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

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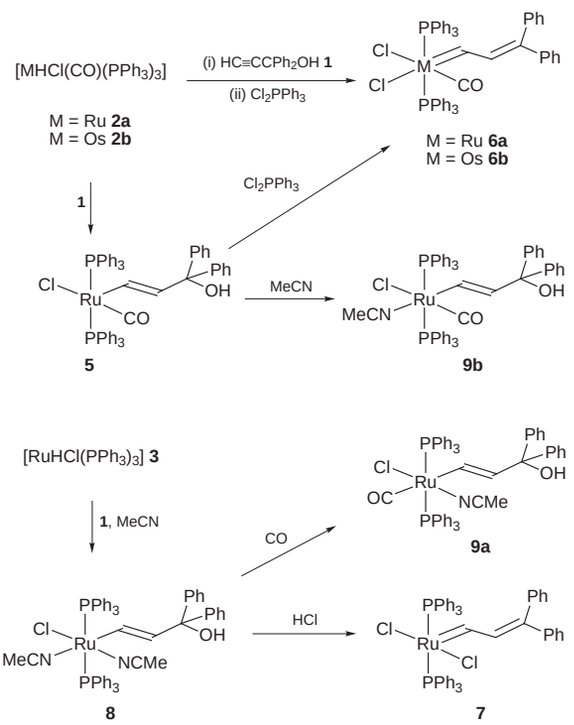
The reactions of $[RuHX(PPh_3)_3]$ (X = Cl, O_2CMe) and $[MHCl(CO)(PPh_3)_3]$ (M = Ru, Os) with 1,1-diphenylprop-2-yn-1-ol provide convenient access to alkynyl, alkenyl, propenylidene, and acetoxyallenyl complexes of divalent ruthenium and osmium, including $[RuCl_2(=CHCH=CPh_2)(PPh_3)_2]$ and the complexes $[Ru(C{\equiv}CCPh_2OH)(O_2CMe)(CA)_2(PPh_3)_2]$ (A = $NCMe_3$, O), protonation (HPF_6) of which provides $[Ru(O_2CMe)(=C=C=CPh_2)(CNCMe_3)_2(PPh_3)_2]PF_6$ or the metallacycle $[Ru\{\kappa^2C,O\text{-}C(=C=CPh_2)O_2CMe\}(CO)_2(PPh_3)_2]PF_6$, respectively.

There is currently enormous interest in the chemistry of alkylidene complexes of divalent ruthenium.[1] 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, $CH=CPh_2$; R′ = Ph, 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 $[RuCl_2(PPh_3)_3]$ reacts with 1,1-diphenylprop-2-yn-1-ol **1** to provide the coordinatively unsaturated allenylidene complex $[RuCl_2(=C=C=CPh_2)(PPh_3)_2]$.[4a] This complex may be easily converted to $[RuCl_2(=C=C=CPh_2)(PCy_3)_2]$ which serves as a conveniently accessible alternative to Grubbs' catalysts for the ring-closure alkene metathesis of α,ω-dienes and dienynes.[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-butadienyl[5] 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 $[MHCl(CO)(PPh_3)_3]$ (M = Ru **2a**, Os **2b**), $[RuHCl(PPh_3)_3]$ **3**, and $[RuH(O_2CMe)(PPh_3)_3]$ **4** with **1**. The results which include convenient routes to alkenyl, alkynyl, allenylidene, propenylidene and acetoxyallenyl complexes are reported herein.

The γ-hydroxyvinyl complex $[Ru(CH=CHCPh_2OH)Cl(CO)(PPh_3)_2]$ **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 $[RuCl_2(=CHCH=CPh_2)(CO)(PPh_3)_2]$ **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 $[MCl_2(=CHR)(CO)(PPh_3)_2]$ long since described by Roper.[1a,b,9]

The coordinatively unsaturated, carbonyl-free complex $[RuCl_2(=CHCH=CPh_2)(PPh_3)_2]$ **7** was shown by Grubbs to result from the reaction of $[RuCl_2(PPh_3)_3]$ 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 $[Ru(CH=CHCPh_2OH)Cl(CO)(NCMe)(PPh_3)_2]$ **9a**, which is an

