Allenylidene Indenyl Ruthenium(II) Complexes as Sources of Highly Functionalized Alkynyl Complexes: Synthesis of the First Bimetallic Derivatives containing a Vinylidene–Carbene Bridge

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The alkynylphosphonioruthenium(II) complex $[\mathrm{Ru}\{-\mathrm{C{\equiv}C{-}C(PMe_3)(H)Ph}\}(\mathrm{PPh_3})_2(\eta{-}\mathrm{C_9H_7})][\mathrm{PF_6}]$ reacts with aldehydes, ketones and phenylisocyanate *via* a Wittig process to afford either enynyl or keteniminyl complexes; $[\mathrm{Ru({=}C{=}C{=}CPh_2)(PPh_3)_2}(\eta\text{-}\mathrm{C_9H_7})]$ $[\mathrm{PF_6}]$ undergoes regioselective nucleophilic attacks at C_γ by the anionic species $[\mathrm{M(CO_5){=}C(OMe)CH_2}]^-$ (M= Cr, Mo, W) to yield binuclear alkynyl-carbene complexes $[(\eta\text{-}\mathrm{C_9H_7})(\mathrm{PPh_3})_2\mathrm{Ru\text{-}C{\equiv}C\text{-}CPh_2\text{-}CH_2\text{-}C(OMe){=}M(CO)_5}]$ which are the precursors of the first vinylidene–carbene bimetallic cationic derivatives $[(\eta\text{-}\ \mathrm{C_9H_7})(\mathrm{PPh_3})_2\mathrm{Ru{=}C{=}C(H){-}CPh_2{-}CH_2{-}C(OMe){=}M(CO)_5}]^+$

Allenylidene complexes are active species in the catalytic cyclization-reconstitutive addition of prop-2-ynyl alcohols with allyl alcohols[1] and as reactive intermediates in the formation of Fischer-type unsaturated carbene complexes of the type alkenyl- oxy- or polienyl-oxy-carbene complexes of chromium, tungsten[2] and ruthenium.[3] We have investigated the synthetic potential of the allenylidene complexes $[\mathrm{Ru\{C{=}C{=}C(R)Ph\}(PPh_3)_2}(\eta{-}\mathrm{C_9H_7})]^+$ (R=H,Ph) for the preparation of highly functionalized alkynyl complexes taking advantage of the regioselective nucleophilic attacks at C_γ.[4] We believed it of interest to find out the influence of the steric and the electronic properties of the metal auxiliary on the coordinated allenylidene moiety. An X-ray diffraction study on $[\mathrm{Ru\{C{=}C{=}CPh_2\}(PPh_3)_2}(\eta{-}\mathrm{C_9H_7})]^+$ shows† that the conformation of the indenyl ligand is such that the benzo ring is orientated *cis* to the allenylidene group *i.e.* over the C_α. Thereby, we expected that regardless of both nucleophilic attacks at C_α and C_γ being theoretically allowed, the protection of C_α would most likely lead to selective transformations favouring the attack at the C_γ.

We now report the synthesis of (*i*) novel unsaturated alkynyl ruthenium complexes obtained through Wittig processes *via* the alkynylphosphonio complex $[\mathrm{Ru\{C{\equiv}C{-}C(H)(PMe_3)Ph\}}$-$(\mathrm{PPh_3})_2(\eta{-}\mathrm{C_9H_7})]$ $[\mathrm{PF_6}]$ **1** (*ii*) the first examples of bimetallic complexes containing difunctionalized hydrocarbon bridges of the type vinylidene-carbene along with analogous binuclear derivatives with bridging alkynyl-carbene ligands and the X-ray crystal structure of one of them, $[(\eta{-}\mathrm{C_9H_7})(\mathrm{PPh_3})_2$-$\mathrm{Ru{-}C{\equiv}C{-}CPh_2{-}CH_2{-}C(OMe){=}W(CO)_5}]$ **6c**.

