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An Unprecedented Ruthenium Allenylidene Complex Containing an Unsaturated Bicyclic System: Formal Addition of 1-Ethynyl-1-cyclohexanol to an Alkenylvinylidene Intermediate Complex

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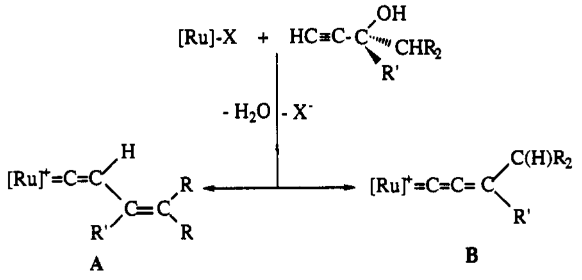
Summary: The stoichiometric activation of 1-ethynyl-1-cyclohexanol by [RuCl(PPh$_3$)$_2$(η-C$_9$H$_7$)] in the presence of NaPF$_6$ allows the formation of the propadienylidene ruthenium complex 1, containing a new spirobicyclic system which is formed through an unprecedented coupling process. The crystal structure of 1 has been determined by X-ray diffraction crystallography.

Ruthenium(II) vinylidene complexes $[Ru]^+{=}C{=}CR_2$ are genuine examples of transition-metal vinylidene complexes and have been widely studied in the last decade. In contrast, the chemistry of the cumulene analogs $[Ru]^+{=}C{=}(C)_x{=}CR_2$ is less developed.[1] Although Dixneuf and co-workers have described as transient species a series of pentatetraenylidene ($x = 3$) ruthenium complexes,[2] actually only a few propadienylidene complexes ($x = 1$) have been isolated, i.e. $[Ru\{{=}C{=}C{=}C(Ph)R\}(PPh_3)Cl(\eta^6\text{-}C_6Me_6)]^+$ (R = Ph, ferrocenyl),[3] $[Ru({=}C{=}C{=}CPh_2)(PPh_3)_2(\eta\text{-}C_5H_5)]^+$,[4] and $[Ru({=}C{=}C{=}CR_2)Cl(dppm)_2]^+$ (R = Me, Ph, *p*-Cl-Ph; R$_2$ = indenylidene group).[2a] The synthetic method is now well established and involves the reaction of 1-alkyn-3-ols with ruthenium(II) chloride complexes.

However, the fate of the dehydration reaction clearly depends on the electronic and steric properties of the metal auxiliary, since protioalkenylvinylidene derivatives **A** can be also formed ([Ru] = $[Ru(PMe_3)_2(\eta\text{-}C_5H_5)]$).[5] This alternative process may limit the scope of the general method used for the synthesis of the allenylidenemetal isomers **B**.



While examining the ability of the indenyl fragment $[Ru(PPh_3)_2(\eta\text{-}C_9H_7)]$ to stabilize these cumulene systems, we have discovered the first example of a formal addition of two molecules of alkynols *via* a metal-promoted double dehydration of 1-ethynyl-1-cyclohexanol, yielding the unprecedented allenylidene complex 1, which contains the bicyclic[3.3.1]non-2-en-9-ylidene moiety.

The reaction of [RuCl(PPh$_3$)$_2$(η-C$_9$H$_7$)], 1-ethynyl-1-cyclohexanol, and NaPF$_6$ in refluxing methanol for 12 h

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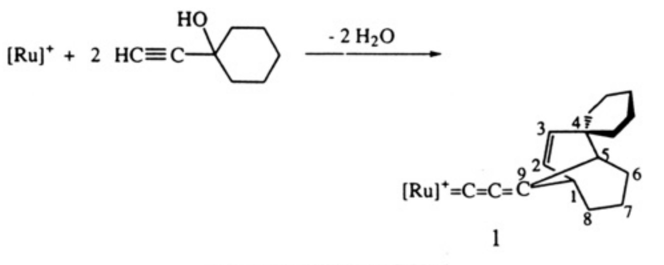
[1] Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197. Antonova, A. B.; Johansson, A. A. *Russ. Chem. Rev.* (*Engl. Transl.*) **1989**, *58*, 693. Werner, H. *Nachr. Chem., Tech. Lab.* **1992**, *40*, 435.



