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The Disproportionation of *cis*-Bicyclo[4.3.0]nona-3,7-diene Catalyzed by $Fe(CO)_5$ and $Cp_2Fe_2(CO)_4$

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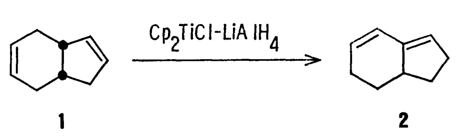
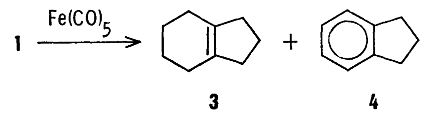
Synopsis. *cis*-Bicyclo[4.3.0]nona-3,7-diene (**1**) was catalytically disproportionated by the use of $Fe(CO)_5$ and $Cp_2Fe_2(CO)_4$ to bicyclo[4.3.0]non-1(6)-ene (**3**) and indan (**4**). However, the same reaction catalyzed by the use of other metal carbonyls gave merely small amounts of **3** and **4**, while those using Pd– and Rh–carbons yielded only **4** and the starting material, **1**, respectively.

A variety of double-bond migration reactions of olefins and dienes catalyzed by transition-metal complexes are well known.¹⁾ Nonconjugated dienes are usually converted into conjugated dienes with $Fe(CO)_5$, and the resulting 1,3-dienes form metal carbonyl complexes.²⁾ Recently, Tureček has reported a titanocene-catalyzed isomerization of *cis*-bicyclo[4.3.0]nona-3,7-diene (**1**) to bicyclo[4.3.0]nona-2,9-diene (**2**) (Eq. 1).³⁾



(1)

However, the reaction of **1** catalyzed by $Fe(CO)_5$ gave bicyclo[4.3.0]non-1(6)-ene (**3**) and indan (**4**) (Eq. 2). In this communication, we wish to report the disproportionation reaction of **1** catalyzed by several iron complexes.



(2)

The reaction of **1** with a catalytic amount of $Fe(CO)_5$ at 230 °C for 4 h gave approximately equal amounts of **3** (40%) and **4** (39%), as well as, an oligomer (7%) containing a small amount of tetracarbonylbis(η^5-4,5,6,7-tetrahydroindenyl)diiron (**5**) (3%).⁴⁾

Figure 1 shows some typical plots of the time conversion curves of **1**, **3**, and **4**. Since about the same amounts of **3** and **4** were obtained in all stages of the reaction, **1** should be disproportionally converted to **3** and **4**. The complex **5** was formed in much larger quantities in the early stage of the reactions. The stoichiometric reaction of **1** and $Fe(CO)_5$ gave **5**, in a yield of 35—40%, in addition to **3** and **4**.⁵⁾

It is interesting to clarify whether the **5** complex is one of the products or a precursor of the disproportionation products. Thus, the reaction of **1** with **5** or tetracarbonylbis(η^5-cyclopentadienyl)diiron (**6**), which is structurally analogous to **5**, as a catalyst, was studied under similar conditions. The results are summarized in Table 1.

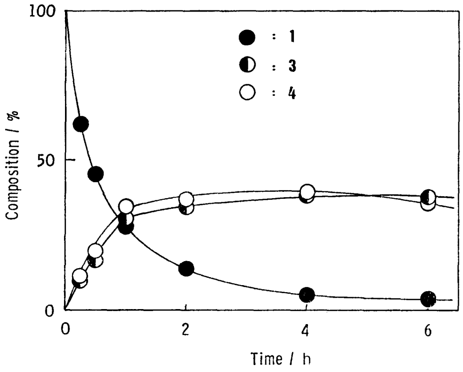


Fig. 1. Disproportionation of 1 catalyzed by $Fe(CO)_5$. $1/Fe(CO)_5=10/1$ (molar ratio), 230 °C

TABLE 1. DISPROPORTIONATION OF **1** BY VARIOUS IRON COMPLEXES$^{a)}$

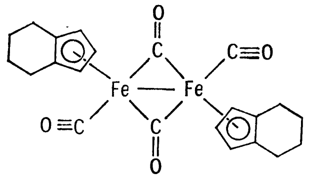
Catalyst	Composition/%$^{b)}$			
	1	**3**	**4**	Oligomers
$Fe(CO)_5$	11.2	39.8	38.5	10.5$^{c)}$
5	44.5	23.6	22.8	9.1
6	6.2	44.2	42.8	6.8

a) The reactions were carried out on 100-mmol scale with **1**/catalyst (molar ratio $\mathbf{1}/Fe(CO)_5=10/1$, $\mathbf{1}/\mathbf{5}=20/1$, $\mathbf{1}/\mathbf{6}=20/1$) at 230 °C for 4 h in an autoclave. b) Estimated on the basis of the **1** used. c) A small amount of **5** was present.

The reaction catalyzed by **5** gave **3** and **4** in a fashion similar to that found in the case of $Fe(CO)_5$, although the reaction rate was only about half as great. However, **5** was not recovered after the reaction because of the decomposition. Similarly, the **6** complex also promoted the disproportionation of **1** to give **3** and **4**. The reaction rate was slightly faster than that by $Fe(CO)_5$, and almost all of the **6** was recovered unchanged. Thus, **6** was found to be an excellent catalyst for the disproportionation of **1**.

