

(3) Å) than the other Os–Os distances in the structure (2.861 (3) and 2.863 (3) Å), and the osmium–carbon distance to the carbonyl carbon approximately trans to C(14) is the shortest in the structure (1.88 (2) Å).

The unsymmetrical conformer observed in the NMR spectrum of **1a** may be identified with the solid-state configuration (Figure 1) and an analogous structure is assumed for **5**. A similar structure may be proposed for the symmetrical form of **1a** (and of **2** and **3**), except with the diene coordinated to the two equatorial positions at one osmium atom. Approximate line shape calculations for **1a** indicate that exchange of the axial and equatorial olefin sites in the unsymmetrical conformer can proceed independently of equilibration via the symmetrical (diequatorial) form. Further mechanistic details await the results of  $^{13}\text{C}$  NMR studies.<sup>10</sup>

Complexes **1b** and **4** are readily distinguished from **1a**, **2**, **3**, and **5** by their infrared spectra<sup>11</sup> and analysis of their  $^1\text{H}$  NMR spectra indicates coordination of the diene in its *s-trans* form. As for **1a**, three two-proton multiplets ( $\tau$  6.60, 7.74, 8.57 in  $\text{CDCl}_3$ ) are seen for **1b**, but the *s*-vicinal protons ( $\text{H}_c$ ,  $\text{H}_c'$ ) resonate at highest field and the protons ( $\text{H}_a$ ,  $\text{H}_a'$ ) trans to the vicinal protons at lowest field. The coupling constants extracted from the iteratively simulated spectrum ( $J_{ab} = 2.47$ ,  $J_{ac} = 7.38$ ,  $J_{ac'} = -0.65$ ,  $J_{bc} = 11.13$ ,  $J_{bc'} = -0.48$ ,  $J_{cc'} = 11.37$  Hz) are generally comparable with those for uncomplexed *s-trans*-1,3-butadiene.<sup>12</sup> Particularly noteworthy is that the *s*-vicinal coupling constant ( $J_{cc'}$ ) is significantly larger for **1b**, **4**,<sup>13</sup> and free butadiene (11.4, 10.6, and 10.4 Hz, respectively) than for **1a**, **5**, and  $\text{Fe}(\text{CO})_3(s\text{-cis-C}_4\text{H}_6)^{6a}$  (4.7, 3.7, and 4.8 Hz, respectively) and free cyclic *s*-cis dienes.<sup>6a,14</sup> Coordination of both ends of an *s-trans* diene necessarily requires two metal centers and the alternative possibilities of diaxial or diequatorial coordination at adjacent osmium atoms can be envisioned. No splitting is seen in the NMR spectrum of **1b** to  $-76^\circ$  and of the more soluble **4** to  $-127^\circ$ , which supports the symmetrical, equatorially bridged structure. This assignment has been substantiated by a single-crystal x-ray diffraction study of **1b**.

Crystals of  $\text{Os}_3(\text{CO})_{10}(s\text{-trans-C}_4\text{H}_6)$  obtained from chloroform solution form in space group  $C2/c$  with a cell of dimensions  $a = 30.638$  (6) Å,  $b = 9.770$  (2) Å,  $c = 13.285$  (3) Å, and  $\beta = 112.82$  (2)°. Data collection and structure determination were performed as before. Refinement of 2473 independent, observed reflections resulted in an  $R$  factor of 0.036. A view of the molecule is presented in Figure 2. Isotropic thermal ellipsoids are shown for carbon atoms C(12) and C(13), which were observed to suffer from severe vibrational disorder. The *s-trans*-butadiene ligand bridges osmium atoms Os(2) and Os(3) with the olefin groups bound in equatorial positions. The Os(2)–Os(3) bond (2.932 (3) Å) is substantially longer than the other osmium–osmium bonds of the structure (2.856 (3) and 2.857 (3) Å).<sup>15</sup>

These results with complexes **1–5** demonstrate that conjugated dienes can coordinate to a triangular metal framework in several ways. An important factor determining the mode adopted must be interaction between diene substituents and adjacent carbonyl ligands, since the complexes of 1,3-butadiene, the unencumbered parent ligand, display the greatest structural variety. For further information on this point the preparation of complexes with a wider range of diene substituents is being pursued.

