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## Reactivity of Alkenes at a Diruthenium Centre: Combination with Methylene and Oxidative Activation

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The complex  $[Ru_2(CO)(CH_2=CH_2)(\mu-CH_2)(\mu-CO)(\eta-C_5H_5)_2]$  undergoes methylene–ethylene combination on heating to give propene, and ethylene activation upon oxidation with Ag<sup>+</sup> to give the  $\mu$ -vinyl cation  $[Ru_2(CO)_2(\mu-CH=CH_2)(\mu-CH_2)(\eta-C_5H_5)_2]^+$ ; treatment of the latter with H<sup>-</sup> affords  $[Ru_2(CO)_2(\mu-CH_2)(\mu-CHCH_3)(\eta-C_5H_5)_2]$ , which evolves propene more efficiently on heating.

Surface methylene is now accepted as playing the central role in carbon chain growth during the Fischer-Tropsch synthesis, through combination with a surface alkyl,<sup>1</sup> alkene,<sup>2,3</sup> or vinyl.<sup>4</sup> There is evidence for methylene-alkene combination in organometallic complex chemistry, in that  $\mu$ -CH<sub>2</sub> di-iron,<sup>5</sup> di-cobalt,<sup>6</sup> and di-osmium<sup>7</sup> complexes react with ethylene to give propene. It was believed initially that an intermediate containing both co-ordinated ethylene and µ-CH<sub>2</sub> was involved, but more recently it has been suggested, on theoretical grounds, that incoming ethylene reacts directly with µ-CH<sub>2</sub>.8 We report here the synthesis of the first dinuclear metal complex to contain co-ordinated  $\mu$ -CH<sub>2</sub> and ethylene and that it does evolve propene on heating, providing support for the earlier mechanism. However, on oxidation the ethylene ligand in the complex is transformed to  $\mu$ -vinyl, allowing the synthesis of a  $\mu$ -methylene/ $\mu$ -ethylidene complex which evolves propene more efficiently, suggesting a process for alkene homologation on a metal surface.

Photolysis (450 W mercury lamp, silica flask) of an acetonitrile solution of the  $\mu$ -methylene complex  $[Ru_2(CO)_2(\mu-CH_2)(\mu-CO)(\eta-C_5H_5)_2]^9$  generates the aceto-

nitrile derivative  $[Ru_2(CO)(MeCN)(\mu-CH_2)(\mu-CO)(\eta-C_5H_5)_2]$  (1),<sup>†</sup> from which labile acetonitrile is readily dis-

<sup>†</sup> The new complexes were identified by elemental analyses and by mass, i.r. and n.m.r. (1H and 13C) spectroscopy. Selected data (i.r. in  $CH_2Cl_2$ , n.m.r. in CDCl<sub>3</sub>, coupling constants in Hz): (1), v(CO) at 1923s and 1748m cm<sup>-1</sup>; <sup>1</sup>H n.m.r. δ 1.99 (s, 3H, MeCN), 7.04 (s, 1H of  $\mu$ -CH<sub>2</sub>), and 9.50 (s, 1H of  $\mu$ -CH<sub>2</sub>). (2) (ca. 1:1 mixture of cis- and trans-isomers), v(CO) at 1942s and 1765m cm<sup>-1</sup>; <sup>1</sup>H n.m.r. δ 1.64 (AB q, 4H, C<sub>2</sub>H<sub>4</sub>), 1.91 (AB q, 4H, C<sub>2</sub>H<sub>4</sub>), 7.73 (s, 1H of µ-CH<sub>2</sub>), 8.78 (s, 1H of µ-CH<sub>2</sub>), 8.95 (s, 1H of µ-CH<sub>2</sub>), and 9.76 (s, 1H of µ-CH<sub>2</sub>); <sup>13</sup>C n.m.r. δ 39.7 (C<sub>2</sub>H<sub>4</sub>), 43.9 (C<sub>2</sub>H<sub>4</sub>), 122.4 (µ-CH<sub>2</sub>), and 122.6 (µ-CH<sub>2</sub>). (3), v(CO) at 1948s and 1782m cm<sup>-1</sup>;  ${}^{1}$ H n.m.r.  $\delta$  1.17 (dd, J 1 and 8, 1H, CH), 1.62 (dd, J 8 and 11, 1H, CH<sub>2</sub>), 3.36 (dd, J 1 and 11, 1H, CH<sub>2</sub>), 3.74 (s, 3H, Me), 7.64 (s, 1H of µ-CH<sub>2</sub>), and 9.65 (s, 1H of  $\mu$ -CH<sub>2</sub>). (4), v(CO) at 2033s and 1989m cm<sup>-1</sup>; <sup>1</sup>H n.m.r.  $\delta$  3.21 (dd, J1 and 12, 1H of CH<sub>2</sub>), 4.81 (dd, J 1 and 7, 1H of CH<sub>2</sub>), 8.85 (d, J 1, 1H of µ-CH<sub>2</sub>), 10.13 (d, J 1, 1H of µ-CH<sub>2</sub>), and 11.01 (dd, J 7 and 12, µ-CH); <sup>13</sup>C n.m.r. δ 52.4 (CHCH<sub>2</sub>), 138.0 (µ-CH<sub>2</sub>), and 173.6  $(\mu$ -CHCH<sub>2</sub>). (9), v(CO) at 1956s and 1917w cm<sup>-1</sup>; <sup>1</sup>H n.m.r.  $\delta$  2.76 (d, J 7, 3H, Me), 7.05 (s, 1H of μ-CH<sub>2</sub>), 8.17 (s, 1H of μ-CH<sub>2</sub>), and 9.89 (q, J 7, 1H, μ-CH); <sup>13</sup>C n.m.r. δ 41.8 (Me), 105.5 (μ-CH<sub>2</sub>), and 138.5 (µ-CHMe).



