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## Control of intramolecular acetate–allenylidene coupling by spectator co-ligand $\pi$ -acidity

## Karsten J. Harlow, Anthony F. Hill\* and Thomas Welton\*

Department of Chemistry, Imperial College of Science Technology and Medicine, South Kensington, London, UK SW7 2AY. E-mail: a.hill@ic.ac.uk

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The reactions of  $[RuHX(PPh_3)_3]$  (X = Cl, O<sub>2</sub>CMe) and [MHCl(CO)(PPh\_3)\_3] (M = Ru, 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  $[RuCl_2(=CHCH=CPh_2)(PPh_3)_2]$  and the complexes  $[Ru(C=CCPh_2OH)-(O_2CMe)(CA)_2(PPh_3)_2]$  (A = NCMe\_3, O), protonation (HPF<sub>6</sub>) of which provides  $[Ru(O_2CMe)(=C=C=CPh_2)-(CNCMe_3)_2(PPh_3)_2]PF_6$  or the metallacycle  $[Ru\{\kappa^2 C, O-C(=C=CPh_2)O_2CMe\}(CO)_2(PPh_3)_2]PF_6$ , respectively.

There is currently enormous interest in the chemistry of alkylidene complexes of divalent ruthenium.<sup>1</sup> This is inspired primarily by Grubbs' ground-breaking discovery of highly effective and remarkably tolerant alkene metathesis catalysts of the form  $[RuCl_2(=CHR)(PR'_3)_2]$  (R = Ph, CH=CPh<sub>2</sub>; R' = Ph, Cy)<sup>2</sup> which are currently enjoying increasingly wide application in a variety of synthetically useful C-C bond-forming processes.<sup>3</sup> We have recently shown that [RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>] reacts with 1,1-diphenylprop-2-yn-1-ol 1 to provide the coordinatively unsaturated allenylidene complex [RuCl<sub>2</sub>(=C=C=CPh<sub>2</sub>)(P-Ph<sub>3</sub>)<sub>2</sub>].<sup>4a</sup> This complex may be easily converted to [RuCl<sub>2</sub>-(=C=C=CPh<sub>2</sub>)(PCy<sub>3</sub>)<sub>2</sub>] which serves as a conveniently accessible alternative to Grubbs' catalysts for the ring-closure alkene metathesis of  $\alpha, \omega$ -dienes and dienynes.<sup>4b</sup> The reactions of propargylic alcohols with metal hydride complexes however, take a different course, viz. hydrometallation of the alkyne to provide  $\gamma$ -hydroxyvinyl complexes which have been shown to be particularly prone to dehydroxylation, providing either  $\sigma$ -butadienyl<sup>5</sup> or propenylidene<sup>6,7</sup> complexes depending, respectively, on the presence or absence of protons  $\delta$  to the metal. In search of alternative routes to coordinatively unsaturated alkylidenes of ruthenium and osmium, we have investigated the reactions of the complexes [MHCl(CO)(PPh<sub>3</sub>)<sub>3</sub>] (M = Ru 2a, Os 2b), [RuHCl(PPh<sub>3</sub>)<sub>3</sub>] 3, and [RuH(O<sub>2</sub>CMe)(PPh<sub>3</sub>)<sub>3</sub>] 4 with 1. The results which include convenient routes to alkenyl, alkynyl, allenylidene, propenylidene and acetoxyallenyl complexes are reported herein.

The  $\gamma$ -hydroxyvinyl complex [Ru(CH=CHCPh<sub>2</sub>OH)Cl(CO)-(PPh<sub>3</sub>)<sub>2</sub>] **5** forms in high yield from the reaction of **2a** with **1** (Scheme 1).† Treating **5** with Cl<sub>2</sub>PPh<sub>3</sub> results in the high yield conversion to the propenylidene complex [RuCl<sub>2</sub>(=CHCH=CPh<sub>2</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub>] **6a**.†‡ The analogous osmium complex **6b** † may be similarly obtained in 75% yield directly from **2b**, **1** and Cl<sub>2</sub>PPh<sub>3</sub>. The complexes **6** may be viewed as analogues of the benzylidene complexes [MCl<sub>2</sub>(=CHR)(CO)(PPh<sub>3</sub>)<sub>2</sub>] long since described by Roper.<sup>1*a*,*b*,9</sup>