Sufficient evidence has not been provided to establish a detailed reaction pathway for the disproportionation of **1**. However, it may be noted that the first step in the disproportionation is the hydrogen-migration reaction of **1** to a conjugated diene, followed by a reaction with $Fe(CO)_5$ to give diene iron tricarbonyl complexes, such as **7**, **8**, or **9**, which are not isolated. Then, the iron atom abstracts an allylic hydrogen, yielding a π-allyl-hydro-iron complex (**10**),⁶⁾ which seems to be an essential intermediate for the disproportionation of **1**, followed by intra- or intermolecular hydrogen transfer with other organic or iron species to produce **3** and **4**.

The disproportionation of **1** catalyzed by **5** and **6** is probably initiated by the homolytic cleavage of **5**



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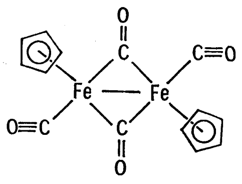

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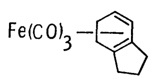

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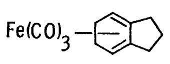

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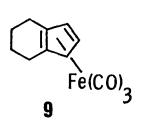

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$\pi\text{-}C_9H_{11}\text{-}FeH(CO)_3$

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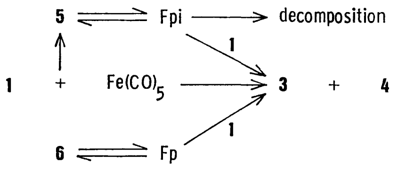
and **6** to dicarbonyl(η^5-3,4,5,6-tetrahydroindenyl)iron (Fpi), and dicarbonyl(η^5-cyclopentadienyl)iron (Fp) fragments,7) which then react with **1** to yield a diene iron complex. Subsequently, the reaction proceeds through a path analogous to that followed by $Fe(CO)_5$ to produce **3** and **4**. The outline of the disproportionation catalyzed by iron complexes is presented in Scheme 1.



Scheme 1. Outline of Disproportionation of **1** Catalyzed by **5** and **6**.

The difference in catalytic activity between **5** and **6** may be due to the ease of their homolytic cleavage and the stability of the resulting Fpi and Fp moieties in the course of the reaction.

The same reaction catalyzed by several metal carbonyls, such as Cr, Mn, Mo, and $Cp_2Mo_2(CO)_6$, gave only small amounts of **3** and **4**. No disproportionation product was obtained by the reaction of **1** catalyzed by Pd- and Rh-carbons, which are typical hydrogenation catalysts; *i.e.*, the dehydrogenated product, **4**, was exclusively produced by Pd, and the starting material, **1**, was recovered only by the use of Rh-carbon.

Experimental

The melting points are uncorrected. The IR spectra were taken with a JASCO-A202 spectrometer. The ^1H-NMR and ^{13}C-NMR spectra were recorded with a JEOL PMX-60 and a JNM-PS-100 FT-NMR spectrometer respectively. The mass spectra were measured with a JEOL-01SG apparatus. The GLC analyses were carried out on a Yanagimoto G1800 apparatus.

Materials. *cis*-Bicyclo[4.3.0]nona-3,7-diene (**1**) was prepared by a procedure reported previously.8)

Tetracarbonylbis(η^5-cyclopentadienyl)diiron (**6**) was prepared accordingly to the King method.9)

Tetracarbonylbis(η^5-4,5,6,7-tetrahydroindenyl)diiron (**5**) was prepared as follows: *cis*-Bicyclo[4.3.0]nona-3,7-diene **1** (12.0 g, 100 mmol) was allowed to react with $Fe(CO)_5$ (19.6 g, 100 mmol) in an autoclave at 230 °C for 4 h. After the filtration of the reaction mixture, the filtrate was dissolved in dichloromethane (200 dm^3). The crystals which separated out were collected and recrystallized from a solution of dichloromethane and hexane (1:9); ^{13}C-NMR ($CDCl_3$) δ 22.1(t), 22.6(t), 83.4(d), 89.2(d), 104.1(s), 214.0(s), 217.2(s); IR (KBr) 634, 831, 1432, 1754, 1951, 2920 cm^{-1}; MS *m*/*e* 462 (M^+), 175, 171 (base peak), 115, 91; Found: C, 57.11; H, 4.79%. Calcd for $C_{22}H_{22}O_4Fe_2$: C, 57.18; H, 4.80%.

Disproportionation Catalyzed by $Fe(CO)_5$. A mixture of **1** (12.0 g, 100 mmol) and a catalytic amount of $Fe(CO)_5$ (1.96 g, 10 mmol) was heated in an autoclave under a nitrogen atmosphere at 230 °C for 1—6 h. The reaction mixture was then poured into hexane to separate the **5**. After the removal of **5** and the solvent, bicyclo[4.3.0]non-1(6)-ene, **3** and **4**, were isolated; **3**, ^1H-NMR (CCl_4) δ 1.66 (m, 4H), 1.76 (m, 2H), 1.92 (m, 4H), 2.13—2.16 (m, 4H); ^{13}C-NMR ($CDCl_3$) δ 21.9(t), 23.4(t), 26.6(t), 36.3(t), 134.1(s); **4**, ^1H-NMR (CCl_4) δ 1.82 (q, 2H), 2.54 (t, 4H), 6.34 (s, 4H); ^{13}C-NMR ($CDCl_3$) δ 25.3(t), 32.8(t), 124.2(d), 125.9(d), 143.9(s).

Compound **3** was hydrogenated on Pd-carbon to *cis*-perhydroindene, which was also formed by the hydrogenation of **1**.

*Disproportionation Catalyzed by **5** and **6**.* The reaction was performed by the above procedure.

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