Acid-Catalysed C–H Activation of Ethene and Linking of Alkynes at a Diruthenium Centre

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The Ru=Ru double-bonded μ-alkyne complexes $[Ru_2(\mu\text{-}CO)(\mu\text{-}RC_2R)(\eta\text{-}C_5H_5)_2]$ react slowly or not at all with ethene and alkynes even under forcing conditions, but in the presence of acid C–H activation of ethene and alkyne-linking occur rapidly at room temperature to give di-μ-vinyl complexes $[Ru_2(CO)(\mu\text{-}CR{=}CHR)(\mu\text{-}CH{=}CH_2)(\eta\text{-}C_5H_5)_2]$ and metallacyclopentadiene complexes $[Ru_2(CO)(\mu\text{-}C_4R_4)(\eta\text{-}C_5H_5)_2]$ respectively; the acid catalysis is shown to proceed *via* the formation of a Ru≡Ru triple-bonded μ-vinyl cation $[Ru_2(\mu\text{-}CO)(\mu\text{-}CR{=}CHR)(\eta\text{-}C_5H_5)_2]^+$.

Carbon–hydrogen bond activation and carbon–carbon bond formation at transition metal centres are fundamental processes which attract considerable attention. Relatively little is yet known, however, about the nature and the extent of these processes at a dinuclear metal centre, although our recent studies indicate that C–C bond formation can occur very readily.[1–4] We now report that a μ-alkyne diruthenium system can be induced to effect C–H activation of ethene at room temperature and 1 atm by acid catalysis and identify the steps involved. The acid-catalysed linking of alkynes (C–C bond formation) in the same system is also described.

The μ-alkyne complexes $[Ru_2(\mu\text{-}CO)(\mu\text{-}RC_2R)(\eta\text{-}C_5H_5)_2]$ **1**[5] contain a short Ru=Ru double bond, but this unsaturation is not reflected in high reactivity because of the kinetic stabilisation provided by the steric protection of the cyclopentadienyl ligands and alkyne substituents. Thus, **1a** reacts slowly over 6 h with ethene (1 atm) only above 110 °C to give a low (12%) yield of the di-μ-vinyl complex $[Ru_2(CO)\{\mu\text{-}C(CF_3){=}CHCF_3\}(\mu\text{-}CH{=}CH_2)(\eta\text{-}C_5H_5)_2]$ **2a**,† while **1b** does not react even at 150 °C. However, in the presence of tetrafluoroboric acid the activation energy for this ethene addition process is dramatically reduced. Thus, **1a** now affords **2a** in 65% yield *at room temperature* within 2 h, while **1b** is induced to give **2b**,† albeit only in 5% yield.

