

The coupling of methylene and vinyl ligands at a ruthenium(II) centre

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The reaction of $[\text{Ru}(\text{CH}=\text{CH}_2)\text{Cl}(\text{CO})(\text{PPh}_3)_2]$ with diazomethane provides the allyl complex $[\text{Ru}(\eta^3\text{-CH}_2\text{CHCH}_2)\text{Cl}(\text{CO})(\text{PPh}_3)_2]$ which is also the product of the reactions of $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$ with either allene or propyne and which reacts subsequently with $\text{NaS}_2\text{CNMe}_2$ to provide $[\text{RuH}(\text{S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)_2]$ and allene.

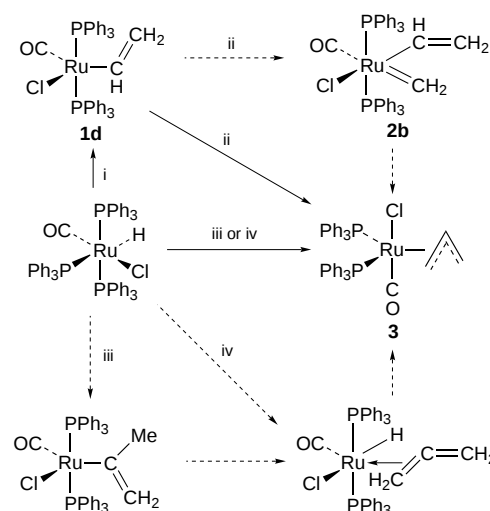
In a recent review,¹ Maitlis *et al.* drew attention to the potential significance of the coupling of vinyl and methylene groups in the Fischer–Tropsch synthesis. In particular the oxidation of $[\text{Rh}_2(\mu\text{-CH}_2)_2(\text{CH}=\text{CH}_2)_2(\eta\text{-C}_5\text{Me}_5)_2]$ by AgBF_4 in acetonitrile was shown to provide $[\text{Rh}(\eta^3\text{-CH}_2\text{CHCH}_2)(\text{NCMe})(\eta\text{-C}_5\text{Me}_5)]\text{BF}_4$,² whilst diazomethane addition to the diruthenium complex $[\text{Ru}_2(\mu\text{-CH}=\text{CH}_2)(\text{CO})_3(\eta\text{-C}_5\text{H}_5)_2]^+$ followed by deprotonation provides $[\text{Ru}_2(\mu\text{-CHCH}=\text{CH}_2)(\mu\text{-CO})(\text{CO})(\eta\text{-C}_5\text{H}_5)_2]$.³ The operation of these couplings on bimetallic systems, whilst clearly significant in understanding Fischer–Tropsch processes, begs the question do they occur on monometallic systems? Werner and coworkers have reported that the reaction of $[\text{RuCl}(\text{C}(\text{Ph})_2)(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)]$ with vinyl magnesium bromide provides the allyl complex $[\text{Ru}(\eta^3\text{-CH}_2\text{CHCH}_2)(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)]$.⁴ The complex $[\text{Ru}(\text{CH}=\text{CH}_2)(\text{C}(\text{Ph})_2)(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)]$ is an attractive intermediate, however as the authors point out, the product is also consistent with direct nucleophilic attack at the carbene carbon. Such a process is typical of coordinatively saturated carbene complexes of divalent ruthenium.⁵ Here, we report the unambiguous observation of the coupling of a vinyl and a methylene ligand on a ruthenium system. Furthermore, we show an unusual β -elimination process of the resulting η^3 -allyl ligand which may be induced by dithiocarbamate coordination.

