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First Isolable Pentatetraenylidene Metal Complex Containing the $Ru{=}C{=}C{=}C{=}C{=}CPh_2$ Assembly. A Key Intermediate To Provide Functional Allenylidene Complexes

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Organometallics containing a carbon-rich, conjugated chain are currently attracting interest either for their materials properties,[1] especially nonlinear optical properties,[2] or as polymer precursors.[3] Those containing a M=C bond show additional potential for synthesis of highly unsaturated organic molecules due to the powerful synthetic utility of carbene complexes.[4] Examples of $M(C)_4M$ metal complexes containing a 1,3-butadiyne-1,4-diyl bridge in bimetallic,[1c,5,6] and polymer systems[3b,7] have been reported, but only a few bimetallic systems containing a bis-carbene[8] or bis-vinylidene[5b,c,9] bridging chain are known. Recently, new strategies have been put into action for access to a novel type of organometallic cumulenes $M{=}(C)_nM$ (n = 3,[10] 4,[6] 5[11]).[12]

Since the first discovery of allenylidene metal complexes $M{=}C{=}C{=}CR_2$,[13] a variety of allenylidene derivatives have been prepared,[14] but the most straightforward method is based on the activation of propargylic alcohol derivatives by ruthenium complexes.[15] Recently, a butatrienylidene metal species has been suggested to result from the moiety $RuC{\equiv}CC(OCOCF_3)CMe_2$.[16] The direct formation of allenylidenes (**I**) (eq 1) by 1,3 elimination of H–OH from propargyl alcohol derivatives[15] suggested that higher metallacumulene (**II**), containing five consecutive double bonds, could be generated by suitable activation of diyne derivatives by 1,5 elimination of H–OY.

$$RuX + HC{\equiv}CCR_2OH \rightarrow H_2O + [Ru{=}C{=}C{=}CR_2]X\ (\mathbf{I})$$
$$MX + HC{\equiv}CC{\equiv}CCR_2OY \rightarrow HOY + [M{=}C{=}C{=}C{=}C{=}CR_2]X\ (\mathbf{II}) \quad (1)$$

This strategy has been used in the direct activation of the diyne $H(C{\equiv}C)_2CPh_2OSiMe_3$ by ruthenium(II) complexes, $RuCl_2(PR_3)(C_6Me_6)$,[17] $RuCl_2[N(CH_2CH_2PPh_2)_3]$,[15c] and $RuCl_2(Ph_2PCH_2PPh_2)_2$,[15d] but has led to the formation of alkenyl allenylidenes, suggesting the generation of a $Ru{=}C{=}C{=}C{=}C{=}CPh_2$ intermediate that was never observed.

We now report the formation of the first isolable complex containing a $M{=}C{=}C{=}C{=}C{=}CR_2$ assembly, $[Ru{=}C{=}C{=}C{=}C{=}CPh_2(Cl)(Ph_2PCH_2CH_2PPh_2)_2]PF_6$ (**4**), its X-ray diffraction characterization, and evidence of the electrophilicity of the C(3) carbon atom that allows nucleophilic addition affording functional allenylidenes.

Under the conditions in which a vinylidene–ruthenium species is formed and immediately deprotonated,[18] the reaction of *cis*-$RuCl_2(Ph_2PCH_2CH_2PPh_2)_2$ (**1**) in THF with 2 equiv of the diyne **2** in the presence of both $NaPF_6$ and NEt_3 at room temperature gave the formation of the yellow monosubstituted *trans*-chlorodiynyl complex **3** (53%)[19] (Scheme 1). The addition of 1 equiv of $Ph_3C^+PF_6^-$ in THF, in an attempt to eliminate the leaving group of **3**, led to immediate formation of a deep blue cationic cumulene **4** (70%).[19] The pentatetra-1,2,3,4-enylidene–metal assembly of complex **4** is indicated by ^{13}C NMR showing the resonances as quintuplets for four "naked" carbon nuclei of the cumulene chain [δ_{ppm}(RuC(1)C(2)C(3)C(4)C(5)Ph_2) (J_{PC}): C_1, 316.35 (14.6 Hz); C(2), 206.7 (2.6 Hz); C(3), 167.63 (2.3 Hz); (C(4), 160.25 (2 Hz); C(5), 165.44 (s)] and by a single crystal X-ray diffraction study.