† The new complexes were characterised by elemental analyses and IR and NMR (^1H, $^{13}C\{^1H\}$ and $^{19}F\{^1H\}$) spectra. Selected data: **2a**, orange crystals, ν(CO) (hexane) at 1985s cm^{-1}; ^1H NMR ($CDCl_3$), δ 10.66 (dd, *J* 10, 7 Hz, *CH*=CH_2), 5.41 (s, C_5H_5), 4.94 (s, C_5H_5), 4.21 (dd, *J* 7, 2 Hz, CH=CH_2), 1.97 (dd, *J* 10, 2 Hz, CH=CH_2) and 1.46 (q, *J* 10 Hz, $CHCF_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ 202.4 (s, CO), 165.5 (s, *C*H=CH_2), 154.4 (q, *J* 43 Hz, *C*CF_3), 131.5 (q, *J* 274 Hz, CF_3), 128.9 (q, *J* 274 Hz, CF_3), 89.9 (s, C_5H_5), 83.6 (s, C_5H_5), 56.9 (q, *J* 37 Hz, *C*HCF_3) and 49.7 (s, CH=*C*H_2); $^{19}F\{^1H\}$ NMR ($CDCl_3$), δ −53.8 (dq, *J* 12, 10 Hz, $CHCF_3$) and −50.1 (q, *J* 12 Hz, CF_3). **4**, orange crystals, ν(CO) (CH_2Cl_2) at 1888s cm^{-1}; ^1H NMR (CD_2Cl_2), δ 5.23 (s, C_5H_5), 5.15 (s, C_5H_5), 2.95 (q, *J* 10 Hz, $CHCF_3$), 2.46 (s, MeCN) and 2.28 (s, MeCN); $^{13}C\{^1H\}$ NMR [$(CD_3)_2CO$] δ 218.0 (s, CO), 152.0 (q, *J* 37 Hz, *C*CF_3), 132.1 (s, CN), 131.9 (q, *J* 276 Hz, CF_3), 128.7 (s, CN), 128.1 (q, *J* 275 Hz, CF_3), 89.0 (s, C_5H_5), 87.9 (s, C_5H_5), 68.0 (qq, *J* 36, 3 Hz, *C*HCF_3), 4.0 (s, Me) and 3.5 (s, Me); $^{19}F\{^1H\}$ NMR (CD_2Cl_2), δ −55.2 (dq, *J* 12, 10 Hz, $CHCF_3$) and −48.7 (q, *J* 12 Hz, CF_3). **6**, yellow crystals, ν(CO) (CH_2Cl_2) at 2027s cm^{-1}; ^1H NMR [$(CD_3)_2CO$] δ 12.52 (q, *J* 8, 1 Hz, *CH*Me), 5.61 (s, C_5H_5), 5.51 (s, C_5H_5), 3.85 (q, *J* 9 Hz, $CHCF_3$), 3.28 (d, *J* 7Hz, CH*Me*) and 2.64 (s, MeCN); $^{13}C\{^1H\}$ NMR [$(CD_3)_2CO$], δ 194.9 (s, *C*HMe), 162.4 (q, *J* 37 Hz, *C*CF_3), 131.4 (s, CN), 129.8 (q, *J* 273 Hz, CF_3), 126.2 (q, *J* 276 Hz, CF_3), 93.7 (s, C_5H_5), 90.1 (s, C_5H_5), 70.1 (q, *J* 33 Hz, $CHCF_3$), 43.7 (s, CH*Me*) and 3.6 (s, *Me*CN); $^{19}F\{^1H\}$ NMR [$(CD_3)_2CO$], δ −54.5 (dq, *J* 12, 9 Hz, $CHCF_3$) and −50.9 (q, *J* 12 Hz, CF_3). **7c**, purple-red crystals, ν(CO) (hexane) at 1951s cm^{-1}; ^1H NMR ($CDCl_3$), δ 5.22 (s, C_5H_5), 5.11 (s, C_5H_5); $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ 196.2 (s, CO), 146.5 (q, *J* 44 Hz, *C*CF_3), 127.8 (q, *J* 271 Hz, CF_3), 123.2 (q, *J* 271 Hz, CF_3), 87.4 (s, C_5H_5) and 86.8 (s, C_5H_5); $^{19}F\{^1H\}$ NMR ($CDCl_3$), δ −52.8 (q, br, *J* 13 Hz, CF_3) and −47.3 (q, br, *J* 13 Hz, CF_3).

The structure of **2a**‡ has been established by X-ray diffraction and the results are summarised in Fig. 1 and in its caption. As implied by the spectroscopic evidence, the Ru–Ru single bond of **2a** is bridged by two vinyl ligands derived from the μ-$CF_3C{\equiv}CCF_3$ ligand of **1a** and ethene respectively, with both vinyls interacting with Ru(1) through σ bonds and with Ru(2) through η^2 interactions. The bond lengths indicate that the CF_3-substituted vinyl ligand binds more strongly to Ru(2) and more weakly to Ru(1) than does the unsubstituted vinyl, consistent with it being the more effective π-acceptor and poorer σ-donor.

There is strong evidence that the acid-catalysed addition of ethene to the complexes **1** follows the sequence **1** → **3** → **5** → **2**

