

Control of intramolecular acetate–allenylidene coupling by spectator co-ligand π -acidity

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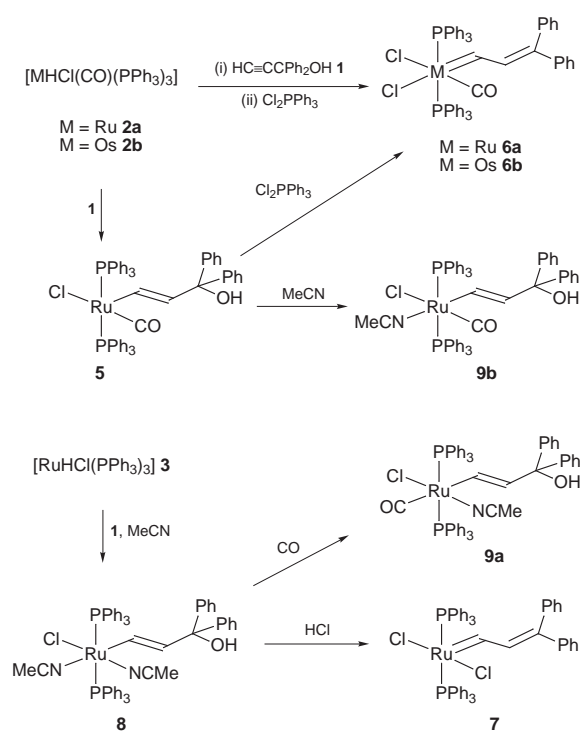
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The reactions of $[\text{RuHX}(\text{PPh}_3)_3]$ ($\text{X} = \text{Cl}, \text{O}_2\text{CMe}$) and $[\text{MHCl}(\text{CO})(\text{PPh}_3)_3]$ ($\text{M} = \text{Ru}, \text{Os}$) with 1,1-diphenylprop-2-yn-1-ol provide convenient access to alkynyl, alkenyl, propenylidene, and acetoxyallenyl complexes of divalent ruthenium and osmium, including $[\text{RuCl}_2(\text{=CHCH}=\text{CPh}_2)(\text{PPh}_3)_2]$ and the complexes $[\text{Ru}(\text{C}\equiv\text{CCPh}_2\text{OH})(\text{O}_2\text{CMe})(\text{CA})_2(\text{PPh}_3)_2]$ ($\text{A} = \text{NCMe}_3, \text{O}$), protonation (HPF_6) of which provides $[\text{Ru}(\text{O}_2\text{CMe})(\text{=C}=\text{C}=\text{CPh}_2)(\text{CNCMe}_3)_2(\text{PPh}_3)_2]\text{PF}_6$ or the metallacycle $[\text{Ru}\{\kappa^2\text{C}, \text{O}(\text{=C}=\text{CPh}_2)\text{O}_2\text{CMe}\}(\text{CO})_2(\text{PPh}_3)_2]\text{PF}_6$, respectively.