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(19) (a) Data for **3**: IR (KBr) $\nu(C{\equiv}C)$ = 2177(s) and 2029(s) cm^{-1}; $^{31}P\{^1H\}$ NMR (121.50 MHz, $CDCl_3$) δ 49.12 (s, 4 PPh_2); ^1H NMR (300.134 MHz, $CDCl_3$) δ 2.67 (m, PCH_2CH_2P), 0.13 (s, $OSiMe_3$); $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$) δ 127.10 (quint, $Ru\mathit{C}{\equiv}$, $^2J_{PC}$ = 15.2 Hz), 94.07 (s, $RuC{\equiv}\mathit{C}$), 79.90 (s, $RuC{\equiv}C\mathit{C}{\equiv}$), 68.03 (s, $RuC{\equiv}CC{\equiv}\mathit{C}$), 64.33 (s, $RuC{\equiv}CC{\equiv}C\mathit{C}$), 0.02 (s, $OSiMe_3$). (b) Data for **4**: IR (KBr) $\nu(C{=}C{=}C)$ = 2024(s) and 1918(m) cm^{-1}; $^{31}P\{^1H\}$ NMR (121.50 MHz, CD_2Cl_2) δ 39.56 (s, 4 Ph_2P), −143.90 (sept, PF_6, J_{PF} = 713 Hz); ^1H NMR (300.134 MHz, CD_2Cl_2) δ 2.78 and 2.61 (m, PCH_2CH_2P); ^{13}C NMR (75.47 MHz, CD_2Cl_2) δ 316.35 (quint, $Ru{=}\mathit{C}$, $^2J_{PC}$ = 14.6 Hz) 206.7 (quint, $Ru{=}C{=}\mathit{C}$, $^3J_{PC}$ = 2.6 Hz), 167.63 (quint, $Ru{=}C{=}C{=}\mathit{C}$, $^4J_{PC}$ = 2.3 Hz), 160.25 (quint, $Ru{=}C{=}C{=}C{=}\mathit{C}$, $^5J_{PC}$ = 2 Hz), 165.44 (s, $Ru{=}C{=}C{=}C{=}C{=}\mathit{C}$).

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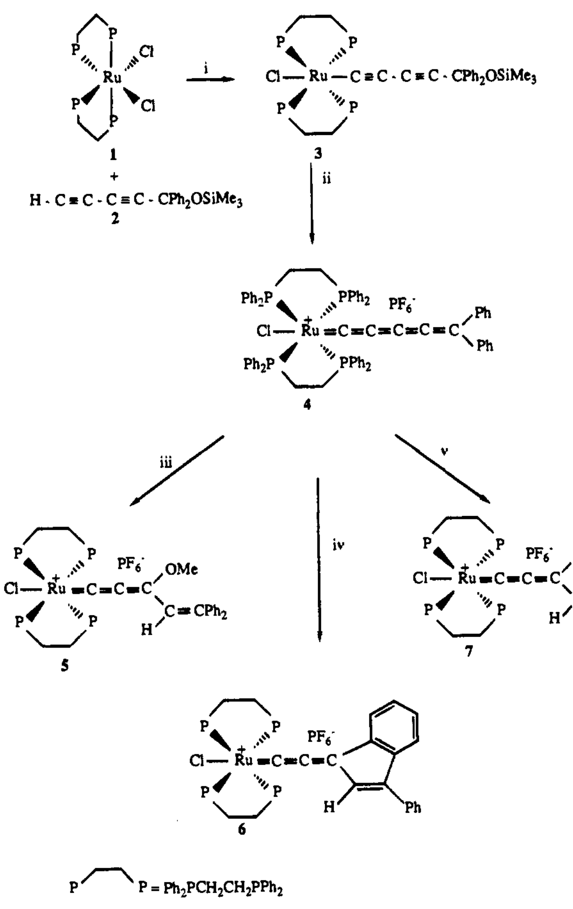
Scheme 1[a]



[a] Reagents and conditions at room temperature: (i) **1** (0.5 mmol), $NaPF_6$ (1 mmol), THF (50 mL), **2** (1 mmol), and Et_3N (2 mmol), 4 h; (ii), **3** (0.25 mmol), $Ph_3C^+PF_6^-$ (0.25 mmol), CH_2Cl_2 (25 mL), 0.5 h; (iii) **4** (0.25 mmol), MeOH (50 mL), 2 h; (iv) **4** (0.25 mmol), $CHCl_3$ (25 mL), 24 h; (v) **4** (0.25 mmol), CH_2Cl_2 (25 mL), Et_2NH (2.5 mmol), 2 h.

The molecular structure of **4** is shown in Figure 1[20] and establishes the *trans* positions of the chloride and cumulene ligands, with a good collinearity of the ClRu=C=C=C=C=C moiety. The short Ru=C distance [1.891(9) Å] is typical of a (vinylidene)C–Ru linkage.[18] The carbon–carbon distances in the cumulene chain are consistent with sp character of the carbon atoms. It is noteworthy that the C(2)–C(3) bond distance is significantly shorter than in related allenylidene–ruthenium complexes.[15a,21,22]

The novel isolated pentatetraenylidene–ruthenium derivative **4** displays an electrophilicity of carbon C(3) as indicated by the addition of methanol to **4**, affording the deep red alkenyl allenylidene **5** (80%), and that of $HNEt_2$, giving the orange complex **7** (65%)[23] (Scheme 1). It is noteworthy that the derivative analogous to the precursor **3**, but containing two $Ph_2PCH_2PPh_2$ (dppm) ligands, when treated under the conditions of reaction **3** → **4**, never allowed the isolation of the pentatetraenylidene intermediate analogous to **4**,[21] thus showing that a slight modification of the chelating ligand drastically influences the stability of pentatetraenylidene complex.

