

## Synthesis of Butadiene *via* Vinyl–Ethylene Combination at a Diruthenium Centre

Gregg C. Bruce, Selby A. R. Knox,\* and Andrew J. Phillips

*Department of Inorganic Chemistry, The University, Bristol BS8 1TS, UK*

Treatment of the  $\mu$ -vinyl cation  $[\text{Ru}_2(\text{CO})(\text{MeCN})(\mu\text{-CO})(\mu\text{-CH=CH}_2)(\eta\text{-C}_5\text{H}_5)_2]^+$  with ethylene (1 atm, 25 °C) gives two isomers of  $[\text{Ru}_2(\text{CO})_2(\mu\text{-H})(\mu\text{-CH}_2\text{=CHCH=CH}_2)(\eta\text{-C}_5\text{H}_5)_2]^+$ , containing (*S*)-*cis*- or (*S*)-*trans*-butadiene; deprotonation is effected with KOH/ethanol to afford the neutral (*S*)-*trans*-butadiene complex  $[\text{Ru}_2(\text{CO})_2(\mu\text{-CH}_2\text{=CHCH=CH}_2)(\eta\text{-C}_5\text{H}_5)_2]$ .

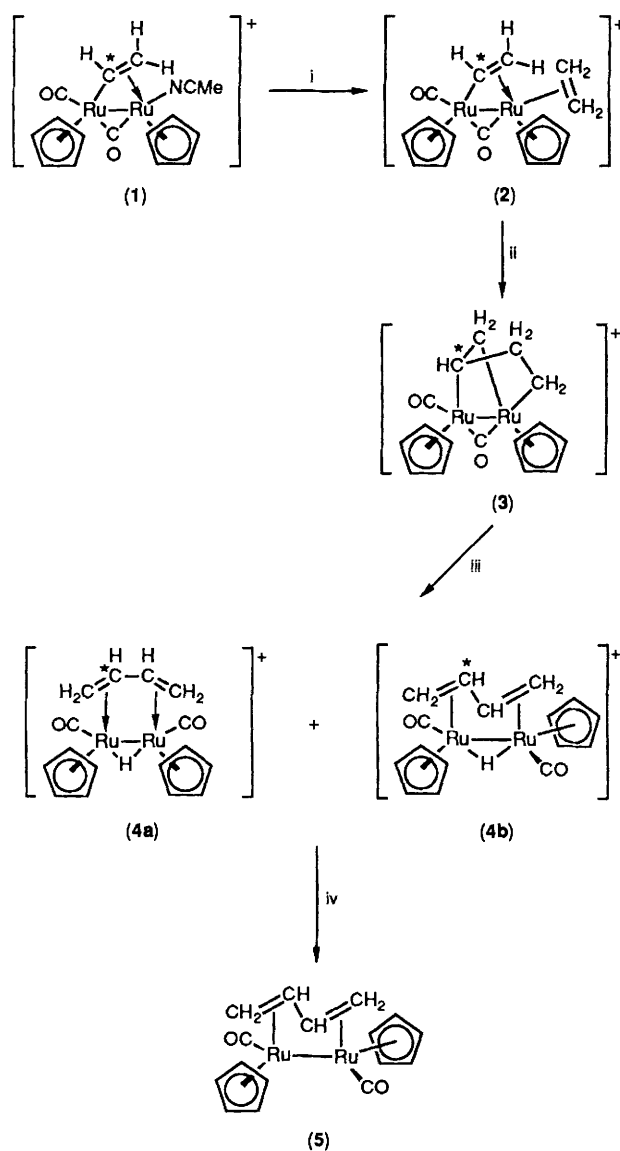
It has recently been suggested that surface vinyl groups may play a significant role in the carbon chain growth which characterises the Fischer–Tropsch Synthesis.<sup>1</sup> In an extension of our studies on the combination of hydrocarbon species at dinuclear metal centres,<sup>2,3</sup> we have investigated the reactivity

of  $\mu$ -vinyl at a diruthenium centre, discovering that it does indeed readily take part in carbon–carbon bond formation processes. We report here on the combination of  $\mu$ -vinyl with ethylene, which occurs at room temperature and atmospheric pressure to yield co-ordinated butadiene.

