

Selective C α -C β bond cleavage by water in allenylidene and alkenylvinylidene ruthenium complexes

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Received (in Basel, Switzerland) 4th January 1999, Accepted 27th January 1999

The Ru(II) complex *mer,trans*-[(PNP)RuCl₂(PPh₃)] [PNP = MeCH₂CH₂N(CH₂CH₂PPh₂)₂] reacts in refluxing THF with propargyl alcohols HC≡CCRR'OH (R = R' = Me, Ph; R = Me, R' = Ph) yielding either the allenylidene complex *fac,cis*-[(PNP)RuCl₂{C=C=CPh₂}] or the alkenylvinylidene derivatives *fac,cis*-[(PNP)RuCl₂{C=C(H)C(R)=CH₂}] (R = Me, Ph); treatment of all these complexes in CH₂Cl₂ or THF with water results in the formation of the ruthenium carbonyl *fac,cis*-[(PNP)RuCl₂(CO)] and free alkenes H₂C=CRR' (R = R' = Me, Ph; R = Me, R' = Ph) via regioselective C α -C β bond cleavage.

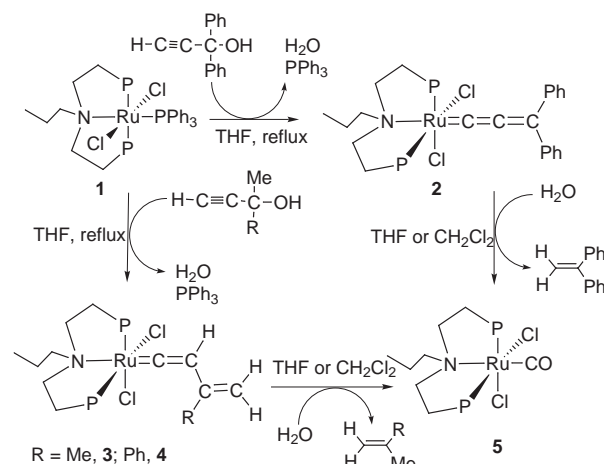
Understanding and rationalizing the reactivity of transition metal complexes containing allenylidene ligands, M=C=C=CR₂, is a topic of much current interest in organometallic chemistry.¹⁻³ Sound motivations arise from the increasing applications of allenylidene complexes, especially of ruthenium derivatives, to various catalytic reactions involving C-C bond formation.⁴

As a general trend, nucleophiles may attack either the C α or C γ carbon atom in allenylidene ligands affording Fischer-type carbenes or alkynyl compounds, respectively.⁵ The addition of water has been found to take place selectively at C α to give unsaturated hydroxycarbenes.⁶ At least in one case, however, there was the suspicion that water might be able to cleave a C-C bond in an allenylidene ligand but no experimental evidence was reported supporting this hypothesis.⁷ The question regarding the hydrolytic C-C bond cleavage in allenylidenes and homologous ligands is not of trivial importance given the wide use of their metal complexes as catalyst precursors in a variety of homogeneous processes, especially in reactions where new C-C bonds are formed.^{4,8} For this reason, we decided to investigate the reactions of both allenylidene and alkenylvinylidene complexes with water. Ruthenium was the metal of choice as it is known to effectively stabilize cumulene complexes and it also constitutes the essential ingredient in many C-C bond forming reactions.^{4,8}

Following the well known Selegue's synthetic protocol,⁹ the neutral allenylidene complex *fac,cis*-[(PNP)RuCl₂{C=C=CPh₂}] **2** was obtained in 78% yield by refluxing *mer,trans*-[(PNP)RuCl₂(PPh₃)] **1**¹⁰ and 1,1-diphenylprop-2-yn-1-ol in THF (Scheme 1).[†]

Complex **2**¹¹ was authenticated by means of standard spectroscopic techniques as well as a single-crystal X-ray analysis (Fig. 1).[‡] The crystallographic study confirmed the *fac* stereochemistry of the PNP ligand and the *trans* disposition of the diphenylallenylidene ligand and the nitrogen donor atom.¹²

While π -alkyne coordination (A) and alkyne to vinylidene tautomerization (B) are common steps to any propargyl alcohol activation, the eventual dehydration process of the hydroxyvinylidene intermediate may occur with different regioselectivity (Scheme 2). Either allenylidene (C) or alkenylvinylidene derivatives may indeed form depending on the presence of hydrogens on the carbon atom proximal to the OH group. If there are no hydrogens, the allenylidene products are stable,