The coordinatively unsaturated, carbonyl-free complex [RuCl<sub>2</sub>(=CHCH=CPh<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>] **7** was shown by Grubbs to result from the reaction of [RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>] with 3,3-diphenyl-cyclopropene<sup>2*a*</sup> 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  $\gamma$ -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 [Ru(CH=CHCPh<sub>2</sub>OH)Cl(CO)(NCMe)(PPh<sub>3</sub>)<sub>2</sub>] **9a**, which is an



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-[Ru(C=CCPh<sub>2</sub>OH)(O<sub>2</sub>CMe)(PPh<sub>3</sub>)<sub>3</sub>] 10 (Scheme 2).† The mechanism presumably involves alkyne hydrometallation, as above, followed by oxidative addition of a second alkyne C–H bond to provide [RuH(C=CCPh<sub>2</sub>OH)(CH=CHCPh<sub>2</sub>OH)-(O<sub>2</sub>CMe)(PPh<sub>3</sub>)<sub>2</sub>] 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 <sup>13</sup>C-{<sup>1</sup>H} and <sup>31</sup>P-{<sup>1</sup>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  $[Ru(C=CCPh_2-OH)(O_2CMe)(CO)_2(PPh_3)_2]$  **11**. Similarly, addition of two equivalents of 1,1-dimethylethyl isocyanide leads to formation of  $[Ru(C=CCPh_2OH)(O_2CMe)(CNCMe_3)_2(PPh_3)_2]$  **12**, whilst excess isocyanide provides the cationic complex *mer*-[Ru(C= CCPh\_2OH)(CNCMe\_3)\_3(PPh\_3)\_2]<sup>+</sup> **13**<sup>+</sup>, readily isolated as the tetrafluoborate salt [**13**]BF<sub>4</sub>. By analogy with the dehydroxylation of  $\gamma$ -hydroxyvinyl ligands, the  $\gamma$ -hydroxyalkynyl ligands in **11** and **12** are also prone to dehydroxylation although the final products differ depending on the nature ( $\pi$ -acidity) of the co-



ligands. Thus the reaction of **12** with HPF<sub>6</sub> provides an allenylidene complex *viz*. [Ru(O<sub>2</sub>CMe)(=C=C=CPh<sub>2</sub>)(CNCMe<sub>3</sub>)<sub>2</sub>-(PPh<sub>3</sub>)<sub>2</sub>]PF<sub>6</sub> ([**14**]PF<sub>6</sub>). Amongst the spectroscopic data for **14**<sup>+</sup>, the intense infrared absorption at 1970 cm<sup>-1</sup> is characteristic of the allenylidene ligand.

The protonation of 11 with  $HPF_6$  however takes a different course although an allenylidene complex akin to 14<sup>+</sup> is clearly involved. The product obtained is formulated as the metallacyclic complex  $[Ru{\kappa^2 C, O-C(=C=CPh_2)O_2CMe}(CO)_2(PPh_3)_2]$ - $PF_6$  [15]  $PF_6$ ) on the basis of spectroscopic data.<sup>†</sup> 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.<sup>11</sup> Complex 15<sup>+</sup> 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  $\pi$ -acidity of the coligands CO and CNCMe<sub>3</sub>. By far the majority of allenylidene complexes of Group 8 metals involve strong donor co-ligands coordinated *trans* to the allenylidene,  $1^{c}$  a feature which may be expected to deactivate the allenylidene towards nucleophilic attack. Whilst the isocyanide ligands in 12 and  $14^+$  are only modest  $\pi$ -acids, the carbonyl ligand coordinated *trans* to the allenylidene in the carbonyl analogue of 14<sup>+</sup> may be expected to strongly activate the allenylidene towards attack by the internal acetate nucleophile.