Addition of one equivalent of Me<sub>3</sub>NO to an acetonitrile solution of the  $\mu$ -vinyl complex [Ru<sub>2</sub>(CO)<sub>2</sub>( $\mu$ -CO)( $\mu$ -CH=CH<sub>2</sub>)( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>][BF<sub>4</sub>]<sup>+</sup> generates the acetonitrile derivative [Ru<sub>2</sub>(CO)(MeCN)( $\mu$ -CO)( $\mu$ -CH=CH<sub>2</sub>)( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>]<sup>+</sup> (**1**)<sup>†</sup> quantitatively. Bubbling ethylene through a dichloromethane solution of this species at room temperature for 3 h results in the formation of an approximately 50:50 mixture of the isomeric (*S*)-*cis*- and (*S*)-*trans*-butadiene complexes [Ru<sub>2</sub>(CO)<sub>2</sub>( $\mu$ -H)( $\mu$ -CH<sub>2</sub>=CHCH=CH<sub>2</sub>)( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>]<sup>+</sup> (**4a**, **b**),<sup>†</sup> isolated in over 90% yield. Crystals of pure (**4b**) were separated but these proved unsuitable for an X-ray diffraction study. However, the structures of the isomers were clearly indicated by their <sup>1</sup>H and <sup>13</sup>C NMR spectra, in comparison with those of known complexes with bridging (*S*)-*cis*- and (*S*)-*trans*-butadiene.<sup>5–8</sup> Moreover, deprotonation of the mixture with KOH in ethanol gave the neutral (*S*)-*trans*-butadiene complex [Ru<sub>2</sub>(CO)<sub>2</sub>( $\mu$ -CH<sub>2</sub>=CHCH=CH<sub>2</sub>)( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] (**5**) in 85% yield, previously obtained by us from the reaction of butadiene with a diruthenium precursor and structurally established by X-ray diffraction.<sup>8</sup> The deprotonation is irreversible; treatment of (**5**) with HBF<sub>4</sub> does not give (**4**).

The (*S*)-*cis*- and (*S*)-*trans*-butadiene ligands in (**4a**) and (**4b**) are associated with Ru<sub>2</sub>(CO)<sub>2</sub>( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub> units which also adopt *cis* and *trans* stereochemistry, respectively. NMR studies show that the isomers do not interconvert in solution, but the high yield of (**5**) obtained on deprotonation of the mixture reveals that isomerisation of (*S*)-*cis*-butadiene to the *S*-*trans* form must occur during this process, presumably *via* a temporary dissociation of one of the double bonds to allow the required rotation about both the central C–C bond of the hydrocarbon and the metal–metal bond.

In the light of our recent studies of the reactions of ethylene<sup>2</sup> and allene<sup>3</sup> with acetonitrile complexes the first step in the formation of (**4a**) and (**4b**) will be the displacement of labile acetonitrile from (**1**), to give the transient  $\mu$ -vinyl/ethylene complex (**2**), as shown in Scheme 1. No spectroscopic evidence was obtained for this species, indicating that carbon–carbon bond formation occurs rapidly once ethylene is co-ordinated. A labelling study employing (**1**) enriched in <sup>13</sup>C at the  $\alpha$ ( $\mu$ )-carbon of the vinyl revealed that the label progressed to an inner diene carbon of (**4a**) and (**4b**) (see asterisks in Scheme 1). Likewise, use of a  $\mu$ -CD=CH<sub>2</sub> vinyl ligand gave only  $\mu$ -CH<sub>2</sub>=CDCH=CH<sub>2</sub> products. These observations are consistent only with carbon–carbon bond formation between ethylene and the  $\alpha$ ( $\mu$ )-vinyl carbon. The process can be viewed as a reductive elimination (2Ru–C → C–C), which will create the dimetallacycle (**3**) containing a sixteen-electron ruthenium centre. The latter then promotes  $\beta$ -elimination of an originally



Scheme 1. i, C<sub>2</sub>H<sub>4</sub>, 1 atm, 25°C; ii, reductive-elimination; iii,  $\beta$ -elimination; iv, KOH, ethanol.

ethylenic hydrogen, restoring electronic saturation to the dimetal centre and generating the products (**4a**) and (**4b**) directly. There are two such  $\beta$ -hydrogens in (**3**) and butadiene arises co-ordinated in either the *S*-*cis* or *S*-*trans* mode depending on which of these hydrogens undergoes  $\beta$ -elimination. The approximately 50:50 mixture of (**4a**) and (**4b**) produced shows that there is no significant discrimination.

It is noteworthy that the  $\mu$ -vinyl precursor of (**1**) is obtained by oxidation of the ethylene complex [Ru<sub>2</sub>(CO)<sub>3</sub>(C<sub>2</sub>H<sub>4</sub>)( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>]<sup>2</sup> so that what is described here completes a sequence for the coupling of two ethylene molecules at a dinuclear metal centre.

The ease with which ethylene/vinyl combination occurs at a diruthenium centre contrasts sharply with ethylene/methylene combination, which was observed only above 200 °C.<sup>2</sup> When this is considered in association with our recent observation that  $\mu$ -methylene combines with allene at room temperature,<sup>3</sup> a picture is beginning to emerge. This is that carbon–carbon bond formation at a dinuclear metal centre, a reductive

