

Hydrogenation and Dimerization of Bicyclo[2.2.1]hepta-2,5-diene Catalyzed by Cobalt(I) Complexes

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(Received October 9, 1985)

Synopsis. Bicyclo[2.2.1]hepta-2,5-diene **1** was hydrogenated to bicyclo[2.2.1]hept-2-ene **2** and tricyclo[2.2.1.0^{2,6}]heptane **3** in a 70:30 ratio and dimerized to Binor-S **4** by [CoX(PPh₃)₃]-BF₃·Et₂O catalysts (X=halogen). **1** was dimerized to **4–7** having tricyclo[2.2.1.0^{2,6}]heptane skeletons by a [Co(SCN)(PPh₃)₃]-ZnBr₂-Zn system in THF.

Conjugated dienes were selectively hydrogenated to terminal olefins by [CoX(PPh₃)₃]-BF₃·Et₂O systems (X=halogen),¹⁾ but to *cis*-olefins by [Co(SCN)(PPh₃)₃]-ZnBr₂-Zn systems.²⁾ Although bicyclo[2.2.1]hepta-2,5-diene **1** is a nonconjugated diene, π -electron systems are supposed to interact through the through-space overlap.³⁾ When **1** was treated with the [Co(SCN)(PPh₃)₃]-ZnBr₂-Zn catalyst in the presence of hydrogen in 1,2-dimethoxyethane, bicyclo[2.2.1]hept-2-ene **2** (37%) and tricyclo[2.2.1.0^{2,6}]heptane **3** (31%) were formed with dimers (32%).²⁾

The hydrogenation of **1** with a [CoBr(PPh₃)₃]-BF₃·Et₂O catalyst was attempted to give small amounts of **2** and **3** and large amounts of dimers (Table 1). The yield of hydrogenation increased slightly when **1** and

BF₃·Et₂O were dropwise added to the cobalt complex solution. The ratio of **3**/**2** is lower than that (45/55) in the [Co(SCN)(PPh₃)₃]-ZnBr₂-Zn system.

The dimers exclusively consist of endo-*cis*-endo-heptacyclo[5.3.1.1^{2,6}.1^{4,12}.1^{9,11}.0^{3,5}.0^{8,10}]tetradecane, **4**, usually designated as "Binor-S."⁴⁾ [CoX(PPh₃)₃] alone has no activity toward the reaction of **1**. When **1** was treated with [CoX(PPh₃)₃] and BF₃ in bromobenzene under a nitrogen atmosphere, **4** was selectively produced in a short time. BF₃·Et₂O is superior to ZnBr₂ and AlCl₃ as the cocatalyst (Table 2). Silver perchlorate reacted with [CoCl(PPh₃)₃] to give a cationic complex, [Co(PPh₃)₃]⁺,⁵⁾ which was highly selective for the formation of **4** although the yield was low. Lewis acids serve as the production of cationic cobalt complexes. Only slight differences were observed on the reactivity and product composition between halogens in [CoX(PPh₃)₃].

Schrauzer et al. have stressed that the formation of **4** with [Zn[Co(CO)₄]₂] proceeds via a π -complex multicenter process which involves an intermediate containing one molecule of **1** coordinated to each of two cobalt atoms.⁴⁾ However, dimerization of **1** to **4** has occurred over mononuclear cationic complexes, binuclear catalysts not being uniquely active for its formation.⁵⁾ It is now recognized that monomeric cationic d⁸ phosphine complexes including Co, Rh, and Ir are active for the selective formation of **4**.⁶⁾

Haloarenes and arenes are suitable solvents for the reaction, but ethers (tetrahydrofuran and anisole) and dichloromethane are ineffective. Excess of **1** had no effect on the composition of dimers unlike the case with [Zn[Co(CO)₄]₂] that **4** was obtained exclusively using only a high catalyst to **1** ratio.^{4a)}

The dimerization of **1** with the [Co(SCN)(PPh₃)₃]-ZnBr₂-Zn system in THF gave dimers, **4–7** and an unidentified dimer(4%):

Table 1. Hydrogenation and Dimerization of **1** with [CoX(PPh₃)₃]-BF₃·Et₂O Catalysts

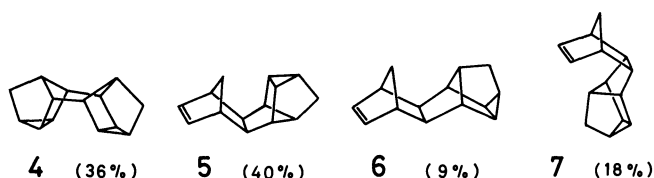
X	Time min	Yield/%	
		Hydrogenated products (2 : 3)	Dimers (4) ^{a)}
Cl	60	5.5 (72:28)	84 (94)
Br ^{b)}	90	19 (68:32)	81 (99)

a) Selectivity of **4** in dimers. b) **1** (2.0 mmol) and BF₃·Et₂O (0.4 mmol) in C₆H₅Cl (5 ml) was added dropwise over 55 min.

