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THE REACTIONS OF SUBSTITUTED METHINYLTRICOBALT ENNEACARBONYLS WITH NORBORNADIENE

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SUMMARY

The reactions of substituted methinyltricobalt enneacarbonyls, $XCCo_3(CO)_9$, with norbornadiene were investigated. When the apical substituent X was alkyl, aryl or F, the known complexes $XCCo_3(CO)_7$(Norb) were obtained. The complexes $(C_7H_9)CCo_3(CO)_9$ and $(C_8H_9O)CCo_3(CO)_9$ were isolated from the reaction of $HCCo_3(CO)_9$. $BrCCo_3(CO)_9$ or $ClCCo_3(CO)_9$ catalyzed the dimerization reaction in methylene dichloride of norbornadiene to give Binor S (1,2,4: 5,6,8-dimetheno-*s*-indacene).

INTRODUCTION

Many transition metal clusters have been synthesized and their reactions investigated. In the reactions of substituted methinyltricobalt enneacarbonyls, $XCCo_3(CO)_9$, it has been reported that the two types of reactions take place depending upon the apical substituent, X. When the apical substituent, X, is alkyl, aryl or F, substitution reactions take place to give complexes of the type $XCCo_3(CO)_mL_n$, where L is a tertiary phosphine[1], arsine[1], arene[2], norbornadiene[3,4], or cyclooctatetraene[5]. On the other hand, when the apical substituent X is Br or Cl, the reactions accompanying the C–X bond cleavage occur to produce complexes, such as $CH_3O_2CCCo_3(CO)_9$[6,7], $[CCo_3(CO)_9]_2$[8,9], $OC[CCo_3(CO)_9]_2$[9], $Co_5(CO)_{15}C_3H$[10], $Co_6(CO)_{18}C_4$[11], and $Co_8(CO)_{24}C_6$[12]. It has also been reported that $HCCo_3(CO)_9$ reacted with organomercurials to give alkyl or aryl substituted methinyltricobalt enneacarbonyls[13].

We have found that the two different types of complexes were formed in the reactions of $XCCo_3(CO)_9$ with norbornadiene, depending upon the apical substituent X. It was also found that norbornadiene was converted selectively to Binor S (1,2,4: 5,6,8-dimetheno-*s*-indacene)[14] in the presence of a catalytic amount of $BrCCo_3(CO)_9$ in refluxing methylene dichloride. We wish to report here the results of these experiments.

EXPERIMENTAL

IR spectra of the products were taken on a Jasco Model I 402G spectrometer, and NMR spectra were recorded on a Hitachi Perkin–Elmer R-20 instrument, using tetramethylsilane as internal standard. Mass spectra were measured with a JMS-07S mass spectrometer. Molecular weights were measured in benzene or methylene dichloride solutions using a Knauer Vapor Pressure Osmometer.

Gas chromatography

The reaction products, dimers of norbornadiene, were analyzed using a 3 m polyethylene glycol 20M column with a Shimazu Gas Chromatograph, Model GC-2C. Conditions were as follows: column temperature, 200°C; carrier gas (helium) speed, 60–70 ml/min; internal standard, n-hexadecane.

Formation of $XCCo_3(CO)_7(Norb)$

A typical procedure is as follows. A solution of $XCCo_3(CO)_9$ (0.3 g) and norbornadiene (0.3 g) in hexane (20 ml) was heated under reflux in an atmosphere of nitrogen for 3 h with stirring. After removal of solvent and excess norbornadiene, the residue was extracted with hexane, and chromatographed on a silica gel column. A first purple eluate (hexane as eluant) afforded a small amount of unchanged $XCCo_3(CO)_9$. A second black eluate (benzene/hexane 3/7 as eluant) afforded black crystals of $XCCo_3(CO)_7(Norb)$, on evaporation, which were recrystallized from hexane at −20°C. The yields and analytical data of these complexes are summarized in Table 1.