1

[Ru]= $[Ru(PPh_3)_2(\eta\text{-}C_9H_7)]$

results[6] in the formation of an air-stable orange solid characterized by elemental analyses and mass spectrum (FAB; $M^+ = 953$) as the hexafluorophosphate salt of the cationic complex **1** (55% yield), which can be formulated as a formal adduct of the metal auxiliary $[Ru(PPh_3)_2(\eta\text{-}C_9H_7)]^+$ and two dehydrated molecules of 1-ethynyl-1-cyclohexanol. The ^{13}C NMR spectrum[6] of **1** exhibits typical resonances of an allenylidene fragment at δ 304.48 (C_α, t, $^2J(P,C) = 19.4$ Hz), 191.07, and 186.83 (C_β and C_γ) ppm, and the IR spectrum shows a ν(C=C=C) absorption band at 1952 cm^{-1}. The ^1H NMR spectrum shows a pattern more complex than that expected for the resonances of the cyclohexyl protons.

Since the structure could not be elucidated unambiguously from this information, a single-crystal X-ray structural determination was carried out.[7] The structure shows the cationic complex **1** (Figure 1) to have a nearly linear allenylidene fragment, with typical Ru–C_α (1.889(5) Å), C_α–C_β (1.256(7) Å), and C_β–C_γ (1.339(7) Å) bond lengths. The observed differences from the values expected for double bonds are due to the contribution of the resonance form [Ru]—C≡CC$^+$(R)$_2$. These distances may be compared with those shown by the complex $[Ru(=C=C=CPh_2)(PMe_3)_2(\eta\text{-}C_5H_5)][PF_6]$.[4] The most remarkable feature in the structure is the presence of the 4-spirocyclohexanebicyclo[3.3.1]non-2-en-9-ylidene moiety, with the 9-carbon atom being C_γ of the metallapropadienylidene chain. The C1′–C2′ distance (1.33 (1) Å) shows the typical bond length of a double carbon–carbon bond.

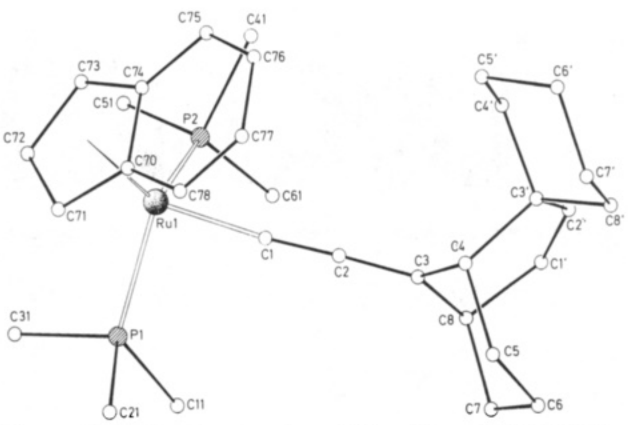


Figure 1. Molecular structure of the cation of [**1**][PF_6]. For clarity aryl groups of the triphenylphosphine ligands are omitted (C* = centroid of the indenyl ring). Selected distances (Å) and angles (deg): Ru–C1, 1.889(5); Ru–C*, 1.942(5); C1–C2, 1.256(7); C2–C3, 1.339(7); C1′–C2′, 1.33(1); Ru–P1, 2.312(1); Ru–P2, 2.311(1); Ru–C1–C2, 173.6(4); C1–C2–C3, 173.2(5); C2–C3–C4, 123.8(5); C2–C3–C8, 122.5(5); P1–Ru–P2, 102.7(1).

However, the reaction of $[RuCl(PPh_3)_2(\eta\text{-}C_9H_7)]$, 1-ethynyl-1-cyclohexanol, and $NaPF_6$ in refluxing methanol for 15 min results in the dehydration of only one molecule of 1-ethynyl-1-cyclohexanol and the formation of the protioalkenylvinylidene cationic complex **2** as a yellow-orange powder[8] (66% yield) (Scheme 1). This complex can be readily deprotonated to yield the enynyl complex **3**.[8] The reaction is reversible, since **3** can be reprotonated by the addition of an equimolar amount of $HBF_4{\cdot}OEt_2$. Similarly, the reaction of **3** with $MeOSO_2CF_3$ results in the electrophilic addition of Me^+ to C_β of the enynyl complex, leading to the triflate salt of the alkenylvinylidene cationic complex **4**.[8,9] On the other hand, the reaction of **2** with 1-ethynyl-1-cyclohexanol gives complex **1**.

