

# Specific alkylidene coupling of the labile diruthenium bridging methylene complex $[(\eta\text{-C}_5\text{H}_5)_2\text{Ru}_2(\mu\text{-CH}_2)(\text{CO})_2(\text{MeCN})]$ with diazoalkanes ( $\text{N}_2=\text{CR}_2$ ) giving alkenic products

Munetaka Akita,<sup>\*a</sup> Ruimao Hua,<sup>a</sup> Selby A. R. Knox,<sup>\*b</sup> Yoshihiko Moro-oka,<sup>\*a</sup> Sadahiro Nakanishi<sup>a</sup> and Michael I. Yates<sup>b</sup>

<sup>a</sup> Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226, Japan

<sup>b</sup> School of Chemistry, University of Bristol, Bristol, UK BS8 ITS

**Reaction of the labile diruthenium bridging methylene complex  $[(\eta\text{-C}_5\text{H}_5)_2\text{Ru}_2(\mu\text{-CH}_2)(\mu\text{-CO})(\text{CO})(\text{MeCN})]$  with diazoalkanes ( $\text{N}_2=\text{CR}^1\text{R}^2$ ) results in specific C–C coupling to give alkenic products, i.e. the bridging alkenyl complex  $[(\eta\text{-C}_5\text{H}_5)_2\text{Ru}_2(\mu\text{-CH}=\text{CHR}^1)(\mu\text{-H})(\text{CO})_2]$  ( $\text{R}^2 = \text{H}$ ) or alkene  $\text{CH}_2=\text{CR}^1\text{R}^2$  ( $\text{R}^1, \text{R}^2 \neq \text{H}$ ).**

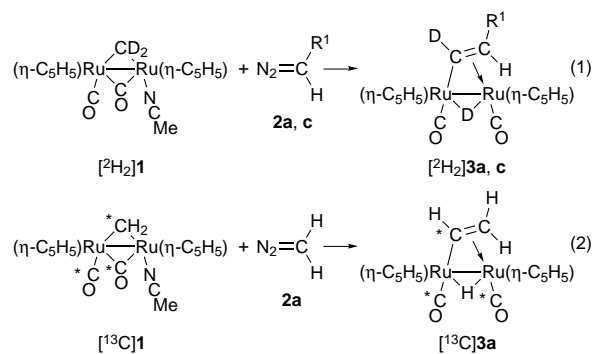
C–C coupling mediated by transition-metal-alkylidene species is involved in many useful stoichiometric and catalytic organic transformations such as alkene cyclopropanation, metathesis and acetylene polymerization,<sup>1</sup> and most of the active species are mononuclear  $[\text{M}=\text{CR}_2]$  with an electrophilic vacant p orbital.<sup>2a,b</sup> In contrast, polynuclear bridging alkylidene species  $[\text{M}_n(\mu\text{-CR}_2)]$  appear to be sluggish with respect to C–C coupling, in particular, coupling with another  $\text{CR}_2$  species, though they are recognized as better model compounds for surface-bound methylene species.<sup>3</sup> This is probably due to the  $\sigma$  character of the  $\text{M}=\text{CR}_2$  bonds,<sup>2c</sup> and few successful examples of alkylidene coupling on a polynuclear system have been reported so far.<sup>3</sup> Herein we disclose the effective and specific C–C coupling of a labile diruthenium bridging methylene species  $[(\eta\text{-C}_5\text{H}_5)_2\text{Ru}_2(\mu\text{-CH}_2)(\mu\text{-CO})(\text{CO})(\text{MeCN})]$  **1**<sup>4</sup> with diazoalkanes ( $\text{N}_2=\text{CR}^1\text{R}^2$  **2**), a reaction relevant to the carbon-chain propagation mechanism of catalytic CO hydrogenation.

When an ethereal solution of diazoalkane **2** was added to the labile bridging methylene species **1** at room temp. an instantaneous reaction took place with gas evolution (Scheme 1). In the case of the reaction with monosubstituted diazoalkane  $[\text{N}_2=\text{CR}^1\text{H}$  ( $\text{R}^2 = \text{H}$ );  $\text{R}^1 = \text{H}$  **a**,  $\text{Me}$  **b**,  $\text{SiMe}_3$  **c**,  $\text{Ph}$  **d**,  $\text{CO}_2\text{Me}$  **e**], the bridging alkenyl complexes  $[(\eta\text{-C}_5\text{H}_5)_2\text{Ru}_2(\mu\text{-CH}=\text{CHR}^1)(\mu\text{-H})(\text{CO})_2]$  **3a–e**<sup>†,‡</sup> were isolated in good yields after TLC separation. The products **3** were readily characterized on the basis of the NMR data<sup>†</sup> [(i) the separated  $\text{C}_\alpha\text{H}_\alpha$  and  $\text{C}_\beta\text{H}_\beta$  signals of the bridging alkenyl ligand ( $\mu\text{-C}_\alpha\text{H}_\alpha=\text{C}_\beta\text{H}_\beta\text{R}^1$ ) and (ii) the hydride signal appearing around  $\delta -15$ ] and the absence

