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A Novel Type of Carbon−Carbon Double Bond Cleavage of 1,1-Disubstituted Alkenes on a Triruthenium Polyhydrido Cluster

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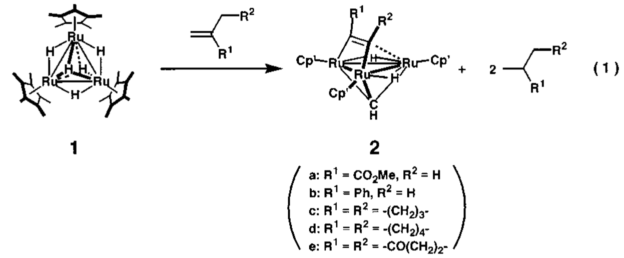
Since the early 1980s, cleavage of carbon−hydrogen and carbon−carbon bonds by soluble transition metals has been of special interest in organometallic chemistry because of its applicability to the functionalization of saturated hydrocarbons. While there is vast chemistry of selective alkane C−H bond activation using unsaturated mononuclear species of transition metals as an activator,[1] there has been a relatively small number of successful examples of C−C bond cleavage mediated by transition metal complexes.[2] Over the past 10 years we have dealt with the activation of organic substrates on multimetallic sites and demonstrated that metal−polyhydride clusters effectively activate even C−H bonds of alkanes with thermal excitation as a result of the cooperative action of the metal centers.[3] The advantageous properties of a multimetallic system over a monometallic one in the substrate activation are its capability of multiple coordination of the substrate to the metal centers and the multielectron transfer between the substrate and the metal centers. Such remarkable properties of the multimetallic system very probably enable us to activate not only a carbon−carbon single bond[4] but also a double bond. We report herein an unprecedented mode of activation of the C−C double bond of 1,1-disubstituted alkenes mediated by a trinuclear pentahydride complex of ruthenium $\{(\eta^5\text{-}C_5Me_5)Ru\}_3(\mu\text{-}H)_3(\mu_3\text{-}H)_2$ (**1**).

The reaction of **1** with excess amount (5 equiv) of methyl methacrylate in toluene at 80 °C for 48 h resulted in the quantitative formation of a new product $(Cp'Ru)_3(\mu_3\text{-}CH{=}CCO_2Me)(\mu_3\text{-}CH)(\mu\text{-}H)_2$ (**2a**) ($Cp' = \eta^5\text{-}C_5Me_5$) together with 2 equiv of 2-methylbutanoic acid as detected by NMR spectroscopy (eq 1). The new compound **2a** was isolated as a dark-red crystalline solid in 87% yield and assigned as a μ_3-alkyne−μ_3-methylidyne complex on the basis of the ^1H and ^{13}C NMR spectral data. Complex **1** reacts with 1,1-disubstituted alkenes such as α-methylstyrene, methylenecyclopentane, methylenecyclohexane, and α-methylene-γ-butyrolactone in a similar manner to lead to the exclusive formation of the corresponding μ_3-alkyne−μ_3-methylidyne complexes **2b**−**2e**. The reaction was, of course, accompanied with the formation of a hydrogenated product of the 1,1-disubstituted alkene used.



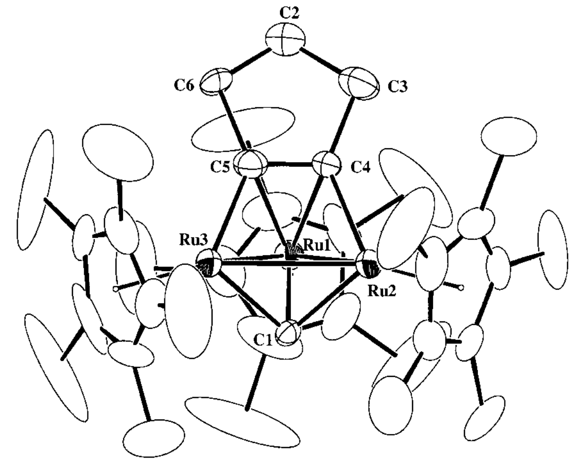


Figure 1. Molecular structure of **2c**. Selected bond lengths (Å): Ru2−Ru3 2.7770(9), Ru1−Ru2 2.7208(9), Ru1−Ru3 2.7060(9), Ru1−C4 2.232(10), Ru1−C5 2.198(9), Ru2−C4 2.031(8), Ru3−C5 2.045(9), Ru−C1av 2.008, C4−C5 1.33(1).