Taking into account that the protioalkenylvinylidene complex **2** is a precursor of **1**, we propose the mechanism

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(2) (a) Pirio, N.; Touchard, D.; Toupet, L.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1991**, 980. (b) Wolinska, A.; Touchard, D.; Dixneuf, P. H.; Romero, A. *J. Organomet. Chem.* **1991**, *421*, 217. (c) Romero, A.; Peron, D.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1990**, 1410. (d) Romero, A.; Vegas, A.; Dixneuf, P. H. *Angew. Chem.* **1990**, *102*, 210. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 215.

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(4) Selegue, J. P. *Organometallics* **1982**, *1*, 217.

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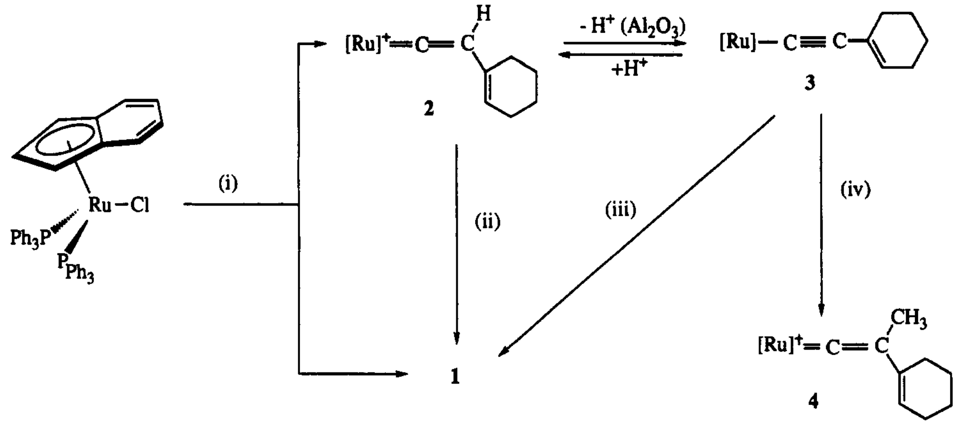
(6) To a solution of $[RuCl(PPh_3)_2(\eta\text{-}C_9H_7)]$ (0.15 g, 0.2 mmol) in 45 mL of methanol were added sodium hexafluorophosphate (0.08 g, 0.5 mmol) and 1-ethynyl-1-cyclohexanol (0.06 g, 0.5 mmol). The reaction mixture was refluxed for 12 h, the solvent was removed, and the crude product was extracted with dichloromethane. Concentration and addition of diethyl ether afforded 0.12 g (55%) of **1** as an orange solid. IR (CH_2Cl_2): ν 1952 cm^{-1} (C=C=C). IR (KBr): ν 1940 (C=C=C), 839 cm^{-1} (PF_6). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.5 MHz): δ 49.56 ppm. ^1H NMR (CD_2Cl_2, 300 MHz): δ 1.20–2.17 (m, 16H, CH_2), 2.60 (m, 1H, CH), 2.86 (m, 1H, CH), 4.91 (t, 1H, $J = 2.7$ Hz, Ind_5), 5.39 (m, 2H, Ind_5), 5.43 (m, 1H, C=C(H)CH), 5.90 (d, 1H, $J = 9.6$ Hz, C=CH), 6.34 (m, 1H, Ind_6), 6.51 (m, 1H, Ind_6), 6.96–7.39 (m, 30H Ph, 2H Ind_6). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.4 MHz): δ 18.32, 22.08, 22.84, 26.27, 32.83, 34.24, 35.25, 39.97 (CH_2), 46.11 (C), 52.27, 58.42 (CH), 86.11, 86.64, 97.12, 110.72, 112.26 (Ind), 123.18–140.07 (Ph, C=C Ind), 191.07, 186.83 (C_β, C_γ), 304.48 (t, $J(C,P) = 19.4$ Hz, C_α).