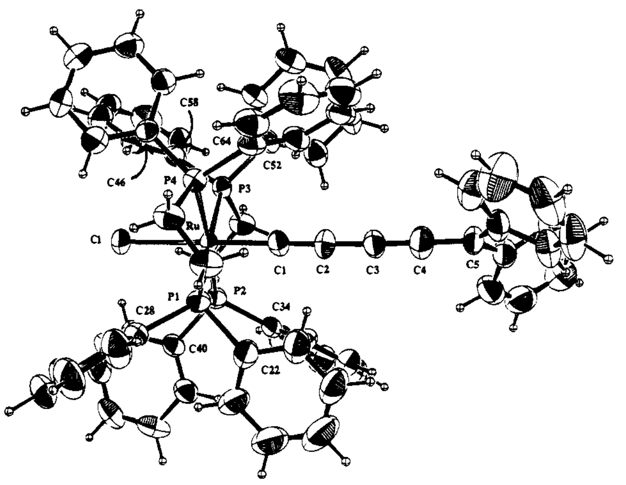


Figure 1. Molecular structure of cation $[Ru{=}C{=}C{=}C{=}C{=}CPPh_2(Cl)(Ph_2PCH_2CH_2PPh_2)_2]^+$ (**4**) (ORTEP view). For clarity, the C–H atoms of phenyl groups are scaled down. Selected bond distances (Å) and angles (deg): Ru–P(1) 2.417(3), Ru–P(2) 2.408(3), Ru–P(3) 2.441(3), Ru–P(4) 2.421(3), Ru–Cl 2.430(3), Ru–C(1) 1.891(9), C(1)–C(2) 1.25(1), C(2)–C(3) 1.30(1), C(3)–C(4) 1.24(1), C(4)–C(5) 1.36(1); Cl–Ru–C(1) 178.8(4), Ru–C(1)–C(2) 179(1), C(1)–C(2)–C(3) 178.(1), C(2)–C(3)–C(4) 179.(1), C(3)–C(4)–C(5) 178.(1).

Complex **4** is stable in THF, but in chloroform at room temperature it is slowly transformed (24 h) *via* the intramolecular reaction into product **6** (92%), corresponding to the electrophilic substitution by carbon C(3) of one ortho proton of a phenyl group (Scheme 1). Thus the transformation of **4** into **5**, **6**, and **7** prove that the pentatetraenylidene species is the key intermediate to afford functional allenylidenes from the pentadiyne **2**.

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Supplementary Material Available: Methods of data collection and lists of spectral data and elemental analyses for the products; lists of complete crystallographic data (24 pages); tables of observed and calculated structure factors (27 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(20) Crystal data for 4: monoclinic, *Cc*, $a = 14.748(4)$ Å, $b = 18.703(3)$ Å, $c = 23.330(7)$ Å, $\beta = 90.35(3)°$, $V = 6435(2)$ Å^3, $Z = 4$, final $R = 0.047$ for 4504 observations with $I > 3\sigma(I)$. The whole structure was refined by the full-matrix least-squares techniques (use of *F* magnitude; x, y, z, β_{ij} for Ru, P, Cl, and C atoms, x, y, z, β for F atoms and dichloromethane molecule, and x, y, z fixed for H atoms, 744 variables and 4504 observations; $w = 1/\sigma(F_o)^2 = [\sigma^2(I) + (0.04F_o^2)^2]^{-1/2}$ with the resulting $R = 0.047$, $R_w = 0.042$, and $S_w = 1.91$ (residual $\Delta\varrho \leq 0.24$ eÅ^{-3}).

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(22) The short C(2)–C(3) distance [1.30(1) Å] is not consistent with a C(3) carbenium center or a partial C(1)–C(2) triple bond character, as observed in a bis-allenylidene complex.[21]

(23) Such allenylidenes containing a basic amine could not be obtained from direct activation of **2** as deprotonation takes place, leading to a diynyl ruthenium derivative.[17] The complex **7** shows in ^{13}C NMR a high-field (Ru=C) carbon nucleus $\delta = 210.25$ ppm. This is consistent with addition of the amino group on C(3) as in $[Ru{=}C{=}C{=}C(NPh_2)CH{=}CPh_2(Cl)(PMe_3)(C_6Me_6)PF_6$ ($\delta = 213.04$ ppm).[17] Addition to carbon C(1) would lead to a much lower field signal, as in $[Ru{=}C(OMe)CH{=}C{=}C{=}CPh_2]^+$ ($\delta = 295.13$ ppm).[24]

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