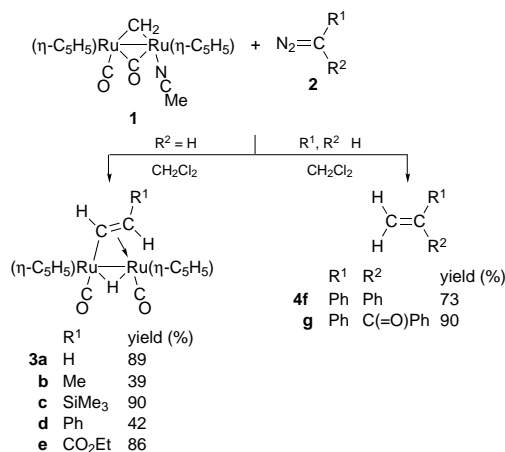
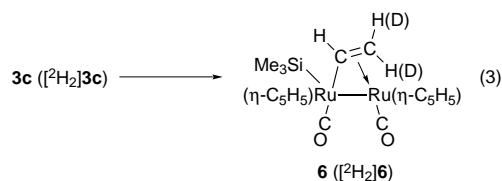
of a bridging CO stretching vibration. Derivatives of **3** including the structurally characterized **3b** have been previously obtained by a different route.<sup>5</sup> The reaction of **1** with disubstituted diazoalkane **2** [ $\text{R}^1 = \text{R}^2 = \text{Ph}$  **f**;  $\text{R}^1 = \text{Ph}$ ,  $\text{R}^2 = \text{C}(\text{=O})\text{Ph}$  **g**] afforded alkene  $\text{CH}_2=\text{CR}^1\text{R}^2$  **4f,g** and only a complicated mixture of organometallic products; the  $\mu\text{-H}$  signal of **3** could not be detected.

It is remarkable that the reaction conditions of the present C–C coupling are much milder than those of the thermal C–C coupling of the di( $\mu$ -alkylidene) complexes,  $[(\eta\text{-C}_5\text{H}_5)_2\text{Ru}_2(\mu\text{-CR}_2)(\mu\text{-CHR})(\text{CO})_2]$  **5** ( $\text{R} = \text{Me}$  **a**,<sup>6a</sup>  $\text{H}$  **b**<sup>6b</sup>) ( $>200$  °C), and that the selectivity as well as the yield is superior to those of the latter systems.

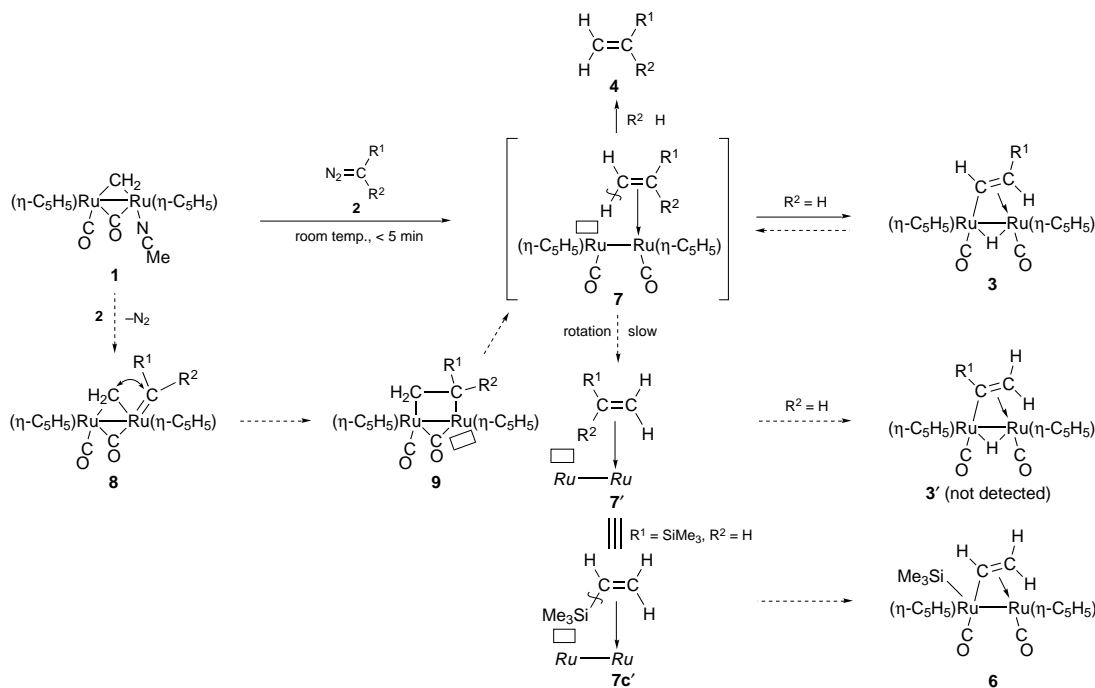
In order to obtain an insight into the reaction mechanism, labelling experiments using  $[\text{}^2\text{H}_2]\text{1}$  ( $\mu\text{-CD}_2$ ) and  $[\text{}^{13}\text{C}]\text{1}$  ( $\mu\text{-}^{13}\text{CH}_2$ ) were carried out. Treatment of  $[\text{}^2\text{H}_2]\text{1}$  with **2a,c** produced  $[\text{}^2\text{H}_2]\text{3a,c}$  where the  $\text{H}_\alpha$  and  $\mu\text{-H}$  atoms were deuterated completely [Scheme 2, eqn. (1)]. Similarly, the  $^{13}\text{C}$ -labelled methylene carbon atom in  $[\text{}^{13}\text{C}]\text{1}$  became the  $\alpha$  carbon atom of the bridging alkenyl ligand in  $[\text{}^{13}\text{C}]\text{3a}$  [Scheme 2, eqn. (2)]. These labelling studies confirm that the C–C coupling is specific and that the  $\alpha\text{-CH}$  and  $\mu\text{-H}$  moieties in **3** come from the bridging  $\text{CH}_2$  ligand in **1**.