Table 2. Dimerization of **1** with [CoX(PPh₃)₃]-Lewis Acid Systems

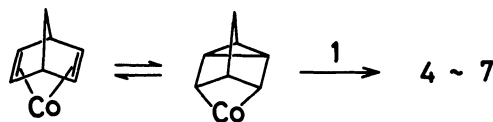
X	Lewis acid ^{a)}	Solvent	Time Conv.		Yield ^{b)} /%	
			h	%	4	Other dimers
Br	BF ₃ Et ₂ O (0.14)	C ₆ H ₅ Br	2	100	98	0
				100	100	0
		C ₆ H ₅ Cl	0.17	—	75	0
				—	85	0
Cl	BF ₃ Et ₂ O (2.0) ^{c)}	C ₆ H ₅ Br	10	99	95	0
		o-CH ₃ C ₆ H ₄ Cl	2	46	32	1.6
				50	35	1.4
		C ₆ H ₅ Br	2	18	2.2	0.5
				55	53	0
		AgClO ₄ (2.0)	14	55	53	0

a) The number in parentheses is the ratio of Lewis acid to the cobalt complex. b) Based on **1** added. c) **1** (21.8 mmol, 1/Co=218) was reacted at 0°C.



The dimers, **4–7**, consist at least of one tricyclo[2.2.1.0^{2,6}]heptane skeleton. The catalytic activity and selectivity of the [Co(SCN)(PPh₃)₃]-ZnBr₂-Zn system are lower than those of [CoX(PPh₃)₃]-BF₃·Et₂O.

Deuteration of **1** by the [Co(SCN)(PPh₃)₃]-ZnBr₂-Zn system occurs specifically via the endo-addition of deuterium.²⁾ The tricyclo[2.2.1.0^{2,6}]heptane skeleton of dimers by both Co(I) complex systems suggests the following likely intermediates:



Tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane (quadricyclane) **8** was treated with [CoBr(PPh₃)₃]-BF₃·Et₂O to give **4** exclusively. **1** was detected during the formation of **4**—**7** by the reaction of **8** with the [Co(SCN)(PPh₃)₃]-ZnBr₂-Zn system.

Experimental

Chlorobenzene, bromobenzene and *o*-chlorotoluene were commercially purified materials and used without further purification. Tetrahydrofuran was heated over lithium aluminium hydride and distilled just before use. Boron trifluoride-diethyl ether complex, zinc bromide, aluminium chloride and silver perchlorate were used without further purification. [CoX(PPh₃)₃] (X=Cl, Br) was prepared according to the method described earlier.⁷⁾ ¹H and ¹³C NMR spectra were recorded on a Nicolet NT-300 and a JEOL FX-100 spectrometer, respectively.

Hydrogenation and Dimerization of 1 with [CoX(PPh₃)₃]-BF₃·Et₂O Catalysts. In a three-necked 100-ml flask [CoX(PPh₃)₃] (0.1 mmol) was placed. Chlorobenzene (10 ml) was added and the flask was dipped in an ice-water bath after several freeze-thaw operations. The flask was filled with atmospheric pressure of hydrogen and BF₃·Et₂O (0.2 mmol) and **1** (2.0 mmol) were added successively. After 60 min the products were analyzed by a Shimadzu 6A gas chromatograph (column for hydrogenated products: 30% Apiezon grease L 2 m, 80°C; column for dimers: 20% SE-30, 2 m, 160°C, and 20% PEG-20M 2 m, 175°C). Hydrogenated products were identified as **2** and **3**.⁸⁾ **4** was identified by comparing its ¹H NMR spectrum with that of an authentic sample.⁴⁾

Dimerization of 1 with [CoX(PPh₃)₃]-Lewis Acid. To a solution of [CoX(PPh₃)₃] (0.1 mmol) and Lewis acid in a solvent (10 ml) under nitrogen was added **1** (5.45 mmol) at r.t. and the mixture was stirred for an appropriate period.

Dimers were analyzed by GLC.

Dimerization of 1 with [Co(SCN)(PPh₃)₃]-ZnBr₂-Zn System. The catalyst was prepared in situ from the reduction of [Co(SCN)₂(PPh₃)₂] (0.3 mmol) with Zn (3.0 mmol) and ZnBr₂ (1.0 mmol) in THF (10 ml) under nitrogen at 17°C.²⁾ After the color of the solution changed from purple to brown (2—3 h), **1** (2.0 mmol) was added and the mixture was stirred at 17°C for 20 h. Dimers were separated by a preparative gas chromatograph (20% SE-30, 2 m, 175°C) and identified by comparing their ¹H and ¹³C NMR spectra with those of authentic samples.⁹⁾

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- 6) Schrauzer et al.⁴⁾ assumed that **1** in conjunction with BF₃·Et₂O reduced [CoCl₂(PPh₃)₂], [RhCl(PPh₃)₃], and [IrCl(CO)(PPh₃)₂] to afford [(Lig)_nM-M(Lig)_n] (M=Co, Rh, Ir, Lig=PPh₃, CO). The assumption is less probable since the addition of AgClO₄ to a [CoCl(PPh₃)₃] solution or that of PPh₃ to [Rh(NBD)₂]⁺ (NBD=**1**)^{5a)} results in the selective production of **4**.
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