There is currently enormous interest in the chemistry of alkylidene complexes of divalent ruthenium.¹ This is inspired primarily by Grubbs' ground-breaking discovery of highly effective and remarkably tolerant alkene metathesis catalysts of the form $[\text{RuCl}_2(\text{=CHR})(\text{PR}'_2)_2]$ ($\text{R} = \text{Ph}, \text{CH}=\text{CPh}_2$; $\text{R}' = \text{Ph}, \text{Cy}$)² which are currently enjoying increasingly wide application in a variety of synthetically useful C–C bond-forming processes.³ We have recently shown that $[\text{RuCl}_2(\text{PPh}_3)_3]$ reacts with 1,1-diphenylprop-2-yn-1-ol **1** to provide the coordinatively unsaturated allenylidene complex $[\text{RuCl}_2(\text{=C}=\text{C}=\text{CPh}_2)(\text{PPh}_3)_2]$.^{4a} This complex may be easily converted to $[\text{RuCl}_2(\text{=C}=\text{C}=\text{CPh}_2)(\text{PCy}_3)_2]$ which serves as a conveniently accessible alternative to Grubbs' catalysts for the ring-closure alkene metathesis of α,ω -dienes and dienyne.^{4b} The reactions of propargylic alcohols with metal hydride complexes however, take a different course, *viz.* hydrometallation of the alkyne to provide γ -hydroxyvinyl complexes which have been shown to be particularly prone to dehydroxylation, providing either σ -butadienyl⁵ or propenylidene^{6,7} complexes depending, respectively, on the presence or absence of protons δ to the metal. In search of alternative routes to coordinatively unsaturated alkylidenes of ruthenium and osmium, we have investigated the reactions of the complexes $[\text{MHCl}(\text{CO})(\text{PPh}_3)_3]$ ($\text{M} = \text{Ru}$ **2a**, Os **2b**), $[\text{RuHCl}(\text{PPh}_3)_3]$ **3**, and $[\text{RuH}(\text{O}_2\text{CMe})(\text{PPh}_3)_3]$ **4** with **1**. The results which include convenient routes to alkenyl, alkynyl, allenylidene, propenylidene and acetoxyallenyl complexes are reported herein.

The γ -hydroxyvinyl complex $[\text{Ru}(\text{CH}=\text{CHCPh}_2\text{OH})\text{Cl}(\text{CO})(\text{PPh}_3)_2]$ **5** forms in high yield from the reaction of **2a** with **1** (Scheme 1).[†] Treating **5** with Cl_2PPh_3 results in the high yield conversion to the propenylidene complex $[\text{RuCl}_2(\text{=CHCH}=\text{CPh}_2)(\text{CO})(\text{PPh}_3)_2]$ **6a**.^{†‡} The analogous osmium complex **6b** may be similarly obtained in 75% yield directly from **2b**, **1** and Cl_2PPh_3 . The complexes **6** may be viewed as analogues of the benzylidene complexes $[\text{MCl}_2(\text{=CHR})(\text{CO})(\text{PPh}_3)_2]$ long since described by Roper.^{1a,b,9}

The coordinatively unsaturated, carbonyl-free complex $[\text{RuCl}_2(\text{=CHCH}=\text{CPh}_2)(\text{PPh}_3)_2]$ **7** was shown by Grubbs to result from the reaction of $[\text{RuCl}_2(\text{PPh}_3)_3]$ with 3,3-diphenylcyclopropene^{2a} but required the non-trivial preparation and handling of 3,3-diphenylcyclopropene. We find that the reaction of **3** with **1** in acetonitrile followed by acid (HCl) work-up provides **7** conveniently and in high yield (83%).[†] The presumed γ -hydroxyvinyl intermediate **8** in this sequence (Scheme 1) has not been fully characterised due to its sensitivity, however carbonylation (1 atmosphere) provides the air stable adduct $[\text{Ru}(\text{CH}=\text{CHCPh}_2\text{OH})\text{Cl}(\text{CO})(\text{NCMe})(\text{PPh}_3)_2]$ **9a**, which is an

