Vinyl Homologation *via* Methyl Migration to μ-Vinyl at a Diruthenium Centre

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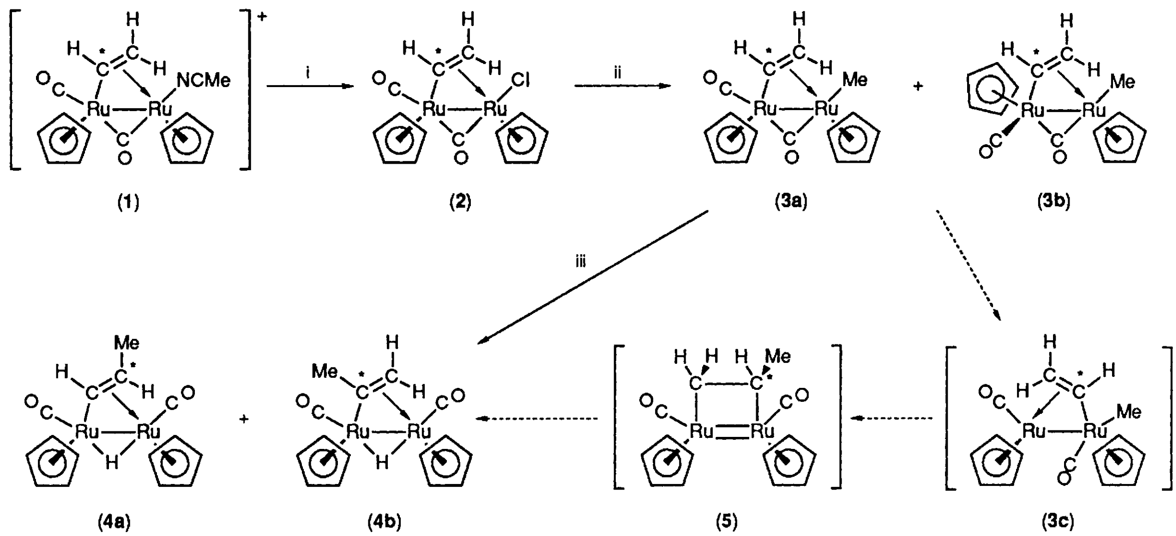
Treatment of the μ-vinyl cation $[Ru_2(CO)(MeCN)(\mu\text{-}CO)(\mu\text{-}CH{=}CH_2)(\eta\text{-}C_5H_5)_2]^+$ with Cl^- gives $[Ru_2Cl(CO)(\mu\text{-}CO)(\mu\text{-}CH{=}CH_2)(\eta\text{-}C_5H_5)_2]$, which in turn reacts with $LiCuMe_2$ at −15 °C to afford $[Ru_2Me(CO)(\mu\text{-}CO)(\mu\text{-}CH{=}CH_2)(\eta\text{-}C_5H_5)_2]$, structurally characterised by *X*-ray diffraction; the latter undergoes methyl migration to the α-carbon of the vinyl at room temperature, yielding the isomeric μ-propenyl complexes $[Ru_2(\mu\text{-}H)(CO)_2(\mu\text{-}CH{=}CHMe)(\eta\text{-}C_5H_5)_2]$ and $[Ru_2(\mu\text{-}H)(CO)_2(\mu\text{-}CMe{=}CH_2)(\eta\text{-}C_5H_5)_2]$.

Recently we described the ready combination of ethylene with a μ-vinyl group at a diruthenium centre to form μ-butadiene.[1] We now report that methyl and μ-vinyl groups also combine under mild conditions at a diruthenium centre, and that the process could model vinyl homologation as a basis for the carbon chain growth of the Fischer–Tropsch synthesis and Ziegler–Natta alkene polymerisation.

When the μ-vinyl cation $[Ru_2(CO)(MeCN)(\mu\text{-}CO)(\mu\text{-}CH{=}CH_2)(\eta\text{-}C_5H_5)_2]^+$ (**1**)[1] is treated with LiCl in dichloromethane–tetrahydrofuran solution the acetonitrile ligand is



Scheme 1. *Reagents and conditions*: i, LiCl; ii, $LiCuMe_2$, −15 °C; iii, 25 °C, 2 days or 50 °C, 2 h.

