

Alkenylvinylidene and allenylidene complexes: evidence for the formation of a metal–trienylidene intermediate

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Reactions of $[\text{Ru}(\text{thf})(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)][\text{PF}_6]$ with buta-1,4-diyne in the presence of nucleophiles give alkenylvinylidene or allenylidene complexes; the results are rationalised in terms of the formation of the intermediate trienylidene cation $[\text{Ru}(\text{C}=\text{C}=\text{C}=\text{CH}_2)(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)]^+$ which undergoes nucleophilic addition at C₃; the X-ray structure of the heteroallenylidene $[\text{Ru}\{\text{C}=\text{C}=\text{CMe}(\text{NPh}_2)\}(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)][\text{PF}_6]$ **2** is determined.

Metal–vinylidene and –allenylidene complexes constitute the first members of a family of unsaturated carbene complexes containing cumulated M=C and C=C double bonds. Whilst the chemistry of vinylidene complexes has been extensively investigated,¹ it is only recently that the higher analogues have received similar attention as a result of the potential material and synthetic applications of long unsaturated carbon chains.² Several methods have been used to prepare metal allenylidene systems, $\text{L}_n\text{M}=\text{C}=\text{C}=\text{CR}_2$, the most useful being the 1,3-dehydration of substituted prop-2-ynyl alcohols.^{1,3} A modification of this method has allowed the preparation of metal–penta-tetraenylidene complex, $[\text{Ru}(\text{C}=\text{C}=\text{C}=\text{C}=\text{CR}_2)(\text{Cl})(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2][\text{PF}_6]$ ⁴ However, this method is obviously not appropriate for the preparation of metallacumulenes with an even number of carbon atoms in the unsaturated chain, of which few examples are known.

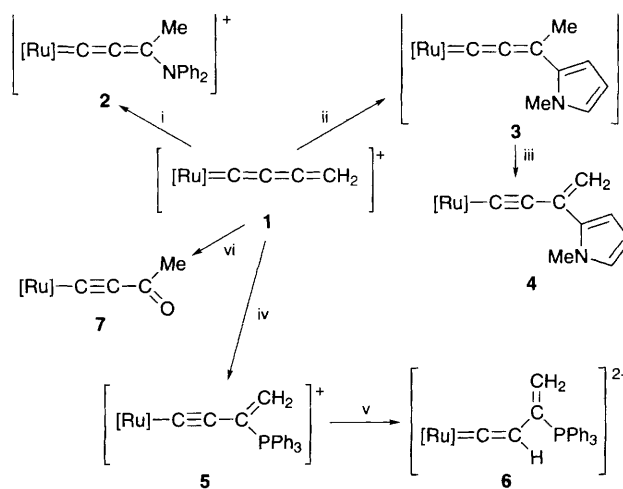
With buta-1,3-diyne, formation of a butatrienylidene complex requires a 1,4 H-shift, whereas the 1,2 H-shift found for alk-1-yne would afford the corresponding ethynylvinylidene complex. *Ab initio* calculations have suggested that free $:\text{C}=\text{C}=\text{C}=\text{CH}_2$ has almost the same stability as $:\text{C}=\text{CH}(\text{C}\equiv\text{CH})$.⁵ In this communication we report several reactions of $[\text{Ru}(\text{thf})(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)][\text{PF}_6]$ with buta-1,3-diyne in the presence of nucleophiles to give novel allenylidene and vinylvinylidene complexes, the formation of which is consistent with the intermediacy of the trienylidene cation $[\text{Ru}(\text{C}=\text{C}=\text{C}=\text{CH}_2)(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)]^+$ **1**.

Thus, reaction of $[\text{Ru}(\text{thf})(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)][\text{PF}_6]$, prepared from $[\text{RuCl}(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)]$ and AgPF_6 , with buta-1,3-diyne in the presence of diphenylamine gave the heteroallenylidene $[\text{Ru}\{\text{C}=\text{C}=\text{CMe}(\text{NPh}_2)\}(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)][\text{PF}_6]$ **2** (Scheme 1) (64%).[†] Confirmation of the identity of **2** was achieved by a single-crystal X-ray study.[‡] A molecule of **2** is shown in Fig. 1, and important bond lengths and angles are summarised. Whilst several allenylidene compounds have been structurally characterised, few contain a cumulenylidene ligand terminated by elements other than carbon.⁶ These studies suggested that there is a significant contribution to the electron distribution from two mesomeric forms:⁷ $[\text{M}=\text{C}=\text{C}=\text{CR}_2]^+ \leftrightarrow [\text{M}-\text{C}\equiv\text{C}-\text{CR}_2]^+$.

