Metallacumulenes: New Allenylidene–Ruthenium Complexes. Crystal Structure of a Cationic $[(Ph_2PCH_2PPh_2)_2(Cl)Ru{=}C{=}C{=}CR^1R^2]^+$ Derivative

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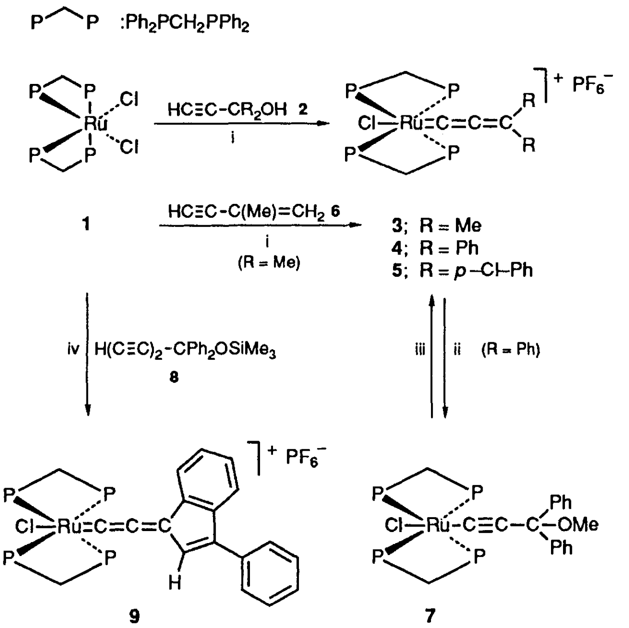
The activation with *cis*-$RuCl_2(Ph_2PCH_2PPh_2)_2$ **1** of $HC{\equiv}C{-}CR_2OH$ and $HC{\equiv}C{-}C(Me){=}CH_2$ leads to allenylidenes *trans*-$(Cl)Ru^+{=}C{=}C{=}CR_2(Ph_2PCH_2PPh_2)_2$ (R = Ph, Me, *p*-Cl-Ph) and that of $HC{\equiv}C{-}C{\equiv}C{-}CPh_2OSiMe_3$ affords a new allenylidene–ruthenium complex **9** *via* an intramolecular *ortho* C–H bond addition.

Metallacumulenes $M{=}(C{=})_4CR_2$ are still hypothetical species[1] in spite of their fundamental and applied interest. Their intrinsic properties resulting from the distribution of electron density and the nature of electrophilic sites in the chain are expected to contrast drastically with those of organic cumulenes[2] or metal-coordinated cumulenes.[3] They have potential as new building blocks for the synthesis of unsaturated organic molecules, by transfer of the carbene-like ligand to alkenes,[4] or for access to polymers[5] or metal-containing polymers.[6]

Although 2-propyn-1-ol derivatives have led to new allenylidene–metal complexes $M{=}(C{=})_2CR_2$,[7] attempts to generate the $Ru{=}(C{=})_4CR_2$ moiety with (η^6-arene)Ru^{II} precursors have provided access to 3-oxo-1,4-pentadienyl–ruthenium, cumulenylcarbene[1] and functional allenylidene[8] derivatives. We have thus undertaken the study of the activation of terminal alkynes with a more sterically hindered ruthenium complex *cis*-$RuCl_2(Ph_2PCH_2PPh_2)_2$ **1** and we now report the route to stable allenylidene–ruthenium compounds, especially *via* the 1,4-shift of the (alkyne) hydrogen atom of isopropenylacetylene, and the first example of an intramolecular addition of a C–H bond to a $Ru{=}(C{=})_4CR_2$ intermediate, with the crystal structure of the resulting novel allenylidene complex.

The reaction of 2-propyn-1-ol derivatives $HC{\equiv}C{-}CR_2OH$ **2** (R = Me, Ph, *p*-Cl–Ph) with the *cis* complex **1** in the presence



Scheme 1 *Reagents and conditions:* i, 2 equiv. of **2** (or **6**), CH_2Cl_2, 2 equiv. of $NaPF_6$, room temp. (4 h); ii, MeOH, 12 equiv. of MeONa, room temp. (2 h); iii, CH_2Cl_2, 10 equiv. of Ph_3CPF_6, room temp. (30 min); iv, 6 equiv. of **8**, CH_2Cl_2, 6 equiv. of $NaPF_6$, 28 °C (28 h)