Complex **1** was prepared in 82% yield by the addition of $\mathrm{PMe_3}$ to the allenylidene complex $[\mathrm{Ru\{{=}C{=}C{=}C(H)Ph\}}$ $(\mathrm{PPh_3})_2(\eta{-}\mathrm{C_9H_7})]^+$ using recently reported methodology.[4]‡ This alkynyl-phophonio complex containing an acidic hydrogen atom at Cγ is an excellent substrate for Wittig reactions leading to the formation of new carbon–carbon double bonds. Thus, the treatment of a THF solution of **1** with 1 equiv. of $\mathrm{Bu^nLi}$ at −20 °C gave rise to an immediate change to a dark-green solution probably containing the ilyde-alkynyl complex $[\mathrm{Ru(C{\equiv}C{-}CPh{=}PMe_3)(PPh_3)_2}(\eta{-}\mathrm{C_9H_7})]$; subsequent addition of benzophenone, cyclohexanone or acetaldehyde, allowing the mixture to reach room temperature resulted in the formation of the new enynyl complexes **2a,b** (65% yield) and **3** (64% yield), respectively (Scheme 1). Complex **3** is obtained as a mixture *ca.* 3 : 1 of the *E* and *Z* stereoisomers. Under analogous conditions the precursor complex **1** reacts with $\mathrm{Bu^nLi}$ and phenyl isocyanate to give the complex **4** (57%), a rare example of a functionalized alkynyl complex containing a keteniminyl moiety. The spectroscopic properties of **2a,b** and **3**‡ are consistent with the presence of the enynyl moieties; in particular the $\nu_{\mathrm{C{\equiv}C}}$ IR absorption (2025–2058 $\mathrm{cm^{-1}}$) and the typical triplet resonance in $^{13}\mathrm{C}$ NMR for the Ru–C≡ carbon nucleus at δ 110.08–114.73 ($^2J_{\mathrm{P,C}}$ 23.2–24.9 Hz). IR and $^{13}\mathrm{C}$ NMR spectroscopic data of complex **4** show the expected signals for the alkynyl-heterocumulene moiety *i.e.* $\nu_{\mathrm{C{=}C{=}N}}$ 1991 $\mathrm{cm^{-1}}$; δ (=C=N) 153.15.

The synthesis of μ-hydrocarbon transition metal complexes without metal–metal bonds are of particular current interest.[5] Since one of the most utilized synthetic methods is based on the reactions between electrophilic and nucleophilic complexes we sought to prepare heterobimetallic derivatives by creating hydrocarbon bridges through C–C coupling reactions between the electrophilic cationic allenylidene complex $[\mathrm{Ru(C{=}C{=}CPh_2)(PPh_3)_2}(\eta{-}\mathrm{C_9H_7})]^+$ and nucleophilic anionic carbene complexes. Thus, the allenylidene complex was treated with lithium salts of the Fischer carbene complexes $[\mathrm{(CO)_5M{=}C(OMe)CH_2}]^-$ (M=Cr, Mo, W). Workup gave the alkynyl carbene bimetallic complexes **5a–c** in 50–75% yield, as shown in Scheme 1. IR, NMR (^{1}H, ^{31}P, ^{13}C) support the proposed formulations and their structures followed readily from these data.‡ The IR spectra showed the expected $\nu_{\mathrm{C{\equiv}C}}$ and ν_{CO} absorptions and the ^{13}C NMR spectra exhibited the downfield M=C [359.98 **5a**, 352.10 **5b**, 335.00 **5c**] and Ru–C [97.74 (t, $^2J_{\mathrm{C,P}}$ 23.3 Hz) **5a**, 97.43 (t, $^2J_{\mathrm{C,P}}$ 25.1 Hz) **5b**, 98.24 (t, $^2J_{\mathrm{C,P}}$ 24.0 Hz) **5c**] resonances.