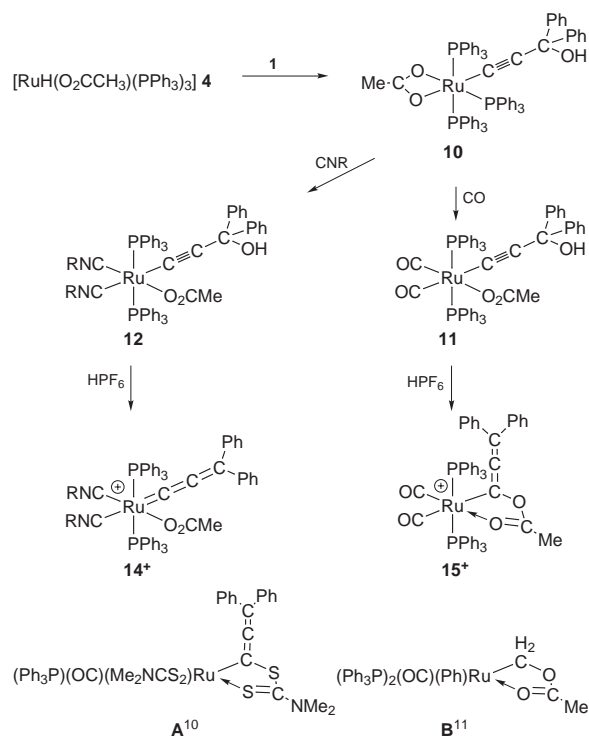


Scheme 1

isomer (CO *trans* to vinyl) of **9b** (MeCN *trans* to vinyl) obtained from **5** and acetonitrile.

The acetate complex **4** reacts with **1** via a quite different sequence, to ultimately provide the alkynyl complex *mer*- $[\text{Ru}(\text{C}\equiv\text{CCPh}_2\text{OH})(\text{O}_2\text{CMe})(\text{PPh}_3)_3]$ **10** (Scheme 2).[†] The mechanism presumably involves alkyne hydrometallation, as above, followed by oxidative addition of a second alkane C–H bond to provide $[\text{RuH}(\text{C}\equiv\text{CCPh}_2\text{OH})(\text{CH}=\text{CHCPh}_2\text{OH})(\text{O}_2\text{CMe})(\text{PPh}_3)_2]$ which undergoes reductive elimination of alkene and re-coordination of phosphine to provide **10**. The facility of the proposed sequence is consistent with the increase in basicity of the acetate ligand in **4** relative to the chloride in **3**, favouring the involvement of tetravalent ruthenium intermediates. The formulation of **10** rests firmly on spectroscopic and FAB-MS data with the *mer* stereochemistry at ruthenium following unequivocally from ^{13}C - $\{^1\text{H}\}$ and ^{31}P - $\{^1\text{H}\}$ NMR data.[†]

Both the acetate chelation and the phosphine coordination in **10** are labile. Thus treating **10** with carbon monoxide (1 atmosphere, 25 °C) results in clean conversion to $[\text{Ru}(\text{C}\equiv\text{CCPh}_2\text{OH})(\text{O}_2\text{CMe})(\text{CO})_2(\text{PPh}_3)_2]$ **11**. Similarly, addition of two equivalents of 1,1-dimethylethyl isocyanide leads to formation of $[\text{Ru}(\text{C}\equiv\text{CCPh}_2\text{OH})(\text{O}_2\text{CMe})(\text{CNCMe}_3)_2(\text{PPh}_3)_2]$ **12**, whilst excess isocyanide provides the cationic complex *mer*- $[\text{Ru}(\text{C}\equiv\text{CCPh}_2\text{OH})(\text{CNCMe}_3)_3(\text{PPh}_3)_2]^+$ **13**⁺, readily isolated as the tetrafluoroborate salt $[\mathbf{13}]\text{BF}_4$. By analogy with the dehydroxylation of γ -hydroxyvinyl ligands, the γ -hydroxyalkynyl ligands in **11** and **12** are also prone to dehydroxylation although the final products differ depending on the nature (π -acidity) of the co-



ligands. Thus the reaction of **12** with HPF₆ provides an allenylidene complex *viz.* [Ru(O₂CMe)(=C=C=CPh₂)(CNCMe₃)₂-(PPh₃)₂](PF₆) (**14**PF₆). Amongst the spectroscopic data for **14**⁺, the intense infrared absorption at 1970 cm⁻¹ is characteristic of the allenylidene ligand.