In the $[\text{Ru}\{\text{C}=\text{C}=\text{CMe}(\text{NPh}_2)\}(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)]^+$ cations the Ru–C(1) [1.94(1), 1.97(1) Å] and C(2)–C(3) [1.36(2), 1.41(2) Å] distances are longer, and C(1)–C(2) [1.22(2), 1.18(2) Å] shorter, than those observed for $[\text{Ru}(\text{C}=\text{C}=\text{CPh}_2)(\text{PMe}_3)_2(\eta\text{-C}_5\text{H}_5)]^+$ [Ru–C(1) 1.884(5), C(1)–C(2) 1.255(8), C(2)–C(3) 1.329(9) Å].⁷ It is likely that the lone pair on the N atom stabilises the $[\text{Ru}(\text{C}\equiv\text{CMe}=\text{NPh}_2)]^+$ tautomer; the short

C–N bond [1.33(2), 1.34(2) Å] is consistent with this interpretation. As predicted by Hoffmann and coworkers,⁸ and confirmed in other examples of these complexes,⁹ the trienylidene ligand is positioned in such a way that the NC(3)C(4) plane coincides with the plane of symmetry in the molecule.

A reaction using *N*-methylpyrrole as the trapping agent yielded the allenylidene $[\text{Ru}\{\text{C}=\text{C}=\text{CMe}(\text{C}_4\text{H}_3\text{NMe})\}(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)][\text{PF}_6]$ **3** (75%). This was characterised by the usual spectroscopic methods[†] and a single-crystal X-ray diffraction study, the details of which will be reported elsewhere. The methyl group is sufficiently acidic to be



Scheme 1 [Ru] = $\text{Ru}(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)$. Reagents: i, NHPH_2 ; ii, *N*-methylpyrrole; iii, LiBu ; iv, PPh_3 ; v, H^+ ; vi, H_2O

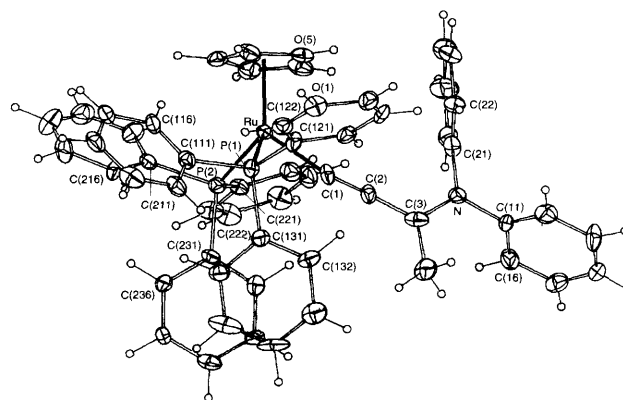


Fig. 1 Plot of cation **2** in $[\text{Ru}\{\text{C}=\text{C}=\text{CMe}(\text{NPh}_2)\}(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)]^+[\text{PF}_6]^-$, showing the atom numbering scheme; cation **1** is similar. Non-hydrogen atoms are shown with 20% thermal ellipsoids; hydrogen atoms have arbitrary radii of 0.1 Å. Significant bond parameters (cation **2**): Ru–P(1) 2.306(4), Ru–P(2) 2.310(5), Ru–C(1) 1.97(1), C(1)–C(2) 1.18(2), C(2)–C(3) 1.41(2), C(3)–N 1.34(2) Å; P(1)–Ru–P(2) 102.0(1), P(1)–Ru–C(1) 92.7(4), P(2)–Ru–C(1) 88.0(4), Ru–C(1)–C(2) 171(1), C(1)–C(2)–C(3) 178(2), C(2)–C(3)–C(31) 120(1), C(2)–C(3)–N 120(1)°.

deprotonated by butyllithium, giving the unusual functionalised acetylide $[\text{Ru}\{\text{C}\equiv\text{CC}(\text{C}_4\text{H}_3\text{NMe-2})=\text{CH}_2\}(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)]$ **4**, characterised by a $\nu(\text{C}\equiv\text{C})$ absorption at 2060 cm^{-1} ; no $\nu(\text{C}=\text{C})$ absorption was present.† The deprotonation is reversible, with water being a strong enough acid to regenerate **3**.