<sup>†</sup> The new complexes were characterised by elemental analyses and by mass, IR (CH<sub>2</sub>Cl<sub>2</sub> solution), and NMR (<sup>1</sup>H and <sup>13</sup>C, *J* in Hz, CD<sub>2</sub>Cl<sub>2</sub> solution unless otherwise stated) spectra. Selected data for (**1**): orange powder,  $\nu$ (CO) 2001s and 1849m cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$  2.34 (s, 3H, MeCN), 3.27 (d, *J* 12, 1H of CH<sub>2</sub>), 5.12 (s, 5H, C<sub>5</sub>H<sub>5</sub>), 5.66 (s, 5H, C<sub>5</sub>H<sub>5</sub>), 5.79 (d, *J* 7.5, 1H of CH<sub>2</sub>), and 10.87 (dd, *J* 7.5, 12, 1H,  $\mu$ -CH); <sup>13</sup>C{<sup>1</sup>H} NMR  $\delta$  4.86 (MeCN), 66.53 (CH<sub>2</sub>), 85.71 (C<sub>5</sub>H<sub>5</sub>), 92.44 (C<sub>5</sub>H<sub>5</sub>), 128.9 (MeCN), 168.7 ( $\mu$ -CH), 197.5 (CO), and 227.6 ( $\mu$ -CO). (**4a**): yellow powder,  $\nu$ (CO) 2019 cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$  -14.74 (s, 1H,  $\mu$ -H), 1.24 (m, 2H), 3.28 (m, 2H), 4.82 (m, 2H), and 5.49 (s, 10H); <sup>13</sup>C{<sup>1</sup>H} NMR (in CD<sub>3</sub>CN)  $\delta$  30.3 (2CH<sub>2</sub>), 46.7 (2CH), 86.4 (2C<sub>5</sub>H<sub>5</sub>), and 204.6 (2CO). (**4b**): yellow powder,  $\nu$ (CO) 1996s cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$  -18.58 (s, 1H,  $\mu$ -H), 2.38 (m, 2H), 2.67 (m, 2H), 3.67 (m, 2H), 5.47 (s, 10H); <sup>13</sup>C{<sup>1</sup>H} NMR (in CD<sub>3</sub>CN)  $\delta$  31.8 (2CH<sub>2</sub>), 53.1 (2CH), 88.6 (2C<sub>5</sub>H<sub>5</sub>), 200.8 (2CO). (**5**) (for comparison):  $\nu$ (CO) (in cyclohexane) 1914 cm<sup>-1</sup>; <sup>1</sup>H NMR (in CDCl<sub>3</sub>)  $\delta$  1.69 (m, 2H), 1.73 (m, 2H), 2.63 (m, 2H), and 5.10 (s, 10H); <sup>13</sup>C{<sup>1</sup>H} NMR (in CDCl<sub>3</sub>)  $\delta$  23.2 (2CH<sub>2</sub>), 48.1 (2CH), 84.5 (2C<sub>5</sub>H<sub>5</sub>), and 206.1 (2CO).

elimination process, creates an unsaturated 32-electron centre and is only favoured when the saturated 34-electron configuration can be readily regained. Co-ordinated allene has sufficient  $\pi$ -electrons to allow this, while for vinyl/ethylene combination the  $\beta$ -elimination process is a source of two additional electrons.  $\beta$ -Elimination is also possible for the dimetallacyclopropane intermediate which will be formed upon ethylene/methylene combination, but an unusual  $\mu$ -allyl ligand would result. The pathway still appears to exist, in that propene is generated at  $>200$  °C, but it is clearly a high energy one.

The study of diene synthesis at a diruthenium centre is being extended to cover a range of alkenes and substituted vinyl ligands. Thus, the reaction of (1) with styrene gives the 1-phenylbutadiene analogues of (4a) and (4b), in an *S-cis*:*S-trans* ratio of 1:3.5. It is clear from this that (a) carbon-carbon bond formation occurs preferentially with the unsubstituted carbon of the alkene and (b) there is now discrimination between the two possible  $\beta$ -hydrogen elimination processes, presumably on steric grounds in each case.

We thank the University of Bristol for the award of an E. S. & A. Robinson Scholarship (to A. J. P.), the SERC for

support, and Johnson Matthey p.l.c. for a loan of ruthenium trichloride.

Received, 5th February 1990; Com. 0/00534G

## References

- 1 J. M. Martinez, H. Adams, N. A. Bailey, and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 1989, 286.
- 2 N. M. Doherty, J. A. K. Howard, S. A. R. Knox, N. J. Terrill, and M. I. Yates, *J. Chem. Soc., Chem. Commun.*, 1989, 638.
- 3 M. J. Fildes, S. A. R. Knox, A. G. Orpen, M. L. Turner, and M. I. Yates, *J. Chem. Soc., Chem. Commun.*, 1989, 1680.
- 4 A. F. Dyke, S. A. R. Knox, M. J. Morris, and P. J. Naish, *J. Chem. Soc., Dalton Trans.*, 1983, 1417.
- 5 M. Tachikawa, J. R. Shapley, R. C. Haltiwanger, and C. G. Pierpoint, *J. Am. Chem. Soc.*, 1976, **98**, 4651.
- 6 K. H. Franzreb and C. G. Kreiter, *Z. Naturforsch., Teil B*, 1982, **37**, 1058.
- 7 J. A. King and K. P. C. Vollhardt, *Organometallics*, 1983, **2**, 684.
- 8 G. S. Lewandos, S. A. R. Knox, and A. G. Orpen, *J. Chem. Soc., Dalton Trans.*, 1987, 2703.