Scheme 1

otherwise they may tautomerize to alkenylvinylidenes (E). Alternatively, the alkenylvinylidene ligand may form *via* direct elimination of water from the hydroxyvinylidene intermediate (D).¹³

Within this mechanistic picture, it was not surprising to find that **1** reacts with either 1,1-dimethyl- or 1-methyl,1-phenylpropyn-1-ol yielding the alkenylvinylidenes *fac,cis*-[(PNP)RuCl₂{C=C(H)C(R)=CH₂}] (R = Me, **3**; Ph, **4**).^{11‡} It was surprising instead to discover that both the allenylidene

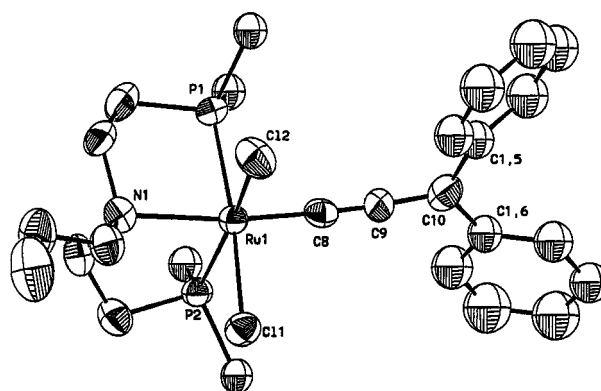
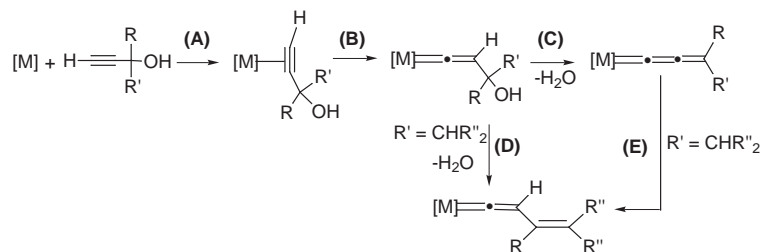


Fig. 1 ORTEP drawing of complex **2**.¹⁸ For sake of clarity only the *ipso* carbon atoms of the phenyl substituents in the PNP ligand are reported. Selected distances (Å) and angles (°): P(1)-Ru(1) 2.314(2), P(2)-Ru(1) 2.289(2), N(1)-Ru(1) 2.335(5), Ru(1)-Cl(1) 2.449(2), Ru(1)-Cl(2) 2.461(2), Ru(1)-C(8) 1.858(7), C(8)-C(9) 1.221(9), C(9)-C(10) 1.376(10), N(1)-Ru(1)-P(1) 82.69(14), N(1)-Ru(1)-P(2) 83.11(15), N(1)-Ru(1)-Cl(1) 90.15(14), N(1)-Ru(1)-Cl(2) 87.96(15), N(1)-Ru(1)-C(8) 173.4(2), P(1)-Ru(1)-P(2) 100.17(8), P(1)-Ru(1)-Cl(1) 171.95(6), P(1)-Ru(1)-Cl(2) 88.49(8), P(1)-Ru(1)-C(8) 90.66(19), P(2)-Ru(1)-Cl(1) 82.52(7), P(2)-Ru(1)-Cl(2) 166.62(6), P(2)-Ru(1)-C(8) 98.35(19), Cl(1)-Ru(1)-Cl(2) 87.59(8), Cl(1)-Ru(1)-C(8) 96.5(2), Cl(2)-Ru(1)-C(8) 91.67(19), Ru(1)-C(8)-C(9) 175.8(6), C(8)-C(9)-C(10) 171.1(7).



Scheme 2

complex **2** and the alkenylvinylidenes **3** and **4** are transformed by water (5 equiv.) into the known carbonyl derivative *fac-cis*-[(PNP)RuCl₂(CO)] (**5**)¹⁴ and the corresponding free alkene H₂C=CRR' (R = R' = Ph; R = Me or Ph, R' = Me). The quantitative formation of 1 equiv. of alkene was shown by GC-MS analysis and NMR spectroscopy (¹H, ¹³C) on both reaction mixtures and samples isolated by TLC. The hydrolysis reactions are quite fast at reflux temperature in either THF or CH₂Cl₂ but take place also at room temperature. When D₂O was employed in the place of H₂O, the alkene was found to regioselectively incorporate two *gem* deuterium atoms (D₂C=CRR') indicating that both terminal hydrogens come from water. Finally, the selective incorporation of ¹⁸O in the carbonyl complex **5**-¹⁸O, $\nu(\text{C}^{18}\text{O})$ 1899 cm⁻¹, was observed when the hydrolysis reactions were carried out with H₂¹⁸O confirming that the C_α-C_β bond scission in either allenylidene or alkenylvinylidene ligand was brought about by water and not by adventitious oxygen.¹⁵