replaced rapidly by chloride, giving $[Ru_2Cl(CO)(\mu\text{-}CO)(\mu\text{-}CH{=}CH_2)(\eta\text{-}C_5H_5)_2]$ (**2**)† in 55% yield. Subsequent reaction of (**2**) with $LiCuMe_2$ in dichloromethane at −15 °C, followed by chromatography on alumina at −30 °C, provides the corresponding methyl derivative $[Ru_2Me(CO)(\mu\text{-}CO)(\mu\text{-}CH{=}CH_2)(\eta\text{-}C_5H_5)_2]$ (**3**)† in 50% yield. The ^1H and ^{13}C NMR spectra of (**3**) reveal the presence of *cis*-(**3a**) and *trans*-(**3b**) isomers in solution, in *ca.* 4 : 1 ratio at room temperature. A crystal selected for *X*-ray diffraction study proved to be of (**3a**);‡ the molecular structure is displayed in Figure 1, showing the *cis* disposition of cyclopentadienyl groups, with the β-carbon of the vinyl *anti* to these and bonded to the same ruthenium as the methyl ligand.

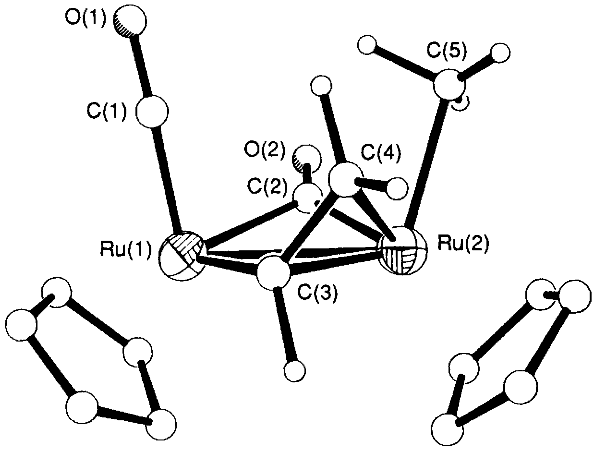


Figure 1. Molecular geometry of (**3a**). Cyclopentadienyl hydrogen atoms have been omitted for clarity. Important molecular geometry parameters include: bond lengths, Ru(1)–Ru(2) 2.735(1), Ru(1)–C(1) 1.847(11), Ru(1)–C(2) 2.110(8), Ru(2)–C(2) 1.957(10), Ru(1)–C(3) 2.022(10), Ru(2)–C(3) 2.140(9), Ru(2)–C(4) 2.206(10), Ru(2)–C(5) 2.144(13), C(3)–C(4) 1.421(14) Å; torsion angle: C(1)–Ru(1)–Ru(2)–C(5) −19.7(5)°.

Although quite stable in the solid state, the mixture of (**3a**) and (**3b**) is unstable in hexane solution at room temperature, transforming slowly over 2 days (or within 2 h at 50 °C) to an approximately 1 : 1 mixture of the isomeric μ-propenyl complexes $[Ru_2(\mu\text{-}H)(CO)_2(\mu\text{-}CH{=}CHMe)(\eta\text{-}C_5H_5)_2]$ (**4a**) and $[Ru_2(\mu\text{-}H)(CO)_2(\mu\text{-}CMe{=}CH_2)(\eta\text{-}C_5H_5)_2]$ (**4b**) in 60% combined yield. Both (**4a**) and (**4b**) have been obtained previously in this laboratory, by a quite different route, and the structure of the former has been established by *X*-ray diffraction.[2]

An experiment employing complex (**1**) labelled with ^{13}C at the α-carbon of the vinyl revealed that the label evolved adjacent to the methyl group of both (**4a**) and (**4b**), as required by methyl migration exclusively to the α-carbon (see asterisks in Scheme 1). Inspection of Figure 1 reveals, however, that on the basis of C···C distances in (**3a**) [C(5)···C(4) 2.76(2), C(5)···C(3) 3.54(2) Å] methyl migration to the β-carbon might have been expected, to afford μ-CHEt and subse-