Roper and coworkers have shown that the coordinatively unsaturated complex $[\text{Ru}(\text{Ph})\text{Cl}(\text{CO})(\text{PPh}_3)_2]$ **1a** reacts with diazomethane to provide a remarkably stable methylene complex $[\text{Ru}(\eta^2\text{-OCPh})\text{Cl}(\text{C}(\text{H})=\text{CH}_2)(\text{PPh}_3)_2]$ **2a**, but that such a reaction has so far failed for the corresponding *trans* β -styryl analogue $[\text{Ru}(\text{CH}=\text{CHPh})\text{Cl}(\text{CO})(\text{PPh}_3)_2]$ **1b**.⁶ An intriguing feature of the reactivity of **2a** is the apparent reluctance of the phenyl and methylene ligands to couple, despite the anticipated stability of the hypothetical product $[\text{Ru}(\text{CH}_2\text{Ph})\text{Cl}(\text{CO})(\text{PPh}_3)_2]$ **1c**. We find that the parent vinyl complex $[\text{Ru}(\text{CH}=\text{CH}_2)\text{Cl}(\text{CO})(\text{PPh}_3)_2]$ **1d**⁷ reacts readily with diazomethane in dichloromethane–diethyl ether to provide high yields of the η^3 -allyl complex $[\text{Ru}(\eta^3\text{-CH}_2\text{CHCH}_2)\text{Cl}(\text{CO})(\text{PPh}_3)_2]$ **3** (Scheme 1), the identity and stereochemistry of which follows unambiguously from spectroscopic data† and two unequivocal syntheses (*vide infra*). Whilst the reaction leading to **3** is unique, the class of compounds has precedent. Related examples, *e.g.* $[\text{Ru}(\eta^3\text{-CH}_2\text{CHCH}_2)\text{Cl}(\text{CO})(\text{PMe}_2\text{Ph})_2]$ have been obtained from the reaction of $[\text{RuCl}_2(\text{CO})_2(\text{PMe}_2\text{Ph})_2]$ with $\text{Bu}^n\text{SnCH}_2\text{CH}=\text{CH}_2$,^{8†} whilst $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$ hydorruthenates 1,3-dienes to provide substituted examples.⁹ Although this result is surprising, the methylene complex $[\text{Ru}(\text{CH}=\text{CH}_2)\text{Cl}(\text{C}(\text{H})=\text{CH}_2)(\text{CO})(\text{PPh}_3)_2]$ **2b** is an obvious intermediate in the formation of **3**. It remains unclear to us why, in the case of **1a** methylene coordination is followed by (reversible) migration of a phenyl group to a carbonyl ligand, but in the case of **1d**, migration of the vinyl ligand occurs selectively and irreversibly to the introduced methylene ligand.

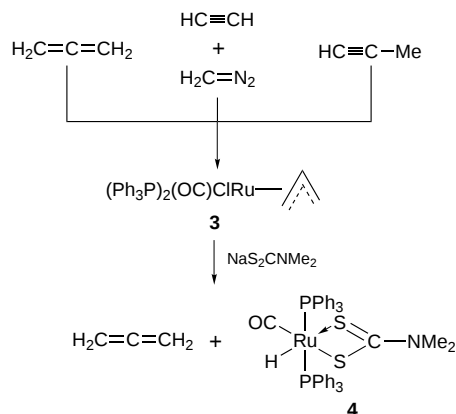
Maitlis' studies of C–C bond forming processes for organorhodium species certainly point to a greater migratory aptitude for vinyl than phenyl ligands.¹ However, since the phenyl complex **2a** has been shown to be in equilibrium with $[\text{Ru}(\text{Ph})\text{Cl}(\text{C}(\text{H})=\text{CH}_2)(\text{CO})(\text{PPh}_3)_2]$ ⁶ the relative mobility of vinyl and phenyl ligands appears not to be the limiting factor here, but more likely one of product development control.

Complex **3** also results from two other approaches. Santos and coworkers have shown that in general, terminal alkynes $\text{RC}\equiv\text{CH}$ ($\text{R} = \text{Ph}, \text{Bu}^t, \text{Bu}^n$) react with $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$ to provide coordinatively unsaturated σ -vinyl complexes $[\text{Ru}(\text{CH}=\text{CHR})\text{Cl}(\text{CO})(\text{PPh}_3)_2]$.¹⁰ We anticipated that a similar hydorruthenation of allene might provide **3** which indeed it does in high yield (Scheme 1). Somewhat surprisingly however, **3** is also the product of the reaction of $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$ with propyne! This result can be explained by the formation of the usually less favoured α -substituted σ -vinyl complex $[\text{Ru}(\text{C}(\text{Me})=\text{CH}_2)\text{Cl}(\text{CO})(\text{PPh}_3)_2]$, which can undergo β -Ru–H elimination to provide $[\text{RuH}(\eta^2\text{-CH}_2\text{CCH}_2)\text{Cl}(\text{CO})(\text{PPh}_3)_2]$ followed by hydorruthenation to provide **3**.