Reaction of $HCCo_3(CO)_9$ and norbornadiene

(*a*). A solution of $HCCo_3(CO)_9$ (0.3 g) and norbornadiene (0.3 g) in hexane (15 ml) was heated under reflux in an atmosphere of nitrogen for 3 h. After removal of solvent, the residue was extracted with hexane, filtered, then chromatographed on a silica gel column. A first eluate (hexane as eluant) gave a small amount of $HCCo_3(CO)_9$. A second eluate (benzene/hexane 1/4 as eluant) afforded 106 mg of purple crystals which were recrystallized from hexane at −70°C to give crystals of $(C_8H_9O)CCo_3(CO)_9$, m.p. 65–66°C. (Found: C, 38.46; H, 1.55. $(C_8H_9O)CCo_3(CO)_9$ calcd.: C, 38.47; H, 1.61%.)

TABLE 1

YIELD AND ANALYTICAL DATA OF $XCCo_3(CO)_7(Norb)$

Complex	*Yield (%)*	*Analysis found (calcd.) (%)*		*Mol. wt. found (calcd.)*
		C	*H*	
$CH_3CCo_3(CO)_7(Norb)$	65	39.22 (39.02)	2.25 (2.24)	486 (492)
$C_6H_5CCo_3(CO)_7(Norb)$	40	45.61 (45.51)	2.54 (2.35)	542 (554)
$CH_3OOCCCo_3(CO)_7(Norb)$	35	38.23 (38.06)	2.18 (2.05)	541 (536)
$C_2H_5OOCCCo_3(CO)_7(Norb)$	40	39.59 (36.29)	2.36 (2.39)	557 (550)
$FCCo_3(CO)_7(Norb)$	18.5	35.90 (36.29)	1.69 (1.61)	

(*b*). A solution of $HCCo_3(CO)_9$ (2 g) and norbornadiene (0.2 ml) in hexane (100 ml) was heated under reflux in an atmosphere of nitrogen for 30 min. After removal of solvent, the residue was dissolved in hexane, filtered, and chromatographed on a silica gel column. A first eluate (hexane as eluant) gave 1.2 g of $HCCo_3(CO)_9$. A second eluate (benzene/hexane 1/9 as eluant) afforded 195 mg of purple crystals of $(C_7H_9)CCo_3(CO)_9$. After recrystallization from methanol the crystalline complex melted at 62–63°C, (Found: C, 38.45; H, 1.56. $(C_7H_9)CCo_3(CO)_9$ calcd.: C, 38.23; H, 1.70%.) A third eluate (benzene/hexane 1/4 as eluant) gave 450 mg of crystals of $(C_8H_9O)CCo_3(CO)_9$.

From the reaction of norbornadiene and $DCCo_3(CO)_9$ (prepared via reaction of $DCBr_3$ with $Co_2(CO)_8$), the complexes $(C_7H_8D)CCo_3(CO)_9$ and $(C_8H_8DO)CCo_3(CO)_9$ were obtained in manner similar to that described above.

Dimerization of norbornadiene

A typical procedure of the dimerization of norbornadiene is as follows. A solution of norbornadiene (3 g) and $BrCCo_3(CO)_9$ (0.3 g) in methylene dichloride (15 ml) was heated under reflux in an atmosphere of nitrogen for 3 h with stirring. After removal of solvent under reduced pressure, the residue was taken up in hexane, filtered, and chromatographed on a silica gel column, using hexane as eluant. The initial colorless hexane eluate contained Binor S, which was recrystallized from ethanol to give pure colorless crystals (m.p. 65°C) in 82% yield. (Found: C, 91.20; H, 8.63. Mol. wt. 183. $C_{14}H_{16}$ calcd.: C, 91.25; H, 8.75%. Mol. wt. 184.) The NMR spectrum exhibited signals at δ 1.9 (4 protons), 1.6 (2 protons), 1.3 (4 protons), and 1.05 ppm (6 protons), which agreed with the data reported by Schrauzer *et al.*[14]. Purple crystals of catalyst were recovered from the second purple hexane eluate (35%).