(7) Crystal data for **1**: $C_{61}H_{57}F_6P_3Ru$; $M_r = 1098.10$; triclinic; space group $P\bar{1}$; $a = 13.92(1)$ Å, $b = 14.512(8)$ Å, $c = 15.503(7)$ Å; $\alpha = 62.70(9)°$, $\beta = 68.57(8)°$, $\gamma = 69.14(6)°$; $V = 2523(4)$ Å^3; $Z = 2$; $\rho_{calc} = 1.44$ g cm^{-3}; $F(000) = 1132$; $\mu = 4.5$ cm^{-1}; red-brown crystal (0.23 × 0.13 × 0.09 mm); of 9641 reflections measured, 6424 used in refinement; PF_6^- anion was affected by some structural disorder; final $R = 0.047$ and $R_w = 0.050$; $w = 1.0/[\sigma^2(F_o) + 0.0003F_o^2]$; parameters refined 641; residual electronic density less than 1.04 e Å^{-3} (0.47 e Å^{-3} excluding the PF_6^- peaks), located near the disordered PF_6^-; maximum parameter shift to esd ratio 0.064; $T = 200$ K; Enraf-Nonius CAD4 diffractometer; λ(Mo Kα) = 0.710 73 Å, ω–2θ scan technique, ($0 < \theta < 25°$).

(8) Selected spectroscopic data are as follows. **2**: IR (KBr) ν 840 cm^{-1} (PF_6^-); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.5 MHz) δ 37.55 ppm; ^1H NMR (CD_2Cl_2, 300 MHz) δ 1.41 (m, 4H, CH_2), 1.64 (m, 2H, CH_2), 2.14 (m, 2H, CH_2), 4.81 (s, 1H, Ru=C=CH), 5.37 (m, 1H, C=CH), 5.50 (d, 2H, $J = 2.7$ Hz, Ind_5), 5.79 (t, 1H, $J = 2.7$ Hz, Ind_5), 5.85 (m, 2H, Ind_6), 6.80 (m, 12H, Ph), 7.23 (m, 12H Ph, 2H Ind_6), 7.43 (m, 6H, Ph); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.4 MHz) δ 22.56, 23.39, 26.38, 30.50 (CH_2), 83.20, 99.74, 116.80 (Ind), 121.58 (C_β), 124.01 (Ind), 124.84 (=C), 129.15–134.45 (Ph, =CH, Ind), 355.36 (t, $J(C,P) = 16.5$ Hz, C_α). **3**: IR (CH_2Cl_2) ν 2066 cm^{-1} (C≡C); IR (KBr) ν 2051 cm^{-1} (C≡C); $^{31}P\{^1H\}$ NMR (C_6D_6, 121.5 MHz) δ 52.35 ppm; ^1H NMR (C_6D_6, 300 MHz) δ 1.90 (m, 4H, CH_2), 2.49 (m, 2H, CH_2), 2.64 (m, 2H, CH_2), 4.95 (d, 2H, $J = 2.1$ Hz, Ind_5), 5.83 (t, 1H, $J = 2.1$ Hz, Ind_5), 6.25 (m, 1H, C=CH), 6.58 (m, 2H, Ind_6), 6.92 (m, 2H, Ind_6), 7.18 (m, 18 H, Ph), 7.39 (m, 4H, Ph), 7.74 (m, 8H, Ph); $^{13}C\{^1H\}$ NMR (C_6D_6, 75.4 MHz) δ 23.68, 23.42, 26.88, 32.61 (CH_2), 75.54, 96.29 (Ind), 104.47 (t, $J(C,P) = 24.5$ Hz, Cα), 109.94 (Ind), 117.22 (C_β), 123.77–140.13 (Ph, C=C, Ind). **4**: IR (KBr) ν 1270 cm^{-1} ($CF_3SO_3^-$); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.5 MHz) δ 39.35 ppm; ^1H NMR (CD_2Cl_2, 300 MHz) δ 0.85 (m, 2H, CH_2), 1.32 (m, 2H, CH_2), 1.47 (m, 2H, CH_2), 1.50 (s, 3H, CH_3), 2.24 (m, 2H, CH_2), 5.30 (m, 2H, Ind_5), 5.54 (m, 2H, Ind_6), 5.68 (m, 1H, Ind_5), 5.96 (m, 1H, C=CH), 6.69 (m, 10H, Ph), 7.11 (m, 2H, Ind_6), 7.30 (m, 14H, Ph), 7.45 (m, 6 H, Ph); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 74.5 MHz) δ 10.38 (CH_3), 22.62, 23.50, 26.81, 26.84 (CH_2), 81.04, 100.12, 116.95 (Ind), 123.98–135.37 (Ph, C_β, C=C, Ind).