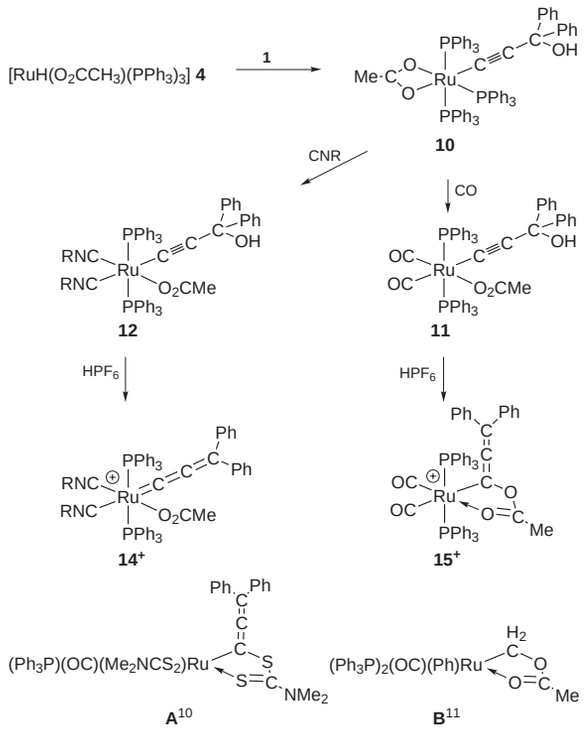


Scheme 1

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*-$[Ru(C{\equiv}CCPh_2OH)(O_2CMe)(PPh_3)_3]$ **10** (Scheme 2).† The mechanism presumably involves alkyne hydrometallation, as above, followed by oxidative addition of a second alkyne C–H bond to provide $[RuH(C{\equiv}CCPh_2OH)(CH=CHCPh_2OH)(O_2CMe)(PPh_3)_2]$ 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 $^{13}C\text{-}\{^1H\}$ and $^{31}P\text{-}\{^1H\}$ 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 $[Ru(C{\equiv}CCPh_2OH)(O_2CMe)(CO)_2(PPh_3)_2]$ **11**. Similarly, addition of two equivalents of 1,1-dimethylethyl isocyanide leads to formation of $[Ru(C{\equiv}CCPh_2OH)(O_2CMe)(CNCMe_3)_2(PPh_3)_2]$ **12**, whilst excess isocyanide provides the cationic complex *mer*-$[Ru(C{\equiv}CCPh_2OH)(CNCMe_3)_3(PPh_3)_2]^+$ **13**$^+$, readily isolated as the tetrafluoborate salt **[13]**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-



Scheme 2 R = CMe_3.

ligands. Thus the reaction of **12** with HPF_6 provides an allenylidene complex *viz.* $[Ru(O_2CMe)(=C=C=CPh_2)(CNCMe_3)_2(PPh_3)_2]PF_6$ ([**14**]PF_6). Amongst the spectroscopic data for $\mathbf{14}^+$, the intense infrared absorption at 1970 cm^{-1} is characteristic of the allenylidene ligand.