The chemistry of η^3 -allyl ligands is enriched by their ability to assume a monohapto coordination mode. We therefore attempted to induce monohapto coordination by replacing the chloride ligand in **3** with a potentially bidentate dithiocarbamate ligand. Surprisingly, the reaction of **3** with $\text{Na}[\text{S}_2\text{CNMe}_2]$ in dichloromethane–ethanol led to the formation of $[\text{RuH}(\text{S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)_2]$ **4** with the organometallic ligand being lost from the coordination sphere. When the reaction was carried out in CDCl_3 – MeOH (10 : 1), ¹H NMR integration confirmed allene as the organic product. The most reasonable course for this reaction would appear to be dissociation of chloride followed by the β -RuH elimination of allene to provide the coordinatively unsaturated, though presumably solvent-stabilised species $[\text{RuH}(\text{CO})(\text{PPh}_3)_2]^+$. Although this type of elimination is unusual, we have observed¹¹ that treating



Scheme 1 Reagents and conditions: i, $\text{H}_2\text{C}=\text{CH}_2$ (CH_2Cl_2 , 25 °C); ii, CH_2N_2 (Et_2O , CH_2Cl_2 , 25 °C); iii, $\text{CH}_3\text{C}\equiv\text{CH}$ (thf , 25 °C then heating); iv, $\text{H}_2\text{C}=\text{C}=\text{CH}_2$ (thf , 25 °C then heating)



Scheme 2

[Ru(CH=CHCH₂PPh₃)Br(CO)(PPh₃)₂]⁺ with Na[S₂CNMe₂] also leads to formation of **4**.

The above transformations taken together constitute the metal-mediated conversion of ethyne or propyne to allene (Scheme 2). The reactions are clearly not catalytic in nature, however they do add a further viewpoint to the complex picture of chain growth in Fischer–Tropsch processes, complimenting recent results obtained by Werner *et al.* for the coupling of vinyl ligands with vinylidenes on mononuclear rhodium centres.¹²

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Footnotes and References

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† Selected data for **3**: (a) complex **1d** (1.00 g) in dichloromethane (35 cm³) was treated with an excess of diazomethane in diethyl ether and stirred for 15 min. Removal of solvent, chromatographic purification (silica gel, CH₂Cl₂ eluent) and crystallisation from CH₂Cl₂–EtOH provided **3**; yield 0.45 g (44%). (b) [RuHCl(CO)(PPh₃)₃] (0.60 g) in allene-saturated thf was stirred for 1 h and then heated under reflux for 2 min. Addition of ethanol and slow concentration provided **3**; yield 0.39 g, (85%). [RuHCl-

(CO)(PPh₃)₃] (0.50 g) in propyne-saturated thf was stirred for 1 h and then heated under reflux for 2 min. Addition of ethanol and slow concentration provided **3**; yield 0.32 g (84%). IR 1933 (Nujol), 1939 (CH₂Cl₂) [ν(CO)] cm⁻¹. NMR (25 °C, CDCl₃). ¹H: δ 2.57 [dd, 2 H, J(HH) 5.28, 12.54, CH₂], 2.97 [d, 2 H, J(HH) 7.26 Hz, CH₂], 5.03 [m (= tt), 1 H, ≡CH], 7.22–7.48 (m, 30 H, C₆H₅). ¹³C{¹H}: δ 202.2 [t, J(PC) 14 Hz], 134.4–127.9 (C₆H₅), 101.6 (≡CH), 62.1 [d, J(PC) 23.7 Hz, CH₂]. ³¹P {¹H}: δ 34.98. FABMS *m/z* (%): 730(3) [M]⁺, 695 (51) [M – Cl]⁺, 689 (73) [M – C₃H₅]⁺, 653 (11) [Ru(CO)(PPh₃)₂]⁺, 625 (17) [Ru(PPh₃)₂]⁺. Anal. Found: C, 65.66; H, 4.75. C₄₀H₃₅ClO₂P₂Ru requires C, 65.80; H, 4.83%.

‡ Notably **1a** rather than **3** is the product of the reaction of [RuHCl(CO)(PPh₃)₃] with Ph₃SnCH₂CH=CH₂.

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