In conclusion, for the first time it has been shown that both allenylidene and alkenylvinylidene ruthenium complexes, dissolved in organic solvents, may react with water producing CO ligands and free alkene *via* regioselective cleavage of the C_α-C_β bond. The hydrolysis of metal vinylidenes has recently been reported to give carbonyl species and the saturated hydrocarbon derived from the homologation of the vinylidene substituent.¹⁵ From allenylidene and alkenylvinylidene complexes, unsaturated hydrocarbons are selectively formed, which may open the door to the alternative synthesis of high-added value alkenes or alkenes selectively deuterated at the unsubstituted end.

This work was supported by the bilateral program «Azione Integrata» between the University of Florence (Italy) and Almeria (Spain) and by the EC contracts INTAS 96-1176 and INCO ERBIC15CT960746.

Notes and references

† Satisfactory elemental analyses were obtained for **2** (red purple crystals), **3** (pink crystals), and **4** (pink red crystals). Selected spectroscopic data for **2**: IR ($\nu_{\text{C-C}}$) 1916 cm⁻¹. ³¹P{¹H} NMR (CD₂Cl₂, 85% H₃PO₄, 294 K), δ 49.12 (s). ¹³C{¹H} NMR (CD₂Cl₂, TMS, 294 K), δ 304.3 (t, ²J_{CP} 19.2 Hz, C_α), 233.8 (s, C_β), 150.8 (s, C_γ). For **3**: IR ($\nu_{\text{C-C}}$) 1610s cm⁻¹. ¹H NMR (CDCl₃, TMS, 294 K), δ 5.16 (t, ⁴J_{HP} 3.3 Hz, 1H, CH), 4.63 and 4.15 (d, ²J_{HH} 1.8 Hz, 1H each, CH₂), 2.28 [s, 3H, CH₃(alkenylvinylidene)]. ³¹P{¹H} NMR (CDCl₃, 85% H₃PO₄, 294 K), 47.81 (s). ¹³C{¹H} NMR (CDCl₃, TMS, 294 K), δ 313.5 (t, ²J_{CP} 18.0 Hz, C_α), 126.6 (s, C_β), 114.2 (s, C_β), 18.5 [s, CH₃(alkenylvinylidene)], confirmed by a DEPT-135 experiment, C_γ, not assigned. For **4**: IR ($\nu_{\text{C-C}}$) 1617s cm⁻¹. ¹H NMR (CD₂Cl₂, TMS, 294 K), δ 5.73 and 5.25 (d, ²J_{HH} 1.6 Hz, 1H each CH₂), 5.10 (t, ⁴J_{HP} 8.2 Hz, 1H, CH). ³¹P{¹H} NMR (CD₂Cl₂, 85% H₃PO₄, 294 K), δ 49.20 (s). ¹³C{¹H} NMR (CD₂Cl₂, TMS reference, 294 K), 350.3 (t, ²J_{CP} 17.5 Hz, C_α), 150.2 (s, C_γ), 122.6 (s, C_β), 113.5 (s, C_β), confirmed by a DEPT-135 experiment.

‡ Crystal data: C₄₆H₄₅Cl₂NP₂Ru, M_w = 845.79, monoclinic, space group P2₁/c, a = 11.881(9), b = 13.446(2), c = 25.264(5) Å, β = 98.00(5)°, V = 3997(3) Å³, Z = 4, D_c = 1.406 g cm⁻³, T = 293(2) K, μ(Mo-Kα) = 0.640 mm⁻¹; red crystal, crystal size 0.23 × 0.35 × 0.29 mm. Enraf Nonius CAD4 diffractometer, 5545 independent reflections. The structure was solved by direct methods (SIR92)¹⁶ and refined (F₀²) using the program SHELX-93.¹⁷ An empiric absorption correction was applied *via* ψ scan (0.97–1.00). The final R, R_w indices [I > 2σ(I)] were 0.0644, 0.1544 for 220

parameters (non-hydrogen atoms anisotropic, hydrogen atoms in idealised positions, C–H = 0.96 Å). CCDC 182/1164.

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