Since only one analogous alkynyl-carbene dinuclear complex has been structurally characterized *i.e.* $[(\eta{-}\mathrm{C_5Me_5})$-$\mathrm{(NO)(PPh_3)Re{-}C{\equiv}C{-}C(OMe){=}W(CO)_5}]$,[6] the single-crystal structural determination of **5c** has been carried out§ (Fig. 1). The crystal structure shows the typical pseudooctahedral three-legged piano-stool coordination around the ruthenium atom, which is linked to the pentacarbonyl tungsten fragment by the chain $\mathrm{{-}C{\equiv}C{-}CPh_2{-}CH_2{-}(MeO)C{=}}$. The structure shows a linear Ru–C≡C–C arrangement defined by typical Ru–Cα single bond and $\mathrm{C_\alpha{\equiv}C_\beta}$ triple bond lengths. Parameters for the $\mathrm{{-}CH_2{-}(MeO)C{=}}$ bonds can be compared with those

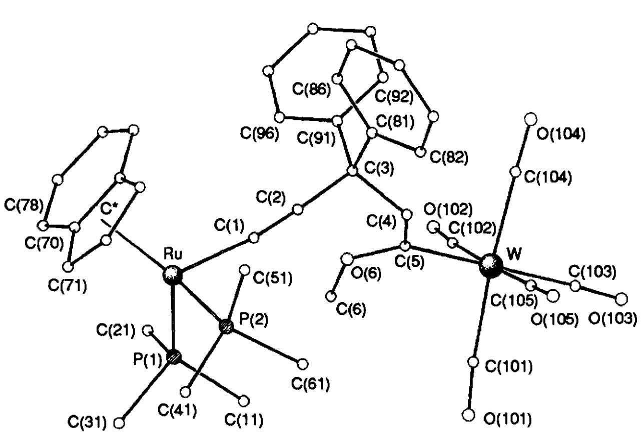
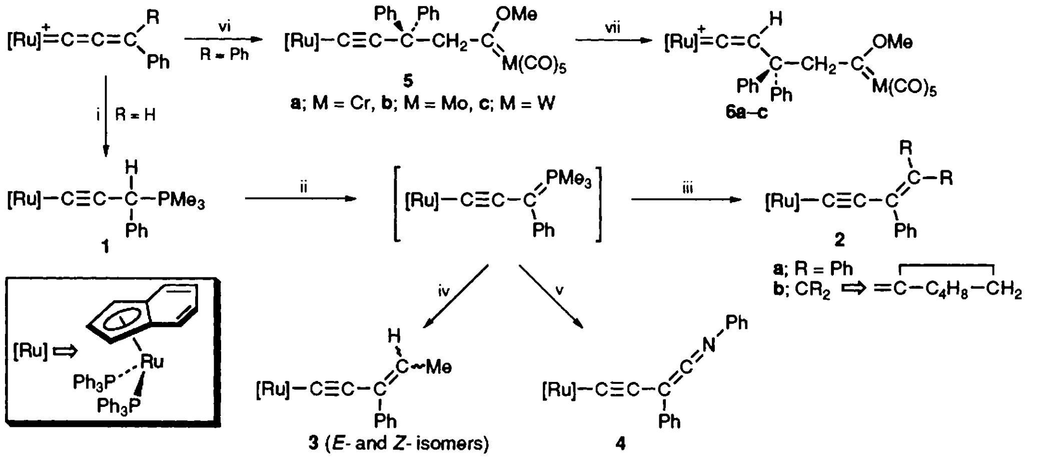


Fig. 1 Molecular structure of $[(\eta{-}\mathrm{C_9H_7})(\mathrm{PPh_3})_2\mathrm{Ru{-}C{\equiv}C{-}CPh_2{-}CH_2{-}C(OMe){=}W(CO)_5}]$ **6c** showing the atomic numbering. For clarity hydrogen atoms and phenyl phosphine groups have been omitted. Main bond distances (Å) and angles (°): Ru–C(1) 2.041(7). C(1)–C(2) 1.201(9). C(2)–C(3) 1.488(10). C(3)–C(4) 1.564(10). C(4)–C(5) 1.499(10). C(5)–O(6) 1.309(8). O(6)–C(6) 1.457(9). W–C(5) 2.186(7). Ru–C(1)–C(2) 172.6(6). C(1)–C(2)–C(3) 173.7(7). O(6)–C(5)–C(4) 107.5(6). W–C(5)–O(6) 131.3(5). W–C(5)–C(4) 121.1(5)