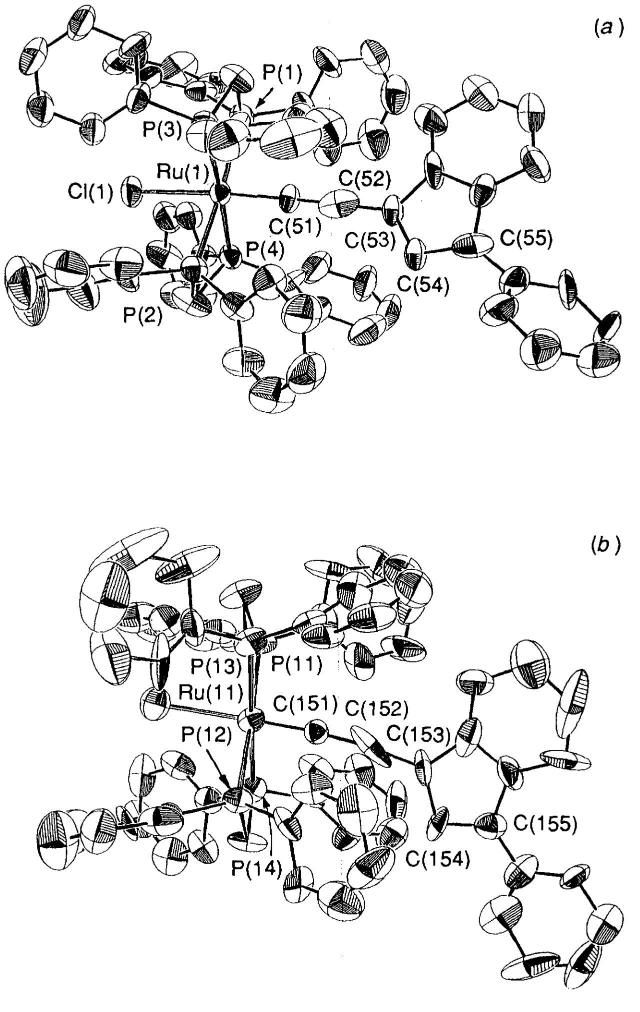


Fig. 1 Molecular structure of cation **9a** (ORTEP view). For clarity, hydrogen atoms are omitted. (*a*) Selected bond distances (Å) and angles (°) for cation **9a**: Ru(1)–Cl(1) 2.439(6), Ru(1)–P(1) 2.351(8), Ru(1)–P(2) 2.361(8), Ru(1)–P(3) 2.376(6), Ru(1)–P(4) 2.385(6), Ru(1)–C(51) 1.85(2), C(51)–C(52) 1.29(3), C(52)–C(53) 1.39(3), C(53)–C(54) 1.43(4), C(54)–C(55) 1.41(3); Cl(1)–Ru(1)–C(51) 175.0(6), Ru(1)–C(51)–C(52) 179.0(2), C(51)–C(52)–C(53) 177.0(2), C(52)–C(53)–C(54) 124.0(2); (*b*) Selected bond distances (Å) and angles (°) for cation **9b**: Ru(11)–Cl(11) 2.421(5), Ru(11)–P(11) 2.407(7), Ru(11)–P(12) 2.381(6), Ru(11)–P(13) 2.379(7), Ru(1)–P(14) 2.363(7), Ru(11)–C(151) 1.67(2), C(151)–C(152) 1.43(3), C(152)–C(153) 1.42(3), C(153)–C(154) 1.50(3), C(154)–C(155) 1.34(3); Cl(11)–Ru(11)–C(151) 176.2(7), Ru(11)–C(151)–C(152) 175.0(1), C(151)–C(152)–C(153) 172.0(2), C(152)–C(153)–C(154) 126.0(2).

of $NaPF_6$ in dichloromethane leads to *trans*-allenylidene–ruthenium(II) complexes **3** (79%), **4** (89%) and **5** (89%)[†] (Scheme 1). The allenylidenes **3–5** are surprisingly stable toward the addition of methanol with respect to $[(\eta^6\text{-arene})(PR_3)ClRu{=}C{=}C{=}CR_2]^+$ intermediates.[7b] Moreover, complex **4** is readily transformed in the presence of MeONa in methanol into its alkynyl derivative **7** (55%)[†] by addition of methoxide at carbon C-3, rather than at the expected electrophilic carbon C-1. It is likely that four of the phenyl groups of the $Ph_2PCH_2PPh_2$ ligands sterically protect the carbon C-1 against nucleophilic additions. Complex **7** on treatment with Ph_3CPF_6 in dichloromethane gives the allenylidene **4** on methoxide elimination.

Complex **1** treated with an excess of isopropenylacetylene **6** in dichloromethane slowly leads to the formation of the *trans*-allenylidene complex **3** (R = Me) (40%).[†] This reaction provides the first direct evidence for the 1,4-shift of the terminal alkyne hydrogen atom of an alkyne to the alkenic C-4 carbon.