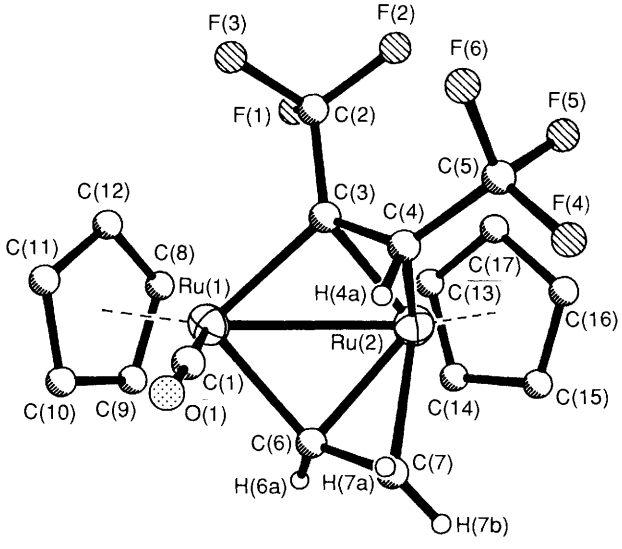
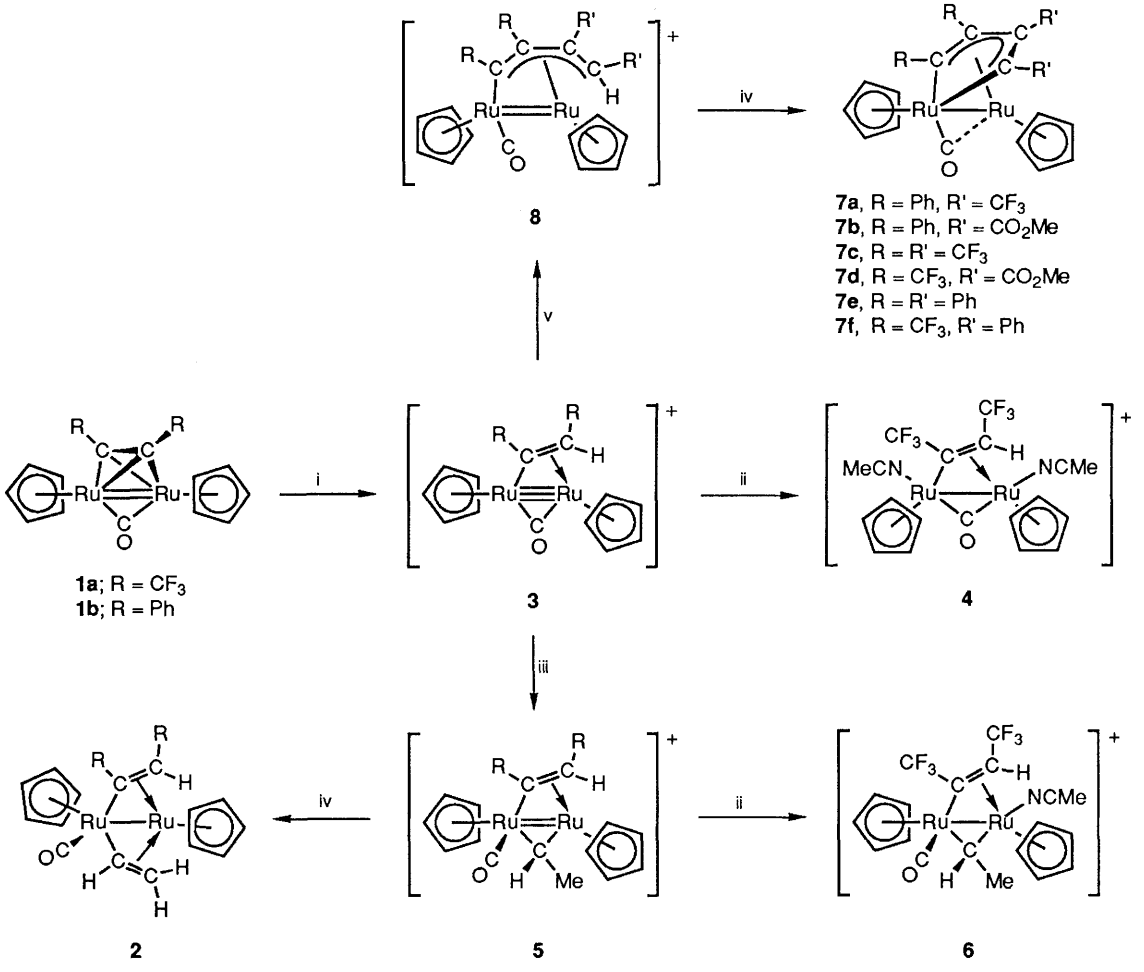


Fig. 1 Molecular geometry of **2a**; cyclopentadienyl hydrogen atoms have been omitted for clarity. Important bond lengths (Å) include: Ru(1)–Ru(2) 2.703(1), Ru(1)–C(1) 1.846(6), Ru(1)–C(3) 2.102(5), Ru(1)–C(6) 2.051(5), Ru(2)–C(3) 2.037(5), Ru(2)–C(4) 2.160(6), Ru(2)–C(6) 2.077(5), Ru(2)–C(7), 2.212(5), C(3)–C(4) 1.451(7), C(6)–C(7), 1.403(8).

‡ *Crystal data* for **2a**: $C_{16}H_{14}F_6ORu_2$, *M* = 538.0, monoclinic, space group $P2_1/n$ (no. 14), *a* = 8.404(1), *b* = 15.334(2), *c* = 13.579(2) Å, β = 99.58(1)°, *V* = 1725.4(4) $Å^3$, *Z* = 4, D_c = 2.07 g cm^{-3}, λ = 0.71073 Å, μ = 18.1 cm^{-1}, *F*(000) = 1040, *T* = 295 K.