With an aprotic nucleophile (PPh_3), the cationic alkenyl-acetylide $[\text{Ru}\{\text{C}\equiv\text{CC}(\text{P}^+\text{Ph}_3)=\text{CH}_2\}(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)][\text{PF}_6]^-$ **5** was isolated, there being no evidence for the formation of an allenylidene complex. The IR spectrum of **5** contained a $\nu(\text{C}\equiv\text{C})$ absorption at 2032 cm^{-1} . The $^{13}\text{C}\{^1\text{H}\}$ spectrum contained resonances assigned to the unsaturated carbon chain at δ 25.6 (CH_2), 110.4 [t, C(1)], 67.9 [C(2)] and 116.6 [d, C(PPh_3)]. Attempts to form the related allenylidene complex $[\text{Ru}\{\text{C}=\text{C}=\text{CMe}(\text{P}^+\text{Ph}_3)\}(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)][\text{PF}_6]_2$ by reaction of **5** with strong acids such as HPF_6 result instead in the formation of the isomeric vinylvinylidene $[\text{Ru}\{\text{C}=\text{CHC}(\text{PPh}_3)=\text{CH}_2\}(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)][\text{PF}_6]_2$ **6**.

The nature of the substituent attached to C(3) of a vinylacetylide complex is critical in determining whether electrophilic attack occurs at C(2), to give an alkenylvinylidene, or at C(4), to give an allenylidene. Thus **5** and $[\text{Ru}\{\text{C}\equiv\text{CC}=\text{CH}(\text{CH}_2)_4\}(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)]$ are protonated at C(2) to give the corresponding vinylidenes, whereas $[\text{Ru}\{\text{C}\equiv\text{CCMe}=\text{CH}_2\}(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)]$ and **4** react with H^+ at C(4) to give $[\text{Ru}\{\text{C}=\text{C}=\text{CMe}(\text{R})\}(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)]\text{PF}_6$ ($\text{R} = \text{Me}^{10}$ or $\text{C}_4\text{H}_3\text{NMe-2}$). Other electron-rich vinylthynyl complexes $[\text{Ru}(\text{C}_2\text{R})(\text{PMe}_3)_2(\eta\text{-C}_5\text{H}_5)]$ ($\text{R} = \text{cyclohex-1-enyl}$, cyclopent-1-enyl, $\text{CPr}^i=\text{CMe}_2$) also give vinylidenes.¹¹ The reaction between $[\text{Ru}(\text{thf})(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)][\text{PF}_6]$ and buta-1,3-diyne in the presence of water gives $[\text{Ru}\{\text{C}\equiv\text{CC}(\text{O})\text{-Me}\}(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)]$ **7**;¹⁰ formation of **7** can be understood by loss of a proton from an intermediate formed by addition of water to C(3) in **1**.

These observations are consistent with isomerisation of buta-1,3-diyne at the Ru centre via a 1,4 H-shift to give the trienylidene cation **1**. This has precedence in the reactions of $[\text{RuCl}_2(\text{PR}_3)(\eta\text{-C}_6\text{H}_6)]^9$ or $[\text{RuCl}_2\{\text{N}(\text{C}_2\text{H}_4\text{PPh}_2)_3\}]^6$ with 1,3-diynes of the form $\text{HC}\equiv\text{CC}\equiv\text{CR}_2(\text{OH})$. Compound **1**, whilst too reactive to be isolated, reacts with an available nucleophile, initially at C(3), to give an alkenylacetylide complex. Attack of nucleophiles at C(3) in metal trienylidenes is also indicated by formation of a ruthenium–trienylidene–trifluoroacetate ion-pair complex.¹² Further proton migration is required to form **2**, **3** and **7**, as summarised in Scheme 1.

We thank the Australian Research Council for support of this work, and the Deutsche Forschungsgemeinschaft for a Fellowship (P. H.); P. J. L. held an Australian Postgraduate Award.