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## Notes and references

† Selected data for new complexes (satisfactory microanalytical and/or FAB-MS data obtained); IR (Nujol, cm<sup>-1</sup>), NMR (CDCl<sub>3</sub>, 25 °C, ppm) <sup>1</sup>H (270), <sup>31</sup>P (109), <sup>13</sup>C (68 MHz). **5**: yield 97%. IR: 3573 (OH), 1917 (CO). NMR <sup>1</sup>H:  $\delta$  5.40 [d, 1 H, RuCH=*CH*; *J*(HH) = 12.9 Hz], 6.94–7.45 [m, 41 H, Ph + RuCH (obscured)]. <sup>31</sup>P-{<sup>1</sup>H}:  $\delta$  33.2. <sup>13</sup>C{<sup>1</sup>H}:

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δ 80.0 [CPh<sub>2</sub>OH], 139.7 [RuCH=CH], 144.6 [RuCH=CH], 202.3 [t, CO; J(PC) = 14.3 Hz]. This complex was also crystallographically characterised.<sup>12</sup> 6a: yield 95%. IR: 1955 (CO). NMR <sup>1</sup>H:  $\delta$  8.01 [d, 1 H, Ru= CHC*H*; J(HH) = 13.8], 15.93 [d, 1 H, Ru=CH; J(HH) = 13.9 Hz]. <sup>31</sup>P-{<sup>1</sup>H}:  $\delta$  16.7. <sup>13</sup>C-{<sup>1</sup>H}:  $\delta$  146.9 [Ru=CHCH], 154.2 [=CPh<sub>2</sub>], 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 <sup>1</sup>H:  $\delta$  17.50 [dt, 1 H, Os=CHCH; J(HH) = 13.5; J(PH) = 2.0 Hz] (OsCH=CH obscured by Ph resonances). <sup>31</sup>P-{<sup>1</sup>H}:  $\delta = 8.0.$  <sup>13</sup>C-{<sup>1</sup>H}:  $\delta$  151.2 [Os=CHCH], 152.4 [=CPh<sub>2</sub>], 177.6 [t, CO; J(PC) = 9.7 Hz], 278.1 [m, Os=CH]. 7: yield 83%. NMR <sup>1</sup>H:  $\delta$  8.20 [d, 1 H, Ru=CHC*H*; J(HH) = 9.9], 17.74 [dt, 1 H, Ru=CH; J(HH) = 9.9; J(PH) = 9.6 Hz]. <sup>31</sup>P-{<sup>1</sup>H}:  $\delta$  28.9. These data correspond to those previously reported.<sup>2a</sup> 9a: yield 75%. IR: 3564 (OH), 2283 (CN), 1949 (CO). NMR <sup>1</sup>H:  $\delta$  0.82 [s, 3 H, CH<sub>3</sub>], 5.32 [d, 1 H, RuCH=CH; J(HH) = 17.8], 7.59 [d, 1 H, RuCH; J(HH) = 18.5 Hz]. <sup>31</sup>P-{<sup>1</sup>H}:  $\delta$  29.3. <sup>13</sup>C-{<sup>1</sup>H}: δ 2.6 [CH<sub>3</sub>], 80.2 [CPh<sub>2</sub>OH], 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) = 10.3Hz]. **9b**: yield 86%. IR: 3564 (OH), 1944 (CO). NMR <sup>1</sup>H:  $\delta$  1.60 [s, 3 H, CH<sub>3</sub>], 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]. <sup>31</sup>P-{<sup>1</sup>H}:  $\delta$  27.3. **10**: yield 71%. IR: 3558 (OH), 2057(C=C), 1531 (CO<sub>2</sub>). NMR <sup>1</sup>H:  $\delta$  0.92 [s, 3H, CH<sub>3</sub>]. <sup>31</sup>P-{<sup>1</sup>H}:  $\delta 35.5 [d, 2P^A, J(P_AP_B) = 26.8], 50.9 [t, 1 P^B, J(P_AP_B) = 26.8 Hz].