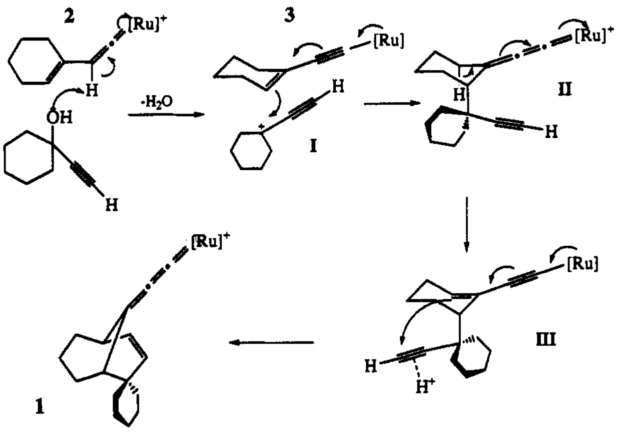
(9) The structure of **4** has been confirmed by an X-ray crystallographic determination. (García-Granda, S.; Borge, J. Personal communication.) It is worth mentioning that the orientations of the indenyl ligand in **1** and **4** are different, since the arene ring orients with respect to the phosphine ligands in either a "closer to" or "further away" fashion.

Scheme 1[a]



[a] Legend: [Ru] = $[Ru(PPh_3)_2(\eta\text{-}C_9H_7)]$; (i) $NaPF_6$ + $HC{\equiv}C\overline{C(OH)CH_2(CH_2)_3CH_2}$; (ii) $HC{\equiv}C\overline{C(OH)CH_2(CH_2)_3CH_2}$; (iii) $HC{\equiv}C\overline{C(OH)CH_2(CH_2)_3CH_2}$ + $MgSO_4$; (iv) $MeOSO_2CF_3$.

Scheme 2. Proposed Mechanism of the Formation of 1 ([Ru] = $[Ru(PPh_3)_2(\eta\text{-}C_9H_7)]$)



illustrated in Scheme 2. We assume that the first step is the dehydration of 1-ethynyl-1-cyclohexanol induced by proton transfer from the vinylidene complex 2, which leads to the formation of the carbocation I. This transient species I is rapidly trapped by the alkynyl complex 3, resulting from the deprotonation of 2, to form the intermediate allenylidene complex II. The final formation of 1 is likely to be based on the acidic character of the proton on the δ-carbon of the allenylidene moiety in II, which is transferred to the terminal alkyne group. This shift allows the intramolecular attack of the alkenyl group in III to give the observed allenylidene complex containing the spirobicyclic system. We assume that the key step of this mechanism is the attack of 3 on the carbocation I simultaneously generated from the starting materials under the reaction conditions.

To prove this, we have explored the reactivity of 3 with 1-ethynyl-1-cyclohexanol using $MgSO_4$ as a Lewis acid to activate the alcohol. The reaction leads readily to the formation of 1 (Scheme 1), while no reaction is observed in the absence of a Lewis acid, showing that the formation of the activated species I seems to be required. On the other hand, the alkynyl complex 3 is also an active species, since the vinylidene complex 2 does not react with the alkynol in the presence of $MgSO_4$. This mechanism is also consistent with the absence of reactivity of the methylvinylidene complex 4 toward 1-ethynyl-1-cyclohexanol.

The above results show for the first time a new type of reaction in the chemistry of metallacumulene systems which represents a good example of the potential utility of these derivatives as building blocks for the synthesis of unsaturated organic fragments. Further studies concerning the scope of these unusual addition reactions as well as the influence of different ancillary ligands in the metallic auxiliary $[RuL_2(\eta\text{-}C_9H_7)]$ on the stabilization of different cumulene systems are underway.

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Supplementary Material Available: Text giving experimental procedures for 2-4 and lists of crystal structure data, positional and thermal parameters, bond lengths and angles, torsion angles, and least-squares planes for 1 (13 pages). Ordering information is given on any current masthead page.

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