Scheme 1 *Reagents and conditions*: i, PMe_3, THF; ii, Bu^nLi (1 equiv.), THF −20 °C; iii, Ph_2CO or $O{=}\overline{C{-}C_4H_8{-}C}H_2$, THF room temp.; iv, MeCHO, THF room temp.; v, PhNCO, THF room temp.; vi, $Li[(CO)_5M{=}C(OMe)CH_2]$, THF −20 °C; vii, HBF_4, Et_2O −20 °C.

of tungsten Fischer-type carbene complexes $[(RC{-}(OR'){=}W(CO)_5]$.[7] The indenyl orientation is in a position between the formal *cis* and *trans* arrangement with respect to the hydrocarbon chain. The *cis* orientation is adopted by the indenyl group in the precursor allenylidene complex $[Ru(C{=}C{=}CPh_2)(PPh_3)_2(\eta{-}C_9H_7)]^+$.†

We have synthesised the first bimetallic complexes containing vinylidene–carbene type hydrocarbon bridges by protonation of diethyl ether solutions of alkynyl-carbene complexes **5a–c** with tetrafluoroboric acid at −20 °C. The treatment led to the formation of the desired tetrafluoroborate complexes (Scheme 1) isolated as yellowish stable solids **6a–c** (52–75% yield), which were characterized analogously to **5a–c**.¶ ^{13}C NMR spectra showed M=C and Ru=C resonances at δ 361.79, 334.08 (t, $^2J_{C,P}$ 17.3 Hz) **6a**, 358.15, 348.44 (t, $^2J_{C,P}$ 17.2 Hz) **6b**, 337.16, 345.52 (t, $^2J_{C,P}$ 18.8Hz) **6c**.

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Footnotes

† S. García-Granda and J. Borge, unpublished results from this laboratory.

‡ The complexes have been fully characterized by elemental analyses and NMR spectroscopy including NOE experiments for the two isomers of **3**.

§ *Crystal data*: $C_{74}H_{66}O_6P_2RuW$, M_r = 1398.20, orange crystal, triclinic, space group $P\bar{1}$, a = 11.858(4), b = 14.00(2), c = 19.46(2) Å, α = 92.5(1), β = 97.87(8), γ = 97.43(6)°, V = 3167(5) Å^3, Z = 2, D_x = 1.47 g cm^{-3}, T = 293 K; crystal dimensions 0.26 × 0.20 × 0.13 mm^3. 11464 reflections measured, range $1 < \theta < 25$ and $-13 < h < 14$, $-16 < k < 16$, $-23 < 1 < 0$; 11105 independent reflections (R_{int} = 0.034); μ = 2.19 mm^{-1}. Final R factors [$I > 2\sigma(I)$], $R1$ = 0.048, $wR2$ = 0.132; 711 parameters, $w = 1/[\sigma^2(F_o^2) + (0.0665{*}P)^2]$ where $P = (\mathrm{Max}(F_o^2,0) + 2{*}F_c^3)/3$; ρ_{max} = 1.02, ρ_{min} = −2.11 eÅ^{-3}; maximum shift/error = 0.006.

Mo-Kα radiation (λ = 0.71073 Å), graphite crystal monochromator; Enraf Nonius CAD4 (ω–2θ technique). Empirical absorption correction was applied (DIFABS), non-H atoms anisotropic, solvent refined as rigid group. The structure was solved by DIRDIF and refined by SHELXL93. Geometrical calculations were made with PARST. Crystallographic plots were made with EUCLID. All calculations were made on a MicroVAX 3400 at the Scientific Computer Center of the University of Oviedo. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors Issue No. 1.

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