^{13}C-{}^{11}H: \delta 24.3 [O_2CCH_3], 76.7 [CPh_2OH], 110.5 [dt, RuC=C; J(P_a,C) \approx J(P_{eq}C) = 17.3], 118.3 [RuC=C], 185.1 [CO_2]. 11: yield 88%. IR:$  $^{3579}$ ,  $^{3561}$  (OH),  $^{2121}$  (C=C),  $^{2051}$ ,  $^{1978}$  (CO). NMR  $^{1}$ H:  $\delta$  1.20 [s, 3 H,  $^{CH_3}$ ].  $^{31}$ P-{ $^{1}$ H}:  $\delta$  31.4.  $^{13}$ C-{ $^{1}$ H}:  $\delta$  22.8 [CH<sub>3</sub>], 75.0 [CPh<sub>2</sub>OH], 106.8 [t, 100.6 ] Ru $C \equiv C$ ; J(PC) = 20.0], 116.2 [t, Ru $C \equiv C$ ; J(PC) = 2.4], 176.2 [CO<sub>2</sub>], 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 (CO<sub>2</sub>). NMR <sup>1</sup>H:  $\delta$  0.81, 0.89 [s × 2, 9 H × 2, CNC(CH<sub>3</sub>)<sub>3</sub>], 1.25 [s, 3 H, O<sub>2</sub>CCH<sub>3</sub>], <sup>31</sup>P-{<sup>1</sup>H}:  $\delta$  38.3. <sup>13</sup>C-{<sup>1</sup>H}:  $\delta$  24.5 [O<sub>2</sub>CCH<sub>3</sub>], 29.8, 30.6  $[CNC(CH_3)_3]$ , 55.6, 56.1  $[CNC(CH_3)_3]$ , 75.1  $[CPh_2OH]$ , 115.2  $[RuC \equiv C]$ , 176.3 [CO<sub>2</sub>]. [**13**]BF<sub>4</sub>: yield 65%. IR: 3563 (OH), 2194 (CN), 2150 (CN), 2111 (C=C). NMR <sup>1</sup>H:  $\delta$  0.81 [s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>], 0.93 [s, 18 H, C(CH<sub>3</sub>)<sub>3</sub>]. <sup>31</sup>P-{<sup>1</sup>H}: δ 34.8. [14]PF<sub>6</sub>: yield 79%. IR: 2184 (CN), 2148 (CN), 1970 (C=C=C), 1587  $(CO_2)$ . NMR <sup>1</sup>H:  $\delta$  0.96 [s, 9 H,  $C(CH_3)_3$ ], 1.08 [s, 9 H,  $C(CH_3)_{3]}$ , 1.11 [s, 3 H, O<sub>2</sub>CCH<sub>3</sub>]. <sup>31</sup>P-{<sup>1</sup>H}:  $\delta$  34.3. [15]PF<sub>6</sub>: yield 88%. IR: 2071 (CO), 2003 (CO), 1598 (C=C=C). NMR <sup>1</sup>H: 1.32 [s, 3H, O<sub>2</sub>CCH<sub>3</sub>]. <sup>31</sup>P-{<sup>1</sup>H}:  $\delta$  22.4. <sup>13</sup>C-{<sup>1</sup>H}:  $\delta$  18.4 [O<sub>2</sub>CCH<sub>3</sub>], 118C [=CPh<sub>2</sub>], 147.4 He C(CO), 2003 (CO), 1598 (C=C=C). 147.4 [t, RuC(OCO), J(PC) = 15.1], 183.6 [O<sub>2</sub>CCH<sub>3</sub>], 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].

<sup>‡</sup> Whilst Cl<sub>2</sub>PPh<sub>3</sub> was found to be the most convenient dehydroxylating agent,<sup>8</sup> similar yields were obtained using anhydrous HCl, OSCl<sub>2</sub> or PhSeCl and the complexes [Ru(CH=CHCR<sub>2</sub>OH)Cl(CO)(PPh<sub>3</sub>)<sub>2</sub>] (CR<sub>2</sub> = *cyclo*-C<sub>6</sub>H<sub>10</sub>, CMe<sub>2</sub>, C<sub>13</sub>H<sub>8</sub>), obtained from **2a** and the appropriate propargylic alcohol.

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