The protonation of **11** with HPF_6 however takes a different course although an allenylidene complex akin to $\mathbf{14}^+$ is clearly involved. The product obtained is formulated as the metallacyclic complex $[Ru\{\kappa^2C,O\text{-}C(=C=CPh_2)O_2CMe\}(CO)_2(PPh_3)_2]PF_6$ ([**15**]PF_6) 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 $\mathbf{15}^+$ 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 $CNCMe_3$. By far the majority of allenylidene complexes of Group 8 metals involve strong donor co-ligands coordinated *trans* to the allenylidene,[1c] a feature which may be expected to deactivate the allenylidene towards nucleophilic attack. Whilst the isocyanide ligands in **12** and $\mathbf{14}^+$ are only modest π-acids, the carbonyl ligand coordinated *trans* to the allenylidene in the carbonyl analogue of $\mathbf{14}^+$ 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^{-1}), NMR ($CDCl_3$, 25 °C, ppm) ^1H (270), ^{31}P (109), ^{13}C (68 MHz). **5**: yield 97%. IR: 3573 (OH), 1917 (CO). NMR ^1H: δ 5.40 [d, 1 H, RuCH=C*H*; *J*(HH) = 12.9 Hz], 6.94–7.45 [m, 41 H, Ph + RuCH (obscured)]. $^{31}P\text{-}\{^1H\}$: δ 33.2. $^{13}C\{^1H\}$: δ 80.0 [*C*Ph_2OH], 139.7 [RuCH=*C*H], 144.6 [Ru*C*H=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=CHC*H*; *J*(HH) = 13.8], 15.93 [d, 1 H, Ru=CH; *J*(HH) = 13.9 Hz]. $^{31}P\text{-}\{^1H\}$: δ 16.7. $^{13}C\text{-}\{^1H\}$: δ 146.9 [Ru=CH*C*H], 154.2 [=*C*Ph_2], 199.0 [t, CO; *J*(PC) = 13.4], 322.1 [t, Ru=*C*H; *J*(PC) = 10.7 Hz]. **6b:** yield 75%. IR 1932 (CO). NMR ^1H: δ 17.50 [dt, 1 H, Os=C*H*CH; *J*(HH) = 13.5; *J*(PH) = 2.0 Hz] (OsCH=C*H* obscured by Ph resonances). $^{31}P\text{-}\{^1H\}$: δ −8.0. $^{13}C\text{-}\{^1H\}$: δ 151.2 [Os=CH*C*H], 152.4 [=*C*Ph_2], 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=CHC*H*; *J*(HH) = 9.9], 17.74 [dt, 1 H, Ru=CH; *J*(HH) = 9.9; *J*(PH) = 9.6 Hz]. $^{31}P\text{-}\{^1H\}$: 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, CH_3], 5.32 [d, 1 H, RuCH=C*H*; *J*(HH) = 17.8], 7.59 [d, 1 H, RuCH; *J*(HH) = 18.5 Hz]. $^{31}P\text{-}\{^1H\}$: δ 29.3. $^{13}C\text{-}\{^1H\}$: δ 2.6 [CH_3], 80.2 [*C*Ph_2OH], 119.6 [NC], 136.4 [t, RuCH=*C*H; *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, CH_3], 5.48 [dt, 1 H, RuCH=C*H*; *J*(HH) = 15.9; *J*(PH) = 2.0], 7.40 [d, 1 H, RuCH, *J*(HH) = 15.9 Hz]. $^{31}P\text{-}\{^1H\}$: δ 27.3. **10**: yield 71%. IR: 3558 (OH), 2057(C≡C), 1531 (CO_2). NMR ^1H: δ 0.92 [s, 3H, CH_3]. $^{31}P\text{-}\{^1H\}$: 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]. $^{13}C\text{-}\{^1H\}$: δ 24.3 [O_2CCH_3], 76.7 [*C*Ph_2OH], 110.5 [dt, RuC≡C; $J(P_{ax}C) \approx J(P_{eq}C)$ = 17.3], 118.3 [RuC≡*C*], 185.1 [CO_2]. **11**: yield 88%. IR: 3579, 3561 (OH), 2121(C≡C), 2051, 1978 (CO). NMR ^1H: δ 1.20 [s, 3 H, CH_3]. $^{31}P\text{-}\{^1H\}$: δ 31.4. $^{13}C\text{-}\{^1H\}$: δ 22.8 [CH_3], 75.0 [*C*Ph_2OH], 106.8 [t, RuC≡C; *J*(PC) = 20.0], 116.2 [t, RuC≡C; *J*(PC) = 2.4], 176.2 [CO_2], 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_2). NMR ^1H: δ 0.81, 0.89 [s × 2, 9 H × 2, $CNC(CH_3)_3$], 1.25 [s, 3 H, O_2CCH_3]. $^{31}P\text{-}\{^1H\}$: δ 38.3. $^{13}C\text{-}\{^1H\}$: δ 24.5 [O_2CCH_3], 29.8, 30.6 [$CNC(CH_3)_3$], 55.6, 56.1 [$CNC(CH_3)_3$], 75.1 [*C*Ph_2OH], 115.2 [RuC≡*C*], 176.3 [CO_2]. [**13**]BF_4: yield 65%. IR: 3563 (OH), 2194 (CN), 2150 (CN), 2111 (C≡C). NMR ^1H: δ 0.81 [s, 9 H, $C(CH_3)_3$], 0.93 [s, 18 H, $C(CH_3)_3$]. $^{31}P\text{-}\{^1H\}$: δ 34.8. [**14**]PF_6: yield 79%. IR: 2184 (CN), 2148 (CN), 1970 (C=C=C), 1587 (CO_2). NMR ^1H: δ 0.96 [s, 9 H, $C(CH_3)_3$], 1.08 [s, 9 H, $C(CH_3)_3$], 1.11 [s, 3 H, O_2CCH_3]. $^{31}P\text{-}\{^1H\}$: δ 34.3. [**15**]PF_6: yield 88%. IR: 2071 (CO), 2003 (CO), 1598 (C=C=C). NMR ^1H: 1.32 [s, 3H, O_2CCH_3]. $^{31}P\text{-}\{^1H\}$: δ 22.4. $^{13}C\text{-}\{^1H\}$: δ 18.4 [O_2CCH_3], 118.6 [=*C*Ph_2], 147.4 [t, Ru*C*(OCO), *J*(PC) = 15.1], 183.6 [O_2CCH_3], 192.0 [t, *C*O; *J*(PC) = 9.7], 198.7 [t, *C*O; *J*(PC) = 11.3], 201.8 [t, RuC=*C*, *J*(PC) = 4.9 Hz].