Scheme 1. Reagents: (i) AgBF<sub>4</sub> or [N(C<sub>6</sub>H<sub>4</sub>Br-p)<sub>3</sub>][PF<sub>6</sub>], (ii) NaBH<sub>4</sub>.

placed when ethylene is bubbled through the solution, to give a 45% yield of  $[Ru_2(CO)(CH_2=CH_2)(\mu-CH_2)(\mu-CO)(\eta-C_5H_5)_2]$  (2).<sup>†</sup> The yellow crystals of (2) were severely disordered and proved unsuitable for an X-ray diffraction study, but the methyl acrylate analogue  $[Ru_2(CO)(CH_2=CH-CO_2Me)(\mu-CH_2)(\mu-CO)(\eta-C_5H_5)_2]$  (3),<sup>†</sup> prepared similarly, allowed the structure of these first polynuclear methylene/ alkene complexes to be firmly established.<sup>‡</sup> The molecular structure of (3) is summarised in Figure 1 and in its caption.

Complex (2) is stable at room temperature, but on heating at 250 °C for 3 h propene (29%) is evolved in association with methane (16%), ethylene (35%), and ethane (20%). That the propene was formed by methylene–ethylene combination, and not via coupling of three methylene groups, was established by synthesising and thermolysing <sup>13</sup>C- and <sup>2</sup>H-labelled (2),  $[Ru_2(CO)(CH_2=CH_2)(\mu-1^3CH_2)(\mu-CO)(\eta-C_5H_5)_2]$  and  $[Ru_2(CO)(CH_2=CH_2)(\mu-CD_2)(\mu-CO)(\eta-C_5H_5)_2]$  respectively. The labelled propene produced was determined by mass spectrometry to be consistent only with methylene–ethylene combination; *i.e.* <sup>13</sup>C C<sub>2</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>4</sub>D<sub>2</sub> were generated. Interestingly, the  $\mu$ -CH<sub>2</sub> and methyl acrylate ligands in (3) are oriented correctly, and with the C(6) and C(31) carbons separated by only 2.8 Å, for their combination to produce linear methyl crotonate in preference to branched methyl



Figure 1. Molecular structure of (3). Important bond lengths: Ru(1)-Ru(2) 2.726(1), Ru(1)-C(5) 2.023(4), Ru(2)-C(5) 2.014(4), Ru(1)-C(6) 2.102(5), Ru(2)-C(6) 2.075(5), Ru(1)-C(31) 2.174(4), Ru(1)-C(32) 2.192(4), C(31)-C(32) 1.392(8) Å.

methacrylate. On heating at 200 °C this is exactly what happens; the homologated alkenes are formed in only low yield, but in a linear:branched ratio of  $\approx 10:1$ . This is strikingly similar to that for the hydrocarbons produced in the Fischer–Tropsch synthesis itself.