The most informative data with respect to the structures of these complexes is derived from the NMR study. A pair of resonances for the alkynic carbon appears in the regions of δ 150−160 and δ 100−130 ppm, and the signal characteristic of the μ_3-methylidyne carbon is observed in the δ 310−320 ppm region in the ^{13}C NMR spectra. The ^1H NMR spectra of **2a** and **2b** exhibit characteristic resonance signals for the terminal hydrogen of the coordinated alkyne around δ 9 ppm, and the resonances for the triply bridging methylidyne ligand of **2a**−**e** appear around δ 14 ppm. The shifts of δ 14 and 310−320 ppm for the methylidyne ligand in the ^1H and ^{13}C NMR spectra, respectively, are comparable to those reported for the μ_3-methylidyne complex of late transition metals.[5] Definitive proof for the proposed structure was provided by X-ray diffraction study on the single crystal of **2c** (Figure 1).

Figure 1 clearly establishes the structural identity of **2c** as a μ_3-alkyne−μ_3-methylidyne complex in which the alkyne ligand is coordinated parallel to one of the three ruthenium bonds. The alkyne ligand is σ-bonded to two ruthenium atoms and π-bonded to the third ruthenium. Formation of the μ_3-alkyne−μ_3-methylidyne complex **2** evidently shows that the carbon−carbon double bond of the 1,1-disubstituted alkene is cleaved, and the resulting two fragments are converted into the μ_3-methylidyne and the μ_3-alkyne moieties, respectively, in the reaction. To our best knowledge, this is the first example of the selective carbon−carbon double bond cleavage of 1,1-disubstituted alkene in cooperation with three metal centers.

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[1] For example: (a) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 352. (b) Hoyano, J. K.; Graham, W. A. G. J. *J. Am. Chem. Soc.* **1982**, *104*, 3723. (c) Watson, P. L. *J. Am. Chem. Soc.* **1983**, *105*, 6491. (d) Burk, M. J.; Crabtree, R. H.; McGrath, D. V. *J. Chem. Soc., Chem. Commun.* **1985**, 1829. (d) Amdtsen, B. A.; Bergman, R. G. *Science* **1995**, *270*, 1970.

[2] For example: (a) Kang, J. W.; Moseley, R.; Maitlis, P. M. *J. Am. Chem. Soc.* **1969**, *91*, 5970. (b) King, R. B.; Efraty, A. *J. Am. Chem. Soc.* **1972**, *94*, 3773. (c) Benfield, F. W. S.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1974**, 1324. (d) Crabtree, R. H.; Dion, R. P. *J. Chem. Soc., Chem. Commun.* **1984**, 1260. (e) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245. (f) Suggs, J. W.; Jun, C.-H. *J. Am. Chem. Soc.* **1986**, *108*, 4679. (g) Bunel, E.; Burger, B. J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 976. (h) Hartwig, J. F.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 2717. (i) Gozin, M.; Weisman, A.; Ben-David, Y.; Milstein, D. *Nature* **1993**, *364*, 699.

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[5] Cavert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1979**, *99*, 5225. (b) Herrmann, W. A.; Plank, J.; Riedel, D.; Ziegler, M. L.; Weidenhammer, K.; Guggolz, E.; Balbach, B. *J. Am. Chem. Soc.* **1981**, *103*, 63. (c) Kolis, J. W.; Holt, E. M.; Shriver, D. F. *J. Am. Chem. Soc.* **1983**, *105*, 7307. (d) Kakigano, T.; Suzuki, H.; Igarashi, M.; Moro-oka, Y. *Organometallics* **1990**, *9*, 2192.