As the allenylidenes **3–5** are much more stable than the isoelectronic derivatives of $(\eta^6\text{-arene})Ru^{II}$,[7b] we have attempted to generate the metallacumulene intermediate $Ru{=}(C{=})_4CPh_2$ directly from the precursor **1**. The reaction of **1** with the pentadiyne derivative **8**, in the presence of $NaPF_6$ at 28 °C, led to the unexpected allenylidene complex **9**, which was isolated in 68% yield[†] (Scheme 1). This compound shows a strong absorption in the IR spectrum at 1934 cm^{-1} [ν(C=C=C)] and in ^{13}C NMR low-field quintuplets for (allenylidene)*C*=Ru [δ 316.1 ($^2J_{P,C}$ 14.6 Hz)] and (allenylidene)*C*=C=Ru [δ 234.1 ($^3J_{P,C}$ 3.3 Hz)] carbon nuclei are observed. A single-crystal X-ray structural analysis was

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[†] Satisfactory elemental analyses were obtained for derivatives **3–9**. *Selected spectroscopic data* for **3**: IR (KBr) 1964 cm^{-1} (vs, ν C=C=C); ^{31}P (^1H) NMR (121.50 MHz, CD_2Cl_2) δ −14.0 (s, Ph_2P), −143.46 (sept, PF_6^-); ^{13}C (^1H) NMR (75.47 MHz, CD_2Cl_2) δ 322.69 (quint, Ru=*C*, $^2J_{PC}$ 13.9 Hz), 199.85 (quint, Ru=C=*C*, $^3J_{PC}$ 2.3 Hz), 173.33 (broad s, =*C*Me_2), 35.24 (s, *Me*).

For **4**: IR (KBr) 1928 cm^{-1} (vs, ν C=C=C); ^{31}P (^1H) NMR (121.50 MHz, CD_2Cl_2) δ −14.83 (s, Ph_2P), −143.92 (sept, PF_6^-); ^{13}C (^1H) NMR (75.47 MHz, CD_2Cl_2) δ 306.72 (quint, Ru=*C*, $^2J_{PC}$ 14.5 Hz), 208.94 (quint, Ru=C=*C*, $^3J_{PC}$ 2.5 Hz), 161.88 (broad s, =*C*Ph_2).

For **5**: IR (KBr) 1921 cm^{-1} (vs, ν C=C=C); ^{31}P (^1H) NMR (121.50 MHz, CD_2Cl_2) δ −14.78 (s, Ph_2P), −143.41 (sept, PF_6^-); ^{13}C (^1H) NMR (75.47 MHz, CD_2Cl_2) δ 307.33 (quint, Ru=*C*, $^2J_{PC}$ 14.3 Hz), 213.92 (broad s, Ru=C=*C*), 156.63 [broad s, =*C*(Ph-Cl-*p*)$_2$].

For **7**: IR (KBr) 2060 cm^{-1} (s, ν C≡C); ^{31}P (^1H) NMR (121.50 MHz, CD_2Cl_2) δ −4.30 (s, Ph_2P); ^1H NMR (300.13 MHz, CD_2Cl_2) δ 2.19 (s, OMe); ^{13}C (^1H) NMR (75.47 MHz, CD_2Cl_2) δ 109.33 (quint, Ru–*C*≡C, $^2J_{PC}$ 14.9 Hz), 107.75 (s, Ru–C≡*C*), 81.83 (s, *C*Ph_2OMe), 51.07 (s, OMe).

For **9**: IR (KBr) 1934 cm^{-1} (vs, ν C=C=C); ^{31}P (^1H) NMR (121.50 MHz, CD_2Cl_2) δ −16.16 (s, Ph_2P), −143.80 (sept, PF_6^-); ^1H NMR (300.13 MHz, CD_2Cl_2) δ 4.52 (s, CH=); ^1H (^{31}P) NMR (300.13 MHz, CD_2Cl_2) δ 5.26, 5.39 (s, –CH_2–, $^2J_{HH}$ 15.7 Hz); ^{13}C (^1H) NMR (75.47 MHz, CD_2Cl_2) δ 316.13 (quint, Ru=*C*, $^2J_{PC}$ 14.6 Hz), 234.07 (quint, Ru=C=*C*, $^3J_{PC}$ 3.3 Hz), 162.18 (broad s, =*C*Ph); 158.82 (quint, Ru=C=C=*C*, $^4J_{PC}$ 2.2 Hz), 130.27 (s, CH=).