In an attempt to induce methylene-ethylene combination by destructive oxidation (2) was treated with an excess of AgBF<sub>4</sub>. No propene was evolved; instead the co-ordinated ethylene was converted to a µ-vinyl ligand, the complex  $[Ru_2(CO)_2(\mu-CH=CH_2)(\mu-CH_2)(\eta-C_5H_5)_2][BF_4]$  (4)<sup>†</sup> being isolated in 42% yield. We have previously observed an EEC mechanism for the oxidatively induced C-H bond cleavage of alkylidenes,10 alkylidynes,11 and vinylidene12 co-ordinated at ruthenium centres, i.e. two one-electron oxidation steps followed by proton loss. However, the cyclic voltammogram (C.V.) of (2) shows a single irreversible oxidation wave at  $E_{ox}$ = 0.78 V (scan rate 200 mV s<sup>-1</sup>) and controlled potential electrolysis (CPE) revealed n = 0.9 F, consistent with a one-electron oxidation followed by hydrogen radical loss.§ In accord, addition of one equivalent of the one-electron oxidant  $[N(C_6H_4-Br-p)_3][PF_6]$  to (2) afforded the hexafluorophosphate analogue of (4) quantitatively.

This unprecedented activation of ethylene at a dinuclear metal centre led us to study the oxidation of the related ethylene and propene complexes  $[Ru_2(CO)(CH_2=CHR)(\mu-CO)_2(\eta-C_5H_5)_2]$  (5; R = H); (6; R = Me).<sup>13</sup> The C.V. of (5) again shows one irreversible oxidation wave, at  $E_{ox} = 0.66$  V (scan rate 100 mV s<sup>-1</sup>), and addition of one equivalent of AgBF<sub>4</sub> to (5) gave the known  $\mu$ -vinyl complex  $[Ru_2(CO)_2(\mu-CH=CH_2)(\mu-CO)(\eta-C_5H_5)_2][BF_4]$  (7).<sup>13</sup> Similar treatment of the propene complex (6) gave  $[Ru_2(CO)_2(\mu-CH=CH_2)(\mu-CO)(\eta-C_5H_5)_2][BF_4]$  (8)<sup>13</sup> as a result of selective C-H bond cleavage. Maitlis *et al.* have recently suggested<sup>4</sup> that vinyl groups may be important metal surface species in the Fischer–Tropsch synthesis, and it is not inconceivable that these vinyls could be derived from alkenes by a process related to that described here.

Each of the  $\mu$ -vinyl cations (4), (7), and (8) is attacked by hydride to afford the corresponding  $\mu$ -alkylidene complex  $[Ru_2(CO)_2(\mu$ -CH<sub>2</sub>)( $\mu$ -CHCH<sub>3</sub>)( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] (9),<sup>†</sup>  $[Ru_2(CO)_2(\mu$ -

<sup>‡</sup> Crystal data for (3): C<sub>17</sub>H<sub>18</sub>O<sub>4</sub>Ru<sub>2</sub>, M = 488.14, monoclinic, space group P2<sub>1</sub>/n (No. 14), a = 14.273(1), b = 9.093(1), c = 14.268(1) Å, β = 111.35(1)°, U = 1724.7(3) Å<sup>3</sup>, T = 298 K, Z = 4,  $D_c = 1.88$  g cm<sup>-3</sup>, F(000) = 960, graphite-monochromated Mo- $K_{\alpha}$  X-radiation ( $\lambda = 0.71073$  Å),  $\mu$ (Mo- $K_{\alpha}$ ) = 17.34 cm<sup>-1</sup>. The structure was solved by heavy atom methods and refined by least squares to R = 0.046 for 5036 unique, observed [ $I > 2\sigma(I)$ ], absorption-corrected intensities with 2.5 < 2 $\theta$  < 60°. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

<sup>§</sup> Carried out at a Pt bead electrode in dichloromethane containing 0.1 mol dm<sup>-3</sup> [Bu<sup>n</sup><sub>4</sub>N][PF<sub>6</sub>] as supporting electrolyte; potentials are vs. the saturated calomel electrode.

CHMe)( $\mu$ -CO)( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] (10),<sup>13</sup> or [Ru<sub>2</sub>(CO)<sub>2</sub>( $\mu$ -CHEt)( $\mu$ -CO)( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] (11)<sup>13</sup> in high yield. Thus, oxidation followed by hydride attack effects an overall isomerisation of alkene to alkylidene in this diruthenium system.

Finally, we note that on heating the di- $\mu$ -alkylidene complex (9) to 250 °C propene is obtained much more efficiently than when (2) is heated at the same temperature (87 vs. 29%); *i.e.* alkylidene–alkylidene combination is more favourable than alkylidene–alkene combination. From this, and other observations reported here, we suggest that while alkylidene–alkene combination does appear to provide a viable pathway for alkene homologation at a dinuclear metal centre, homologation will occur more readily if the alkene first isomerises to an alkylidene.

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