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- An equivalent amount of the corresponding monoolefin was also produced. The minor cluster products accompanying complexes **1–4** were identified as hydridoalkenyl compounds  $\text{HOs}_3(\text{CO})_{10}(\text{CH}=\text{CRR}')$ . See ref 1b and references therein.
- Ions derived from  $\text{H}_2\text{Os}_3(\text{CO})_{10}$  are observed in the mass spectrum of **5**. These presumably result from decomposition of **5** to  $\text{H}_2\text{Os}_3(\text{CO})_{10}$  and benzene, as observed in cyclohexane solution at  $80^\circ$ . This process will be discussed further in a full paper.
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- $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\tau$ ): **2**, 4.85 (m, 1H), 7.51 (s, 3H), 7.74 (dd, 1H), 7.95 (dd, 1H), 9.50 (dd, 1H), 9.84 (dd, 1H); **3**, 7.55 (s, 6H), 7.90 (d, 2H), 9.69 (d, 2H); **5**, 4.44 (m, 2H), 6.25 (m, 2H), 8.15 (t, 4H).
- Infrared evidence ( $\nu_{\text{CO}}$ ,  $\text{C}_6\text{H}_{12}$ ) supports these conclusions in that the spectrum of **1a** (2114 m, 2066 s, 2064 s, 2033 s, 2029 s, 2025 s, 2011 s, 1999 vw, 1992 w sh, 1987 m, 1982 w sh, 1945 w, 1934 w  $\text{cm}^{-1}$ ) contains too many bands for just one species. Rather it is the superposition of the two similar but distinct patterns observed for **2** or **3** and for **5** (2, 2114 m, 2065 s, 2033 s, 2028 s, 2010 s, 1997 w, 1986 m, 1980 w sh, 1932 w  $\text{cm}^{-1}$ ; **3**, 2113 m, 2064 s, 2032 s, 2027 s, 2009 s, 1997 w, 1985 m, 1975 w, 1927 w  $\text{cm}^{-1}$ ; **5**, 2111 m, 2062 s, 2032 s, 2022 s, 2009 s, 1992 w, 1985 m, 1976 w, 1939 w  $\text{cm}^{-1}$ ).
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- A limiting low temperature spectrum of  $^{13}\text{C}$ -enriched **5** has been obtained at  $-108^\circ$  (S. I. Richter, M. Tachikawa, and J. R. Shapley, unpublished results). The pattern observed (2:1:1:1:1:1:1:1, to increasing field) is consistent with the assigned structure, assuming one accidentally degenerate pair of signals.
- $\text{Ir}(\nu_{\text{CO}}$ ,  $\text{C}_6\text{H}_{12}$ ): **1b**, 2109 m, 2063 m, 2047 s, 2019 vs, 1994 s, 1975 m, 1942 vw  $\text{cm}^{-1}$ ; **4**, 2107 m, 2061 m, 2045 s, 2041 s, 2017 vs, 1993 s, 1974 m, 1940 vw  $\text{cm}^{-1}$ .
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Mamoru Tachikawa, John R. Shapley\*

Department of Chemistry, University of Illinois  
Urbana, Illinois 61801

R. Curtis Haltiwanger, Cortlandt G. Pierpont\*

Department of Chemistry, University of Colorado  
Boulder, Colorado 80302  
Received April 6, 1976

## A Novel Catalytic Property of Magnesium Oxide for Hydrogenation of 1,3-Butadiene

Sir:

We wish to report a novel catalytic property of  $\text{MgO}$  which was obtained by evacuating  $\text{Mg}(\text{OH})_2$  at an unusually high temperature,  $1100^\circ\text{C}$ . Although the catalyst did not show any activity for  $\text{H}_2\text{-D}_2$  equilibration, it was active and highly selective for the hydrogenation of 1,3-butadiene to *cis*-2-butene,