Data were collected on a Nicolet P3m diffractometer for a unique quadrant of reciprocal space with $4<2\theta<50°$. The structure was solved by heavy-atom methods and refined by least-squares analysis to *R* 0.031 for 2342 unique, absorption-corrected, observed [$I>2\sigma(I)$] intensity data. Atomic coordinates, bond lengths and angles, and displacement parameters have been deposited with the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



Scheme 1 *Reagents and conditions*: i, H^+; ii, MeCN; iii, C_2H_4 (1 atm, 25 °C); iv, $-H^+$; v, R'C≡CR'

as laid out in Scheme 1. Thus, after mixing dichloromethane solutions of **1a** (ν_{CO} 1808 cm^{-1}) and ethene-saturated $HBF_4{\cdot}OEt_2$, rapid-scanning IR spectroscopy revealed the presence after 20 s of a new cationic species with a bridging carbonyl band at 1868 cm^{-1}, which was gradually replaced over 100 s by a second species displaying a terminal band at 2007 cm^{-1}; this in turn transformed slowly over 2 h to give **2a**. The first-formed species was trapped by acidifying an acetonitrile solution of **1a**, when the complex $[Ru_2(MeCN)_2(\mu\text{-}CO)\{\mu\text{-}C(CF_3)=CHCF_3\}(\eta\text{-}C_5H_5)_2]^+$ **4**† was obtained quantitatively, indicating that initial protonation of the μ-alkyne ligand occurs to give a highly unsaturated μ-vinyl cation $[Ru_2(\mu\text{-}CO)(\mu\text{-}CR{=}CHR)(\eta\text{-}C_5H_5)_2]^+$ **3**. The species derived from the reaction of **3a** with ethene, with the 2007 cm^{-1} band, is sufficiently long-lived that it can be detected by ^1H NMR spectroscopy at 0 °C. This reveals the presence of a μ-ethylidene group [δ 12.38 (q, *J* 7 Hz, 1H) and 3.01 (d, *J* 7 Hz, 3H)], a μ-vinyl proton [δ 3.78 (q, $^3J_{HF}$ 9 Hz, 1H)] and inequivalent cyclopentadienyl ligands [δ 5.10 (s, 5H) and 5.17 (s, 5H)], in accord with the formulation $[Ru_2(CO)(\mu\text{-}CHMe)\{\mu\text{-}C(CF_3)=CHCF_3\}(\eta\text{-}C_5H_5)_2]^+$ **5a**. Although this second unsaturated intermediate could not be isolated it was also trapped by addition of acetonitrile, as the stable complex $[Ru_2(CO)(MeCN)(\mu\text{-}CHMe)\{\mu\text{-}C(CF_3)=CHCF_3\}(\eta\text{-}C_5H_5)_2]^+$ **6**† in 70% yield. In dichloromethane slow dissociation of MeCN from **6** over 20 h resulted in its conversion to **2a** *via* **5a**.

The key to this acid-catalysed C–H activation of ethene is the protonation of a four-electron μ-alkyne ligand to give μ-vinyl complexes **3** which are (*a*) cationic and (*b*) 30-electron species with a formal Ru≡Ru triple bond. They are therefore very electrophilic and coordinate ethene readily compared with neutral 32-electron **1**. The subsequent isomerisation of coordinated ethene to ethylidene at a diruthenium centre, implicit in the generation of **5** from **3**, may be assisted by the unsaturation of the dimetal unit. The unsaturation of **5** is also crucial in allowing a hydrogen of the ethylidene methyl group to be transferred to the dimetal centre in a β-elimination process, followed by proton ejection to give the 34-electron product **2**.

The reactions of alkynes with the complexes **1** are also catalysed by acid. Thus, whereas **1a** and **b** react with alkynes $R'C_2R'$ (R' = CO_2Me or CF_3) under heptane or xylene reflux over 1–4 days to give the metallacyclopentadiene complexes $[Ru_2(CO)(\mu\text{-}C_4R_2R'_2)(\eta\text{-}C_5H_5)_2]$ **7**† in 50–90% yields, in the presence of acid the linking occurs *at room temperature* within 1–2 h to give **7** in 20–75% yields. More striking still, while **1a** and PhC≡CPh do not react even under xylene reflux, addition of a few drops of $HBF_4{\cdot}OEt_2$ to a dichloromethane solution of the reagents at room temperature results in the formation of **7e** in 75% yield after 2 h. The structure of **7c** has been established by X-ray diffraction and will be reported elsewhere with a full account of the thermal alkyne linking reactions.

We suggest that this acid-catalysed alkyne linking involves the 30-electron μ-vinyl cations **3** reacting with an alkyne to give an unsaturated μ-butadienyl cation **8**, which then deprotonates to give **7**, as depicted in Scheme 1. Recent studies in this Laboratory on the reactions of μ-vinyl ligands with alkynes have established that μ-butadienyl complex formation and subsequent deprotonation to metallacyclopentadienyl complexes of type **7** is common.[6]

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