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

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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(PPh_3)$_3$]-$BF_3\cdot Et_2O$ catalysts (X=halogen). **1** was dimerized to **4—7** having tricyclo[2.2.1.$0^{2,6}$]heptane skeletons by a [Co(SCN)(PPh_3)$_3$]-$ZnBr_2$-Zn system in THF.

Conjugated dienes were selectively hydrogenated to terminal olefins by [CoX(PPh_3)$_3$]-$BF_3\cdot Et_2O$ systems (X=halogen),[1] but to *cis*-olefins by [Co(SCN)(PPh_3)$_3$]-$ZnBr_2$-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)(PPh_3)$_3$]-$ZnBr_2$-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(PPh_3)$_3$]-$BF_3\cdot Et_2O$ 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 $BF_3\cdot Et_2O$ were dropwise added to the cobalt complex solution. The ratio of **3**/**2** is lower than that (45/55) in the [Co(SCN)(PPh_3)$_3$]-$ZnBr_2$-Zn system.

Table 1. Hydrogenation and Dimerization of **1** with [CoX(PPh_3)$_3$]-$BF_3\cdot Et_2O$ Catalysts

X	Time min	Yield/% Hydrogenated products (**2**:**3**)	Yield/% 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 BF_3 Et_2O (0.4 mmol) in C_6H_5Cl (5 ml) was added dropwise over 55 min.

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(PPh_3)$_3$] alone has no activity toward the reaction of **1**. When **1** was treated with [CoX(PPh_3)$_3$] and BF_3 in bromobenzene under a nitrogen atmosphere, **4** was selectively produced in a short time. $BF_3\cdot Et_2O$ is superior to $ZnBr_2$ and $AlCl_3$ as the cocatalyst (Table 2). Silver perchlorate reacted with [CoCl(PPh_3)$_3$] to give a cationic complex, [Co(PPh_3)$_3$]$^+$,[1] 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(PPh_3)$_3$].

Table 2. Dimerization of **1** with [CoX(PPh_3)$_3$]-Lewis Acid Systems

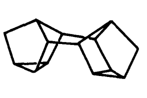
X	Lewis acid[a)]	Solvent	Time h	Conv. %	Yield[b)]/% **4**	Yield[b)]/% Other dimers
Br	BF_3Et_2O (0.14)	C_6H_5Br	2	100	98	0
	(4.1)			100	100	0
	(2.0)	C_6H_5Cl	0.17	—	75	0
		C_6H_5Br		—	85	0
		o-$CH_3C_6H_4Cl$		—	72	0
Cl	BF_3Et_2O (2.0)[c)]	C_6H_5Br	10	99	95	0
	$ZnBr_2$ (1.0)		2	46	32	1.6
	(2.0)		14	50	35	1.4
	$AlCl_3$ (1.0)		2	18	2.2	0.5
	$AgClO_4$ (2.0)		14	55	53	0

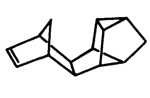
a) The number in parentheses is the ratio of Lewis acid to the cobalt complex. b) Based on **1** added. c) **1** (21.8 mmol, **1**/Co=218) was reacted at 0 °C.

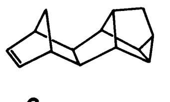
Schrauzer et al. have stressed that the formation of **4** with [Zn[Co(CO)$_4$]$_2$] proceeds via a π-complex multicenter process which involves an intermediate containing one molecule of **1** coordinated to each of two cobalt atoms.[4] However, dimerization of **1** to **4** has occurred over mononuclear cationic complexes, binuclear catalysts not being uniquely active for its formation.[5] It is now recognized that monomeric cationic d^8 phosphine complexes including Co, Rh, and Ir are active for the selective formation of **4**.[6]

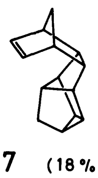
Haloarenes and arenes are suitable solvents for the reaction, but ethers (tetrahydrofuran and anisole) and dichloromethane are ineffective. Excess of **1** had no effect on the composition of dimers unlike the case with [Zn[Co(CO)$_4$]$_2$] that **4** was obtained exclusively using only a high catalyst to **1** ratio.[4a)]

The dimerization of **1** with the [Co(SCN)(PPh_3)$_3$]-$ZnBr_2$-Zn system in THF gave dimers, **4—7** and an unidentified dimer(4%):


4 (36%)

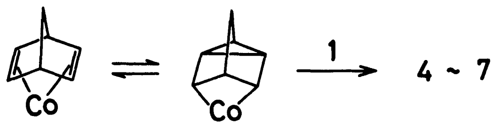

5 (40%)


6 (9%)


7 (18%)

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)(PPh_3)$_3$]-$ZnBr_2$-Zn system are lower than those of [CoX(PPh_3)$_3$]-$BF_3\cdot Et_2O$.

Deuteration of **1** by the [Co(SCN)(PPh_3)$_3$]-$ZnBr_2$-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(PPh_3)$_3$]–$BF_3 \cdot Et_2O$ to give **4** exclusively. **1** was detected during the formation of **4**—**7** by the reaction of **8** with the [Co(SCN)(PPh_3)$_3$]–$ZnBr_2$–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(PPh_3)$_3$] (X=Cl, Br) was prepared according to the method described earlier.[7] ^{1}H and ^{13}C NMR spectra were recorded on a Nicolet NT-300 and a JEOL FX-100 spectrometer, respectively.

Hydrogenation and Dimerization of 1 with [CoX(PPh_3)$_3$]–$BF_3 \cdot Et_2O$ Catalysts. In a three-necked 100-ml flask [CoX(PPh_3)$_3$] (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 $BF_3 \cdot Et_2O$ (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 ^{1}H NMR spectrum with that of an authentic sample.[4]

Dimerization of 1 with [CoX(PPh_3)$_3$]–Lewis Acid. To a solution of [CoX(PPh_3)$_3$] (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)(PPh_3)$_3$]–$ZnBr_2$–Zn System. The catalyst was prepared in situ from the reduction of [Co(SCN)$_2$(PPh_3)$_2$] (0.3 mmol) with Zn (3.0 mmol) and $ZnBr_2$ (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 ^{1}H and ^{13}C NMR spectra with those of authentic samples.[9]

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6) Schrauzer et al.[4] assumed that **1** in conjuction with $BF_3 \cdot Et_2O$ reduced [CoCl$_2$(PPh_3)$_2$], [RhCl(PPh_3)$_3$], and [IrCl(CO)(PPh_3)$_2$] to afford [(Lig)$_n$M-M(Lig)$_n$] (M=Co, Rh, Ir, Lig=PPh_3, CO). The assumption is less probable since the addition of $AgClO_4$ to a [CoCl(PPh_3)$_3$] solution or that of PPh_3 to [Rh(NBD)$_2$]$^+$ (NBD=**1**)[5a] results in the selective production of **4**.

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