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† The new complexes were identified by elemental analyses and by mass, IR, and NMR (^1H and ^{13}C) spectroscopy. Selected data (IR in CH_2Cl_2, NMR in CD_2Cl_2, coupling constants in Hz): (**2**), red crystals, ν (CO) at 1983s and 1824m cm^{-1}; ^1H NMR (1 : 1 *cis* and *trans* isomers) δ 3.43 (d, *J* 11.8, 1H), 3.47 (d, *J* 11.8, 1H), 4.89 (s, 5H), 4.91 (s, 5H), 5.28 (s, 5H), 5.47 (s, 5H), 5.86 (d, *J* 7.7, 1H), 5.98 (d, *J* 7.3, 1H), 10.02 (dd, *J* 7.5, 12.0, 1H), and 10.80 (dd, *J* 7.5, 11.8, 1H); $^{13}C\{^1H\}$ NMR δ 68.8 ($2CH_2$), 85.2 (C_5H_5), 86.3 (C_5H_5), 91.1 (C_5H_5), 91.5 (C_5H_5), 163.7 (μ-CH), 166.9 (μ-CH), 197.9 (CO), 199.1 (CO), 230.8 (μ-CO), and 231.1 (μ-CO). (**3**), orange crystals, ν (CO) at 1953s and 1783m cm^{-1}; ^1H NMR (a) *cis*-isomer: δ 0.44 (s, 3H), 1.12 (dd, *J* 0.6, 10.7, 1H), 3.98 (dd, *J* 0.6, 7.3, 1H), 4.95 (s, 5H), and 5.34 (s, 5H), and 10.63 (dd, *J* 7.3, 10.7, 1H), (b) *trans*-isomer: δ 0.29 (s, 3H), 1.25 (dd, *J* <1, 10.5, 1H), 4.23 (dd, *J* <1, 6.9, 1H), 4.97 (s, 5H), and 5.12 (s, 5H), and 10.01 (dd, *J* 6.9, 10.5, 1H); $^{13}C\{^1H\}$ NMR (a) *cis*-isomer: δ −10.9 (Me), 55.2 (CH_2), 89.3 (C_5H_5), 89.6 (C_5H_5), 158.4 (μ-CH), 201.9 (CO), and 236.9 (μ-CO); (b) *trans*-isomer δ −13.7 (Me), 54.4 (CH_2), 90.0 (C_5H_5), 90.5 (C_5H_5), and 155.3 (μ-CH).

‡ *Crystal data* for (**3a**): $C_{15}H_{16}O_2Ru_2$, M = 430.4, monoclinic, space group $P2_1/n$ (No. 14), a = 7.139(2), b = 22.888(5), c = 9.293(2) Å, β = 108.02(2)°, U = 1443.9(6) Å^3, Z = 4, D_C = 1.98 g cm^{-3}, $\bar{\lambda}$ = 0.71069 Å, μ = 20.5 cm^{-1}, $F(000)$ = 840, 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 to R 0.053 for 2153 unique, absorption-corrected, observed $[I > 2\sigma(I)]$ intensity data. Hydrogen atoms on the vinyl and methyl carbon atoms were refined freely. Atomic co-ordinates, bond lengths and angles, and displacement parameters have been deposited with the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

quently (**4a**) or (**4b**) with the label at the vinyl carbon *not* adjacent to the methyl group. The same is true for the *trans*-isomer (**3b**). This leads us to suggest that migration may actually occur in a third, higher energy isomer (**3c**), formed *via* the well known vinyl σ/π exchange process,[3] in which the methyl is closest to the α-carbon of the vinyl. Methyl migration to this carbon, a reductive–elimination step, will generate the dimetallacyclobutene (**5**), containing an unsaturated 32-electron diruthenium centre which promotes β-hydrogen elimination to afford 34-electron (**4a**) or (**4b**), depending on the hydrogen involved.

It is well known that phenyl migrates more readily to CO than does methyl. Treatment of (**2**) with $LiCuPh_2$ reveals that the same situation holds for migration to μ-vinyl, in that the phenyl analogue of (**4a**) is formed rapidly at −15 °C with only tentative IR observation of the phenyl–vinyl intermediate.

It has recently been proposed that combination of surface vinyl and methylene groups is responsible for the carbon chain growth of the Fischer–Tropsch synthesis.[4] The results reported here suggest another pathway involving vinyl groups, based on vinyl homologation *via* successive methyl migrations and β-hydrogen eliminations. In the course of the homologation μ-CMe=CHR groups must isomerise to μ-$CH=CHCH_2R$ in order to continue linear chain growth, a process known to occur at a dinuclear metal centre.[5] Methyl migration to μ-CMe=CHR will generate branched chain hydrocarbons.

It is interesting to note that there is a strong resemblance between methyl migration to μ-vinyl at a dimetal centre and the alkyl-to-alkene migration at a mono-metal centre usually invoked for Ziegler–Natta alkene polymerisation. In fact, alkene polymerisation can also be envisaged to occur by μ-vinyl homologation through successive alkyl migrations and β-eliminations. A zirconium–aluminium μ-vinyl complex has been shown to act as a precursor of an alkene polymerisation catalyst.[6]

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