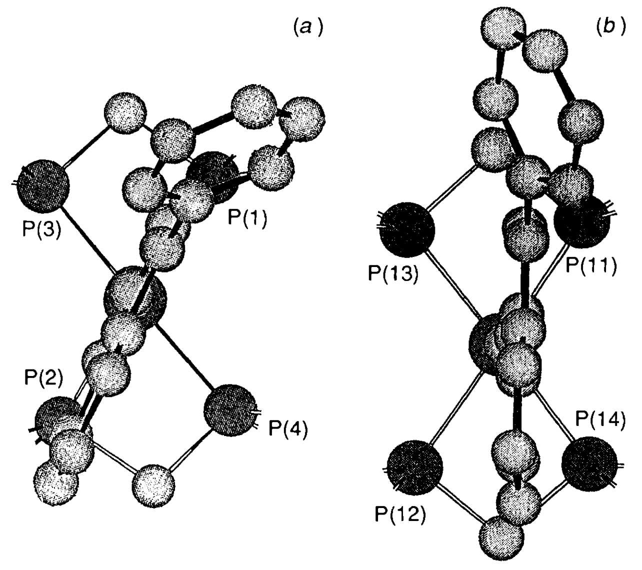

Fig. 2 Views of cations **9a** and **9b** in the C(3)–C(2)–C(1)–Ru axis, (Ph_2P) phenyl groups have been omitted. (*a*) Cation **9a**: approximate angle of the [P(1)–Ru–C(51)] and [C(57)–C(53)–C(52)] planes: 10°; (*b*) Cation **9b**: approximate angle of the [P(11)–Ru–C(151)] and [C(157)–C(153)–C(152)] planes: 28°.

carried out on complex **9**.‡ The ORTEP plot (Fig. 1) establishes the presence of an indenylidene group bonded to one end of a metallacumulene and shows the steric protection by the phenyl groups of C(1) and C(2) carbon atoms. Actually, the whole structure consists of two allenylidene–ruthenium cations **9a** and **9b** with disordered PF_6 anions that have crystallized with one molecule of dichloromethane and one of pentane. The two allenylidene–ruthenium cations are not similar and correspond to two different conformers: the main difference appears in the orientation of the indenyl plane with respect to the phosphorus atoms in the $Ru(P)_4$ plane (Fig. 2).‡ However, it should be noticed that owing to restriction in the programs, it was not possible to include the hydrogen atoms in the calculations and to refine the whole structure in the same set.

The structure suggests that **9** results from the initial formation of the metallacumulene $Ru^+{=}(C{=})_4CPh_2$ intermediate **I**, by $HOSiMe_3$ elimination, followed by the intramolecular addition of an *ortho* C–H bond of a CPh_2 phenyl group at the electrophilic C(3) carbon atom of **I**. This reaction shows, by contrast with the high stability of organic cumulenes $R_2C{=}(C{=})_4CR_2$,[2] that the $M^+{=}(C{=})_4CPh_2$ intermediate **I** is very electrophilic at C(3) and mimics the *ortho* C–H bond addition of a phenyl group toward the ketene ketonic group; as in the Dötz reaction.[9]

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‡ *Crystal data*: $C_{67}H_{54}ClP_4Ru,PF_6,1/2(CH_2Cl_2),1/2(C_5H_{12})$, triclinic, $P\bar{1}$, $a = 13.682(6)$, $b = 22.513(9)$, $c = 23.249(7)$ Å, $\alpha = 112.91(3)$, $\beta = 96.18(3)$, $\gamma = 94.43(4)°$, $V = 6500(2)$ Å^3, $Z = 4$, $D_x = 1.27$ g cm^{-3}, $F(000) = 2748$, $\mu = 4.96$ cm^{-1}. Data were collected on an automatic diffractometer CAD-4 Enraf-Nonius with graphite monochromated Mo-Kα radiation {12809 measured [$2\theta_{max} = 50°$, scan $\omega/2\theta = 1$, $t_{max} = 60$ s, range *hkl*: *h* 0–13, *k* −22–21, *l* −22–22, intensity controls without appreciable decay (0.3%)], 4393 used ($I > 5\sigma(I)$].} After Lorenz and polarization corrections, the structure was solved with a Patterson map which reveals the two Ru atoms. The remaining non-hydrogen atoms of the structure are found after successive scale-factor refinements and Fourier differences. After isotropic (R = 0.12) refinement, solvent molecules of pentane and dichloromethane are found and an absorption correction was made with DIFABS (Walker and Stuart, 1983). The anions PF_6^- appear as disordered. The whole structure was refined by full-matrix least-square techniques with the resulting $R = 0.076$, $R_w = 0.073$ and $S_w = 4.42$. 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.

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