It is also notable that thermolysis of the  $\beta$ -silylethenyl complex **3c** at 100 °C afforded the isomeric silyl-ethenyl complex **6** [eqn. (3)]. The rearrangement of  $[\text{}^2\text{H}_2]\text{3c}$  turned out to be specific as indicated by the formation of  $[\text{}^2\text{H}_2]\text{6}$  with the two  $\beta$ -methylene hydrogen atoms being deuterated completely. Thus the  $\beta\text{-CH}_2$  moiety in **6** originated from the  $\mu\text{-CH}_2$  ligand in **1**.



Scheme 1



Scheme 3  $Ru = Ru(\eta\text{-C}_5\text{H}_5)$ ;  $\square$  = coordinatively unsaturated site

The specific alkylidene coupling and rearrangement can be interpreted in terms of the reaction mechanisms summarized in Scheme 3, involving the coordinatively unsaturated alkene species **7** as a key intermediate. Oxidative addition of a C–H bond in **7** would lead to the  $\mu$ -alkenyl complex **3**, while in the case of the reaction with disubstituted diazoalkane (**2f**, **g**), the alkene **4** may be eliminated from the diruthenium centre due to the steric repulsion. The absence of the regioisomer **3'** and the results of the labelling experiments indicate that the C–H oxidative addition giving **3** must take place before the unsymmetrical structural information of **7** is lost (e.g. via rotation of the alkene ligand leading to **7'**). Because (i) the di( $\mu$ -alkylidene) complex **5** does not undergo C–C coupling under the present reaction conditions and (ii) the symmetrical structure of **5** cannot explain the results of the labelling experiments, the unsymmetrical  $\eta^1$ -alkylidene- $\mu$ -alkylidene species **8** and the dimetallacyclobutane **9** are plausible precursors of **7**. The different reactivities of complexes **8** and **5**, which have the same composition, may be attributed to the relative facility of migratory insertion *cf.* reductive elimination. Finally, thermolysis of the  $\beta$ -silyl ethenyl derivative **3c** is proposed to occur *via* reductive elimination to regenerate **7** with subsequent rotation of the alkene ligand (**7c'**) followed by oxidative addition of the Si–C bond giving rise to the silyl-ethenyl complex **6**.

