10 (s, PMe_2Ph); ^{13}C NMR (75.47 MHz) δ 227.99 (d, Ru=C, $^2J_{PC}$ 28.8 Hz), 161.72, 161.40 (s, Ru=C=C=*C*, =*C*Ph_2}, 132.13 (s, Ru=C=*C*=C), 123.63 ppm (s, =CH, $^1J_{CH}$ 162.7 Hz).

For **6a**: IR (KBr) 2010 cm^{-1} (vs, ν C=C=C); ^1H NMR (300.13 MHz) δ 6.46 (s, CH=), 1.92 (s, C_6Me_6), 1.29 (d, PMe_3, $^2J_{PH}$ 10.8 Hz); ^{31}P (^1H) NMR (121.49 MHz) δ 11.10 (s, PMe_3), −143.41 (sept, PF_6^-); ^{13}C NMR (75.47 MHz) δ 213.04 (d, Ru=C, $^2J_{PC}$ 33.0 Hz), 153.95, 152.10 (s, C=C=*C*–N, =*C*Ph_2}, 123.67 (H*C*=CPh_2, $^1J_{HC}$ 165.5 Hz), 121.02 ppm (s, Ru=C=*C*=C–N).

For **6c**: IR (KBr) 2010 cm^{-1} (vs, ν C=C=C); ^1H NMR (300.13 MHz) δ 6.33 (s, CH=), 1.71 (d, P*Me*, $^1J_{PH}$ 10.5 Hz); ^{13}C NMR (75.47 MHz) δ 210.62 (d, Ru=C, $^2J_{PC}$ 32.2 Hz), 154.98, 150.85 (s, Ru=C=C=*C*, C=*C*Ph_2), 123.16 (HC=, $^1J_{CH}$ 166.4 Hz), 122.75 ppm (s, Ru=C=*C*=C).

For **7a**: IR (KBr) 2215 cm^{-1} (s, ν C≡C) 2060 (s, ν C≡C); ^1H NMR (300.13 MHz) δ 2.05 (s, C_6Me_6), 1.45 (d, PMe_3, $^2J_{PH}$ = 10.5 Hz), 0.12 (s, OSi*Me*$_3$); ^{13}C NMR (75.47 MHz) δ 121.11 (d, Ru–*C*≡C, $^2J_{PC}$ = 39.5 Hz), 86.38, 78.26, 76.75 (s, Ru–C≡*C*–*C*≡*C*–), 68.31 (s, *C*-$OSiMe_3$), 1.65 ppm (s, Si*Me*$_3$).

For **7c**: IR (KBr) 2189 cm^{-1} (s, ν C≡C) 2038 (s, ν C≡C); ^1H NMR (300.13 MHz) δ 1.99 (d, PMe, $^2J_{PH}$ 10.4 Hz), 1.76 (s, C_6Me_6), 0.13 (s, OSi*Me*$_3$); ^{13}C NMR (75.47 MHz) δ 120.23 (d, Ru–*C*≡C, $^2J_{PC}$ 37.2 Hz), 87.83, 78.32, 76.68 (s, Ru–C≡*C*–*C*≡*C*–), 68.37 (s, *C*–$OSiMe_3$), 1.65 ppm (s, Si*Me*$_3$).

‡ *Crystal data*: $C_{35}H_{46}ClOPRuSi$, monoclinic, $P2_1/n$, a = 8.493(3), b = 24.131(5), c = 16.729(2) Å, β = 90.38(1) Å, U = 3428.4(1.5) Å^3, Z = 4, D_c = 1.314 g cm^{-3}, F(000) = 1416, μ_c = 6.31 cm^{-1}. Data collected on a CAD-4 diffractometer with Mo-Kλ radiation [5915 measured ($2 \leq \theta \leq 50°$), 884 used [$I \geq 3\sigma(I)$ reflections]. The structure was solved by Patterson methods and refined by full-matrix least-squares calculations and unit weights. The thermal motion was taken as isotropic for all atoms. The refinement converged at R = 0.076 for observed reflections only. The paucity of data (884 observed reflections) prevented us from testing any anisotropic model (361 parameters) in the refinement process. The poor quality of the crystal structure is due to the unobtainability of bigger crystals. The diffracted spectrum showed a non-homogeneous distribution of intensities in the reciprocal space and most of the reflections had intensities less than 6% of the highest. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

Pr^iOH or $HNPh_2$ and gives access to the 1,2,4-pentatrienyl–ruthenium complexes **4–6**.

The above results show that whereas methanol adds to the Ru=C(1) carbon atom of cations $(\eta^6\text{-arene})(R_3P)(Cl)\text{-}Ru^+(=C=C=CR_2)$,[9] a bulky alcohol or amine preferentially adds to the C(3) atom of 1,2,3,4-pentatrienylidene–ruthenium intermediate.

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