**Table I.** Isotopic Distribution of Products in the Deuteriogenation of 1,3-Butadiene over  $\text{MgO}$  at  $0^\circ\text{C}$

Product	% each product	% of each isotopic species			
		$d_0$	$d_1$	$d_2$	$d_3\text{-}d_8$
1,3-Butadiene	59.0	100.0	0	0	0
1-Butene	2.9	0.7	2.1	97.2	0
<i>trans</i> -2-Butene	6.4	2.5	1.4	96.1	0
<i>cis</i> -2-Butene	31.7	0.4	1.2	98.4	0

**Table II.** Isotopic Distribution of Products in the H<sub>2</sub>-D<sub>2</sub> Equilibration, and the Reaction of 1,3-Butadiene with a Mixture of H<sub>2</sub> + D<sub>2</sub> over MgO at 0 °C

Reactant	Reaction time, min	Product	% each product	% of each isotopic species			
				<i>d</i> <sub>0</sub> or H <sub>2</sub>	<i>d</i> <sub>1</sub> or HD	<i>d</i> <sub>2</sub> or D <sub>2</sub>	<i>d</i> <sub>3</sub> - <i>d</i> <sub>8</sub>
H <sub>2</sub> + D <sub>2</sub>	0	H <sub>2</sub> , HD, D <sub>2</sub>		46.9	0.5	52.6	
	60	H <sub>2</sub> , HD, D <sub>2</sub>		47.4	1.2	51.4	
1,3-Butadiene + H <sub>2</sub> + D <sub>2</sub>	0	H <sub>2</sub> , HD, D <sub>2</sub>		32.7	0.9	66.4	
	60	H <sub>2</sub> , HD, D <sub>2</sub>		31.9	0.9	67.2	
		1,3-Butadiene	1.2	100.0	0	0	0
		1-Butene	3.3	31.3	1.5	67.2	0
		<i>trans</i> -2-Butene	60.8	34.1	1.5	64.4	0
		<i>cis</i> -2-Butene	34.7	26.1	1.0	72.9	0

during which H<sub>2</sub> (or D<sub>2</sub>) maintained its molecular identity; that is, both H (or D) atoms in a H<sub>2</sub> (or D<sub>2</sub>) molecule are incorporated into one hydrogenated molecule. A maintenance of molecular identity of hydrogen, though it is not frequently observed, is one of the characteristics which distinguish a nonmetal heterogeneous catalyst from a metal catalyst. This characteristic has been observed in the hydrogenation of ethylene over Cr<sub>2</sub>O<sub>3</sub>,<sup>1-3</sup> ZnO,<sup>3</sup> and Co<sub>3</sub>O<sub>4</sub><sup>4</sup> and in the hydrogenation of 1,3-butadiene over ZnO<sup>5</sup> and MoS<sub>2</sub>.<sup>6</sup> Over these catalysts, products were limited to those that resulted from an addition of two H (or D) atoms to the original double bond. This fact, combined with the fact that all the hydrogenation catalysts were active for H<sub>2</sub>-D<sub>2</sub> equilibration, has left unsolved the problem as to whether a hydrogen molecule participates in the addition process in its molecular form by one step or in its dissociatively adsorbed form by two steps.

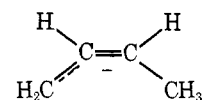
It was reported that MgO showed a high activity for H<sub>2</sub>-D<sub>2</sub> equilibration when heated at 500-750 °C but it lost the activity when heated to very high temperatures.<sup>7</sup> However, MgO evacuated at 1100 °C shows a new catalytic property for hydrogenation, which does not involve the above question.