The present study reveals that alkylidene units on a polynuclear system can be coupled with each other in a quite specific manner under very mild reaction conditions, if they are incorporated into the metal system in an appropriate way. In the present case, the C–C coupling is most probably realized *via* migratory insertion of the  $\eta^1$ -alkylidene- $\mu$ -alkylidene species **8**. A similar alkylidene coupling leading to an alkenic intermediate may occur on a heterogeneous catalyst surface, and, recently, a vinyl species has been proposed as an initiator of the carbon-chain propagation.<sup>3e</sup>

### Footnotes

† Spectroscopic data: **3a** (major isomer),  $\delta_{\text{H}}$  (in  $\text{CDCl}_3$ ) 8.48 (1 H, dd,  $J$  7.8, 12.7 Hz,  $\mu\text{-CH=CH}_2$ ), 5.01, 4.84 (5 H  $\times$  2, s  $\times$  2,  $\text{C}_5\text{H}_5 \times$  2), 4.51 [1 H, d,  $J$  7.8 Hz,  $\mu\text{-CH=CH}_2$  (*cis*)], 2.58 [1 H, d,  $J$  12.7 Hz,  $\mu\text{-CH=CH}_2$  (*trans*)], –14.95 (1 H, s,  $\mu\text{-H}$ );  $\delta_{\text{C}}$  (in  $\text{C}_6\text{D}_6$ ) 203.5, 202.4 (s  $\times$  2, CO), 144.4 (d,  $J$  147 Hz,  $\mu\text{-CH=CH}_2$ ), 84.1 (d,  $J$  176 Hz,  $\text{C}_5\text{H}_5$ ), 83.5 (d,  $J$  178 Hz,  $\text{C}_5\text{H}_5$ ), 53.2

(t,  $J$  156 Hz,  $\mu\text{-CH=CH}_2$ ); IR (in  $\text{CH}_2\text{Cl}_2$ ) 1961, 1913  $\text{cm}^{-1}$ . **3b** (major isomer),  $\delta_{\text{H}}$  (in  $\text{C}_6\text{D}_6$ ) 8.34 (1 H, d,  $J$  11.7 Hz,  $\mu\text{-CH=CH}$ ), 4.76, 4.47 (5 H  $\times$  2, s  $\times$  2,  $\text{C}_5\text{H}_5$ ), 3.54 (1 H, dq,  $J$  5.9, 11.7 Hz,  $\mu\text{-CH=CH}$ ), 1.61 (3 H, d,  $J$  5.9 Hz,  $\text{CH}_3$ ), –14.44 (1 H, s,  $\mu\text{-H}$ ); IR (in  $\text{CH}_2\text{Cl}_2$ ) 1954, 1911  $\text{cm}^{-1}$ . **3c**,  $\delta_{\text{H}}$  (in  $\text{CDCl}_3$ ) 8.78 (1 H, d,  $J$  13.9 Hz,  $\mu\text{-CH=CH}$ ), 5.06, 4.89 (5 H  $\times$  2, s  $\times$  2,  $\text{C}_5\text{H}_5 \times$  2), 2.55 (1 H, d,  $J$  13.9 Hz,  $\mu\text{-CH=CH}$ ), –14.83 (1 H, s,  $\mu\text{-H}$ ); IR (in  $\text{CH}_2\text{Cl}_2$ ) 1958, 1908  $\text{cm}^{-1}$ . **3d** (major isomer),  $\delta_{\text{H}}$  (in  $\text{C}_6\text{D}_6$ ) 9.36 (1 H, d,  $J$  12.5 Hz,  $\mu\text{-CH=CH}$ ), 7.2–7.0 (5 H, m, Ph), 4.80, 4.26 (5 H  $\times$  2, s  $\times$  2,  $\text{C}_5\text{H}_5 \times$  2), 4.64 (1 H, d,  $J$  12.5 Hz,  $\mu\text{-CH=CH}$ ), –14.43 (1 H, s,  $\mu\text{-H}$ ); IR (in  $\text{CH}_2\text{Cl}_2$ ) 1958, 1915  $\text{cm}^{-1}$ . **3e** (major isomer),  $\delta_{\text{H}}$  (in  $\text{CDCl}_3$ ) 10.04 (1 H, d,  $J$  11.7 Hz,  $\mu\text{-CH=CH}$ ), 5.20, 4.91 (5 H  $\times$  2, s  $\times$  2,  $\text{C}_5\text{H}_5 \times$  2), 4.18 (2 H, q,  $J$  6.8 Hz,  $\text{OCH}_2\text{CH}_3$ ), 3.55 (1 H, d,  $J$  11.7 Hz,  $\mu\text{-CH=CH}$ ), 1.29 (3 H, t,  $J$  6.8 Hz,  $\text{OCH}_2\text{CH}_3$ ), –15.04 (1 H, s,  $\mu\text{-H}$ ); IR (in  $\text{CH}_2\text{Cl}_2$ ) 1973, 1923, 1700  $\text{cm}^{-1}$ .

‡ Complex **3** (except for **3c**) is composed of two isomers arising from the different configurations of the Ru auxiliaries ( $\text{C}_5\text{H}_5$  and CO ligands) with respect to the  $\text{Ru}_2(\mu\text{-CH=CHR}^1)(\mu\text{-H})$  core.<sup>5</sup>

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