‡ Whilst Cl_2PPh_3 was found to be the most convenient dehydroxylating agent,[8] similar yields were obtained using anhydrous HCl, $OSCl_2$ or PhSeCl and the complexes $[Ru(CH=CHCR_2OH)Cl(CO)(PPh_3)_2]$ (CR_2 = *cyclo*-C_6H_{10}, CMe_2, $C_{13}H_8$), obtained from **2a** and the appropriate propargylic alcohol.

1 For reviews on the chemistry of alkylidenes of Group 8 metals see (*a*) M. A. Gallop and W. R. Roper, *Adv. Organomet. Chem.*, 1986, **25**, 121; (*b*) W. R. Roper, *J. Organomet. Chem.*, 1986, **300**, 167; (*c*) A. F. Hill, in *Comprehensive Organometallic Chemistry II*, ed. E. W. Abel, F. G. A. Stone and G. Wilkinson, Pergamon, Oxford, 1995, vol. 7.
2 (*a*) S. T. Nguyen, R. H. Grubbs and J. W. Ziller, *J. Am. Chem. Soc.*, 1993, **115**, 9858; (*b*) P. Schwab, M. B. France, J. W. Ziller and R. H. Grubbs, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2039; (*c*) E. L. Dias, S. T. Nguyen and R. H. Grubbs, *J. Am. Chem. Soc.*, 1997, **119**, 3887.
3 A. Fürtsner, *Top. Organomet. Chem.*, 1998, **1**, 37.
4 (*a*) K. J. Harlow, A. F. Hill and J. D. E. T. Wilton-Ely, *J. Chem. Soc., Dalton Trans.*, 1999, 285; (*b*) A. Fürstner, A. F. Hill, M. Liebl and J. D. E. T. Wilton-Ely, *Chem. Commun.*, 1999, 601.
5 M. C. J. Harris and A. F. Hill, *J. Organomet. Chem.*, 1992, **438**, 209.
6 (*a*) M. A. Esteruelas, F. J. Lahoz, E. Oñate, L. A. Oro and B. Zeier, *Organometallics*, 1994, **13**, 4258; (*b*) M. A. Esteruelas, F. J. Lahoz, E. Oñate, L. A. Oro and B. Zeier, B., *ibid.*, 1994, **13**, 1662.
7 K. J. Harlow, A. F. Hill, T. Welton, A. J. P. White and D. J. Williams, *Organometallics*, 1998, **17**, 1916.
8 S. Anderson, D. J. Cook and A. F. Hill, *J. Organomet. Chem.*, 1993, **463**, C3.
9 G. R. Clark, K. Marsden, W. R. Roper and L. J. Wright, *J. Am. Chem. Soc.*, 1980, **102**, 6570.
10 B. Buriez, K. J. Harlow, A. F. Hill, T. Welton, A. J. P. White, D. J. Williams and J. D. E. T. Wilton-Ely, *J. Organomet. Chem.*, 1999, **578**, 264.
11 D. S. Bohle, G. R. Clark, C. E. F. Rickard, W. R. Roper, W. E. B. Shepard and L. J. Wright, *J. Chem. Soc., Chem. Commun.*, 1987, 563; D. S. Bohle, G. R. Clark, C. E. F. Rickard, W. R. Roper and L. J. Wright, *J. Organomet. Chem.*, 1989, **358**, 411.
12 A. J. P. White and D. J. Williams, unpublished work.

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