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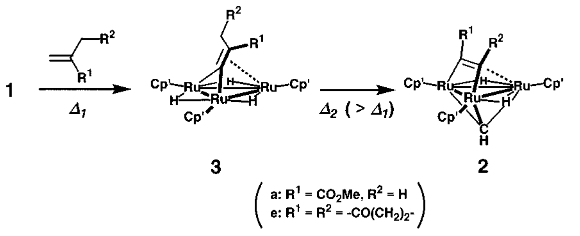
When the reaction of **1** with the 1,1-disubstituted alkene was conducted under milder conditions, formation of an intermediary μ-vinylidene complex was detected. Treatment of **1** with α-methylene−γ-butyrolactone in tetrahydrofuran at room temperature for 21 h led to the quantitative formation of a μ-vinylidene complex **3e** as a result of selective cleavage of the two C−H bonds at the *exo*-methylene carbon. Chromatographic separation of the reaction mixture enabled us to isolate a dark-green crystalline compound **3e** in 80% yield (eq 2). The μ-vinylidene complex was identified on the basis of ^{1}H and ^{13}C NMR spectral data. A notable feature of the ^{13}C NMR data is the appearance of two singlet resonances at δ 322.1 and 74.5 ppm ascribed to the α- and β-carbon, respectively, of the bridging vinylidene moiety. These shifts are comparable to those reported for trinuclear μ_3-vinylidene complexes.[6]

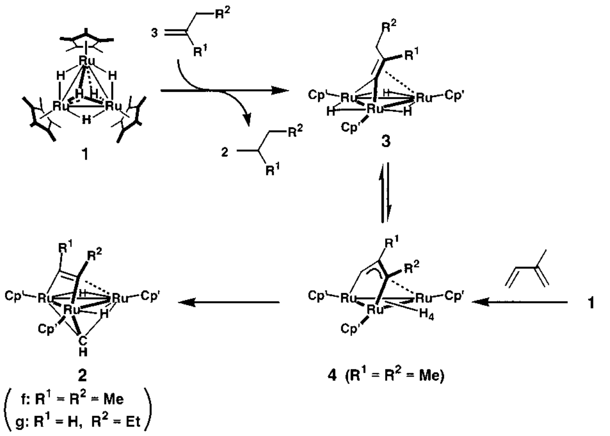


(2)

The proposed structure was confirmed by X-ray diffraction study using a single crystal obtained from the cold (−30 °C) toluene.

In the reaction of **1** with methyl methacrylate in tetrahydrofuran at 60 °C, an intermediary vinylidene complex **3a** was also formed and isolated in 60% yield. The ^{13}CNMR spectrum of **3a** exhibited characteristic signals of the vinylidene group at δ 328.2 (C$_\alpha$) and 78.8 (C$_\beta$). Pyrolysis of the μ-vinylidene complexes **3a** and **3e** proved their intermediacy in the carbon−carbon double bond cleavage. When pyrolysis of the μ-vinylidene complex **3a** in benzene-d_6 at 80 °C was monitored by means of ^{1}H NMR spectroscopy, quantitative conversion of **3a** into the μ_3-alkyne−μ_3-methylidyne complex **2a** was observed. In the pyrolysis of **3e** in toluene at 120 °C, the μ_3-alkyne−μ_3-methylidyne complex **2e** was formed as the sole product and isolated in 51% yield after chromatographic purification.

Scheme 1



In the preceding communication, we reported that trinuclear μ_3-1,3-dimetalloallyl complex (Cp′Ru)$_3$(μ_3-CHCMeCMe)(H)$_4$ (**4**) was formed in the reaction of **1** with isoprene.[7] Interestingly, μ_3-dimetalloallyl complex **4** was converted into a μ_3-alkyne−μ_3-methylidyne complex by way of a μ_3-vinylidene complex when **4** was heated in toluene. Whereas **3f** was exclusively formed at 50 °C, additional heating of **3f** at 80 °C led to a 1/1 mixture of the μ_3-alkyne−μ_3-methylidyne complexes **2f** and **2g**. The results obtained are consistent with the following reaction path (Scheme 1) involving a reversible isomerization between the μ_3-vinylidene complex and the μ_3-1,3-dimetalloallyl complex, followed by carbon−carbon bond cleavage that is likely associated with metal−metal bond cleavage and recombination.

Experiments designed to elucidate the mechanism of carbon−carbon double bond cleavage are under way and the results will be reported in due course.

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Supporting Information Available: Table of ^{1}H and ^{13}C NMR spectral assignments of **2a**−**g**, **3a**, and **3e** and ORTEP diagram, texts describing X-ray procedures, tables of X-ray data, positional and thermal parameters, and distances and angles for **2c** and **3e** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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