Footnotes

† Selected spectroscopic data: (NMR spectra in CDCl_3 , IR spectra in Nujol). For **2**. IR, $\nu(\text{C}=\text{C})$ 1988s, $\nu(\text{PF})$ 842s cm^{-1} ; ^1H NMR, δ 7.7–6.9 (40 H, m, Ph), 4.29 (5 H, s, C_5H_5), 2.11 (3 H, s, Me); $^{13}\text{C}\{^1\text{H}\}$ NMR, δ

219.2 [t, $J(\text{PC})$ 21 Hz, C(1)], 153.0 [s, C(2)], 145.4 [s, C(3)], 135.0–117.6 (m, Ph), 88.7 (s, C_5H_5), 26.4 (s, Me); FAB MS, m/z 909 M^+ , 647 [$\text{M} - \text{PPh}_3$] $^+$. For **3**. IR, $\nu(\text{C}=\text{C})$ 1948s, $\nu(\text{PF})$ 840s cm^{-1} ; ^1H NMR, δ 7.6–7.17 (33 H, m, Ph and $\text{C}_4\text{H}_3\text{N}$), 4.78 (5 H, s, C_5H_5), 4.39 (3 H, s, NMe), 2.06 (3 H, s, Me); $^{13}\text{C}-^1\text{H}$ coupled NMR: δ 256.7 [t, $J(\text{PC})$ 20 Hz, C(1)], 167.4 [s, C(2)], 146.0 [s, C(3)], 140.5 [s, C(2) of $\text{C}_4\text{H}_3\text{N}$], 140.5 [d, $J(\text{CH})$ 189 Hz, C(3) of $\text{C}_4\text{H}_3\text{N}$], 135.6–129.1 (m, Ph), 125.1 and 112.6 [both d, $J(\text{CH})$ 183, 177 Hz, C(4), C(5) of $\text{C}_4\text{H}_3\text{N}$], 90.3 [d, $J(\text{CH})$ 179 Hz, C_5H_5], 38.5 [q, $J(\text{CH})$ 141 Hz, NMe], 27.8 [q, $J(\text{CH})$ 129 Hz, Me]; FAB MS, m/z 821 M^+ , 559 [$\text{M} - \text{PPh}_3$] $^+$. For **4**. IR, $\nu(\text{C}\equiv\text{C})$ 2060s cm^{-1} ; ^1H NMR, δ 7.7–7.0 (33 H, m, Ph, $\text{C}_4\text{H}_3\text{N}$), 4.29 (5 H, s, C_5H_5), 4.22 [1 H, d, $J(\text{HH})$ 5.9 Hz, $\text{C}=\text{CH}_2$], 4.21 [1 H, d, $J(\text{HH})$ 5.9 Hz, $\text{C}=\text{CH}_2$], 3.62 (3 H, s, NMe); $^{13}\text{C}\{^1\text{H}\}$ NMR, δ 138.8–128.7 (m, Ph), 122.5 [s, C(2)], 121.2, 120.2 (both br, $\text{C}_4\text{H}_3\text{N}$), 107.8 and 106.5 [both s, C(3), C(4)], 104.0 [s, C(1)], 85.1 (s, C_5H_5), 38.9 (s, NMe); FAB MS, m/z 820 M^+ , 690 [$\text{Ru}(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)$] $^+$, 558 [$\text{M} - \text{PPh}_3$] $^+$.

‡ Crystal data and refinement details for **2**: $[\text{Ru}\{\text{C}=\text{C}=\text{CMe}(\text{NPh}_2)\}(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)][\text{PF}_6]\cdot 0.5\text{CH}_2\text{Cl}_2$; $\text{C}_{57}\text{H}_{48}\text{F}_6\text{N}_3\text{Ru}\cdot 0.5\text{CH}_2\text{Cl}_2$, $M = 1097.5$, monoclinic, space group Pc , $a = 11.666(10)$, $b = 14.156(13)$, $c = 31.392(8)$ Å, $\beta = 98.01(8)^\circ$, $U = 5134$ Å³, $Z = 4$, $D_c = 1.42\text{ g cm}^{-3}$. Crystal dimensions $0.40 \times 0.35 \times 0.42$ mm, $\mu(\text{Mo-K}\alpha) = 4.45\text{ cm}^{-1}$, $A^*_{\text{min,max}} = 1.15, 1.20$, $F(000) = 2244$. $T = 295\text{ K}$. 5290 'observed' [$I > 3\sigma(I)$] diffractometer data out of 7143 unique independent absorption corrected (monochromatic Mo-K α radiation, $\lambda = 0.71073$ Å; $2\theta_{\text{max}} = 50^\circ$) refined to conventional R on $|F|$ 0.055, R_w (statistical weights) 0.055 (preferred hand). The two independent formula units in the asymmetric unit are pseudosymmetrically related. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/17.

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Received, 17th January 1996; Com. 6/00375C