The protonation of **11** with HPF₆ however takes a different course although an allenylidene complex akin to **14**⁺ is clearly involved. The product obtained is formulated as the metallacyclic complex [Ru{κ²C,O-C(=C=CPh₂)O₂CMe}(CO)₂(PPh₃)₂](PF₆) (**15**PF₆) on the basis of spectroscopic data.[†] We have recently observed the formation of a related metallacycle (**A**, Scheme 2) derived from the intermolecular coupling of an allenylidene ligand with dithiocarbamate,¹⁰ whilst Roper has shown that the coupling of methylene and acetate ligands provides the metallacycle **B**.¹¹ Complex **15**⁺ may therefore be usefully viewed as a hybrid of **A** and **B**. The reason for the dichotomy in products arising from the protonation of **11** and **12** may be understood by considering the π-acidity of the co-ligands CO and CNCMe₃. By far the majority of allenylidene complexes of Group 8 metals involve strong donor co-ligands coordinated *trans* to the allenylidene,¹⁶ a feature which may be expected to deactivate the allenylidene towards nucleophilic attack. Whilst the isocyanide ligands in **12** and **14**⁺ are only modest π-acids, the carbonyl ligand coordinated *trans* to the allenylidene in the carbonyl analogue of **14**⁺ may be expected to strongly activate the allenylidene towards attack by the internal acetate nucleophile.

Acknowledgements

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Notes and references

[†] Selected data for new complexes (satisfactory microanalytical and/or FAB-MS data obtained); IR (Nujol, cm⁻¹), NMR (CDCl₃, 25 °C, ppm) ¹H (270), ³¹P (109), ¹³C (68 MHz). **5**: yield 97%. IR: 3573 (OH), 1917 (CO). NMR ¹H: δ 5.40 [d, 1 H, RuCH=CH; J(HH) = 12.9 Hz], 6.94–7.45 [m, 41 H, Ph + RuCH (observed)]. ³¹P-¹H: δ 33.2. ¹³C-¹H:

δ 80.0 [CPh₂OH], 139.7 [RuCH=CH], 144.6 [RuCH=CH], 202.3 [t, CO; J(PC) = 14.3 Hz]. This complex was also crystallographically characterised.¹² **6a**: yield 95%. IR: 1955 (CO). NMR ¹H: δ 8.01 [d, 1 H, Ru=CHCH; J(HH) = 13.8], 15.93 [d, 1 H, Ru=CH; J(HH) = 13.9 Hz]. ³¹P-¹H: δ 16.7. ¹³C-¹H: δ 146.9 [Ru=CHCH], 154.2 [=CPh₂], 199.0 [t, CO; J(PC) = 13.4], 322.1 [t, Ru=CH; J(PC) = 10.7 Hz]. **6b**: yield 75%. IR 1932 (CO). NMR ¹H: δ 17.50 [dt, 1 H, Os=CHCH; J(HH) = 13.5; J(PH) = 2.0 Hz] (OsCH=CH obscured by Ph resonances). ³¹P-¹H: δ -8.0. ¹³C-¹H: δ 151.2 [Os=CHCH], 152.4 [=CPh₂], 177.6 [t, CO; J(PC) = 9.7 Hz], 278.1 [m, Os=CH]. **7**: yield 83%. NMR ¹H: δ 8.20 [d, 1 H, Ru=CHCH; J(HH) = 9.9], 17.74 [dt, 1 H, Ru=CH; J(HH) = 9.9; J(PH) = 9.6 Hz]. ³¹P-¹H: δ 28.9. These data correspond to those previously reported.^{2a} **9a**: yield 75%. IR: 3564 (OH), 2283 (CN), 1949 (CO). NMR ¹H: δ 0.82 [s, 3 H, CH₃], 5.32 [d, 1 H, RuCH=CH; J(HH) = 17.8], 7.59 [d, 1 H, RuCH; J(HH) = 18.5 Hz]. ³¹P-¹H: δ 29.3. ¹³C-¹H: δ 2.6 [CH₃], 80.2 [CPh₂OH], 119.6 [NC], 136.4 [t, RuCH=CH; J(PC) = 4.3], 153.2 [t, RuCH; J(PC) = 15.1], 198.9 [t, CO; J(PC) = 10.3 Hz]. **9b**: yield 86%. IR: 3564 (OH), 1944 (CO). NMR ¹H: δ 1.60 [s, 3 H, CH₃], 5.48 [dt, 1 H, RuCH=CH; J(HH) = 15.9; J(PH) = 2.0], 7.40 [d, 1 H, RuCH; J(HH) = 15.9 Hz]. ³¹P-¹H: δ 27.3. **10**: yield 71%. IR: 3558 (OH), 2057(C≡C), 1531 (CO₂). NMR ¹H: δ 0.92 [s, 3 H, CH₃]. ³¹P-¹H: δ 35.5 [d, 2 P^A, J(P_AP_B) = 26.8], 50.9 [t, 1 P^B, J(P_AP_B) = 26.8 Hz]. ¹³C-¹H: δ 24.3 [O₂CCH₃], 76.7 [CPh₂OH], 110.5 [dt, RuC≡C; J(P_{ax}C) ≈ J(P_{eq}C) = 17.3], 118.3 [RuC≡C], 185.1 [CO₂]. **11**: yield 88%. IR: 3579, 3561 (OH), 2121(C≡C), 2051, 1978 (CO). NMR ¹H: δ 1.20 [s, 3 H, CH₃]. ³¹P-¹H: δ 31.4. ¹³C-¹H: δ 22.8 [CH₃], 75.0 [CPh₂OH], 106.8 [t, RuC≡C; J(PC) = 20.0], 116.2 [t, RuC≡C; J(PC) = 2.4], 176.2 [CO₂], 194.3 [t, CO; J(PC) = 9.2], 198.5 [t, CO; J(PC) = 11.9 Hz]. **12**: yield 87%. IR: 3567 (OH), 2150 (CN), 2105 (CN), 2073 (C≡C), 1606 (CO₂). NMR ¹H: δ 0.81, 0.89 [s × 2, 9 H × 2, CNC(CH₃)₃], 1.25 [s, 3 H, O₂CCH₃]. ³¹P-¹H: δ 38.3. ¹³C-¹H: δ 24.5 [O₂CCH₃], 29.8, 30.6 [CNC(CH₃)₃], 55.6, 56.1 [CNC(CH₃)₃], 75.1 [CPh₂OH], 115.2 [RuC≡C], 176.3 [CO₂]. **[13]PF₆**: yield 65%. IR: 3563 (OH), 2194 (CN), 2150 (CN), 2111 (C=C). NMR ¹H: δ 0.81 [s, 9 H, C(CH₃)₃], 0.93 [s, 18 H, C(CH₃)₃]. ³¹P-¹H: δ 34.8. **[14]PF₆**: yield 79%. IR: 2184 (CN), 2148 (CN), 1970 (C=C=C), 1587 (CO₂). NMR ¹H: δ 0.96 [s, 9 H, C(CH₃)₃], 1.08 [s, 9 H, C(CH₃)₃], 1.11 [s, 3 H, O₂CCH₃]. ³¹P-¹H: δ 34.3. **[15]PF₆**: yield 88%. IR: 2071 (CO), 2003 (CO), 1598 (C=C=C). NMR ¹H: 1.32 [s, 3 H, O₂CCH₃]. ³¹P-¹H: δ 22.4. ¹³C-¹H: δ 18.4 [O₂CCH₃], 118.6 [=CPh₂], 147.4 [t, RuC(OCO), J(PC) = 15.1], 183.6 [O₂CCH₃], 192.0 [t, CO; J(PC) = 9.7], 198.7 [t, CO; J(PC) = 11.3], 201.8 [t, RuC=C, J(PC) = 4.9 Hz].

‡ Whilst Cl₂PPh₃ was found to be the most convenient dehydroxylating agent,⁸ similar yields were obtained using anhydrous HCl, OSeCl₂ or PhSeCl and the complexes [Ru(CH=CHCR₂OH)Cl(CO)(PPh₃)₂] (CR₂ = *cyclo*-C₆H₁₀, CMe₂, C₁₃H₈), obtained from **2a** and the appropriate propargylic alcohol.

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