The hydrogenation of 1,3-butadiene with D<sub>2</sub>, or a mixture of H<sub>2</sub> and D<sub>2</sub>, and the H<sub>2</sub>-D<sub>2</sub> equilibration were carried out at 0 °C in a recirculation reactor having a volume of about 1510 ml, 0.4 g of a MgO catalyst being used. The catalyst was prepared by evacuating Mg(OH)<sub>2</sub> at 1100 °C for 2 hr. Mg(OH)<sub>2</sub> was a guaranteed reagent of Knato Chemical Co. 1,3-Butadiene, H<sub>2</sub>, and D<sub>2</sub> were purified by passage through 4A molecular sieves at -78 °C. The molar ratio of H<sub>2</sub> (or D<sub>2</sub>) to 1,3-butadiene was 3.0. Composition of H<sub>2</sub>, HD, and D<sub>2</sub> was determined by mass spectrographic analysis. Butenes and 1,3-butadiene were gas chromatographically separated and subjected to mass spectrographic analysis. The positions of D atoms in the products were determined by NMR.

Distributions of D atoms in the products of the reaction of 1,3-butadiene with D<sub>2</sub> are listed in Table I. Preferential formation of *cis*-2-butene containing two D atoms was observed. The NMR spectrum of *cis*-2-butene showed that the intensity ratio of methyl hydrogens to olefinic hydrogens was 2.02, and that peaks of olefinic hydrogen exhibited a 1:2:1 triplet. This indicates that two D atoms in *cis*-2-butene are located at carbon atoms 1 and 4.

In Table II are shown the results of the H<sub>2</sub>-D<sub>2</sub> equilibration and the reaction of 1,3-butadiene with a mixture of H<sub>2</sub> and D<sub>2</sub>. The butenes consist substantially of *d*<sub>0</sub> and *d*<sub>2</sub> isotopic species even at the high conversion of 98.9%. These results clearly demonstrate that MgO evacuated at 1100 °C does not catalyze the H<sub>2</sub>-D<sub>2</sub> equilibration but catalyzes the hydrogenation of 1,3-butadiene by a process in which a hydrogen molecule maintains its molecular identity.

Since D atoms attack carbon atoms 1 and 4, D<sub>2</sub> must be adsorbed dissociatively. Since  $\pi$ -allyl carbanion is most stable in the *cis* form,<sup>8</sup>



preferential formation of *cis*-2-butene indicates that a  $\pi$ -allyl carbanion mechanism is involved with the present catalyst. The mechanism for the deuteriogenation of 1,3-butadiene is suggested to be as follows. Deuterium adsorbs heterolytically to form D<sup>+</sup> and D<sup>-</sup>. At first, D<sup>-</sup> attacks a terminal carbon atom to form  $\pi$ -allyl carbanion as a half hydrogenated state. Since the electron density in a  $\pi$ -allyl carbanion is highest at the other terminal carbon atom, D<sup>+</sup> selectively attacks the carbon atom to form *cis*-2-butene-1,4-*d*<sub>2</sub>. Both D<sup>+</sup> and D<sup>-</sup> on one set of active sites must be assumed not to migrate to other sites, and, therefore, it is suggested that each set of active sites is isolated from the others.

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Hideshi Hattori,\* Yasutaka Tanaka, Kozo Tanabe

Department of Chemistry, Faculty of Science  
Hokkaido University  
Sapporo, 060 Japan

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#### Short-Lived Intermediates. 6. Cyclization of the 1,4-Diradical in Ester Photochemistry. Completion of an Analogy Found Wanting

Sir:

It has been well established that ketones having a  $\gamma$ -hydrogen atom undergo photorearrangement yielding a 1,4-diradical which potentially can (a) return the hydrogen atom to the  $\gamma$ -carbon, (b) eliminate to form an alkene and an enol, or (c) cyclize to form a cyclobutanol.<sup>1</sup> The extensive ketone results would seem to provide an ideal analogy for the structurally and electronically related carboxylate esters. There are, in fact, some examples of esters which undergo reverse  $\gamma$ -hydrogen abstraction to regenerate the original or isomeric ester,<sup>2,3</sup> and many examples of esters which undergo the type II process to yield alkenes and carboxylic acids.<sup>2-8</sup> Heretofore, however, this analogy has been flawed by the striking lack of