Kinetic experiments

Kinetic experiments were carried out as follows. (*a*). A solution of norbornadiene (1 g) in methylene dichloride (5 ml) was heated under reflux in the presence of varying amounts of $BrCCo_3(CO)_9$. Samples were taken from the reaction solution at regular intervals and analyzed by gas chromatography.

(*b*). Hexane solution (1 ml) containing varying amounts of norbornadiene was added to a methylene dichloride solution (5 ml) of $BrCCo_3(CO)_9$ (200 mg). The solution was heated under reflux. Samples were taken from the reaction solution at regular intervals and analyzed by gas chromatography.

RESULTS AND DISCUSSION

Norbornadiene complexes

When norbornadiene reacted with $XCCo_3(CO)_9$, in which the apical substituent X was CH_3, C_6H_5, CH_3O_2C, $C_2H_5O_2C$, or F, the complexes $XCCo_3(CO)_7(Norb)$ were isolated. Physical data of these complexes are summarized in Tables 2 and 3. This type of complex has been recently reported[3,4].

In contrast, the reaction of $HCCo_3(CO)_9$ with norbornadiene in refluxing hexane provided a mixture of two products which could be separated by chromatography on a silica gel column. It was found that these two complexes have the empirical formulae $C_{17}H_9O_9Co_3$ (A) and $C_{18}H_9O_{10}Co_3$ (B) respectively. In the reaction with

TABLE 2

MELTING POINTS AND IR SPECTRA OF $XCCo_3(CO)_7(Norb)$

Complex	*M.p. (°C)*	*ν(CO)[a] (cm⁻¹)*
$CH_3CCo_3(CO)_7(Norb)$	118	2083 m, 2067 (sh), 2030 vs, 1996 vs, 1988 vs, 1968 w, 1958 vw
$C_6H_5CCo_3(CO)_7(Norb)$	151–152	2094 vs, 2052 vs, 2048 vs, 2015 (sh), 2005 w, 1997 m, 1990 m
$CH_3OOCCCo_3(CO)_7(Norb)$	122–123	2099 vs, 2060 vs, 2050 vs, 2030 m, 2010 m, 1990 w
$C_2H_5OOCCCo_3(CO)_7(Norb)$	136	2090 m, 2043 vs, 2023 vs, 2005 s, 1990 m, 1972 w, 1952 vw
$FCCo_3(CO)_7(Norb)$	95	2097 s, 2078 w, 2055 vs, 2050 vs, 2023 m, 1995 w

[a] Hexane solution. s, strong; w, weak; m, medium; v, very; (sh), shoulder.

TABLE 3

NMR DATA OF $XCCo_3(CO)_7(Norb)$[a]

Complex	*δ (ppm)*	*No. of proton*	*Assignment*
$CH_3CCo_3(CO)_7(Norb)$	4.40	3	CH_3
	0.50	2	CH_2 of Norb
	2.50	2	CH of Norb
	3.30	4	=CH of Norb
$C_6H_5CCo_3(CO)_7(Norb)$	7.85	2	phenyl
	7.15	3	
	0.30	2	CH_2 of Norb
	2.50	2	CH of Norb
	3.40	4	=CH of Norb
$CH_3O_2CCCo_3(CO)_7(Norb)$	3.82	3	CH_3
	0.45	2	CH_2 of Norb
	3.00	2	CH of Norb
	3.70	4	=CH of Norb
$C_2H_5O_2CCCo_3(CO)_7(Norb)$	1.27	3	CH_3 of ethyl
	4.55	2	CH_2 of ethyl
	0.50	2	CH_2 of Norb
	3.13	2	CH of Norb
	3.85	4	=CH of Norb
$FCCo_3(CO)_7(Norb)$	0.40	2	CH_2 of Norb
	3.00	2	CH of Norb
	3.60	4	=CH of Norb

[a] Solvent, C_6D_6; TMS as internal standard.

TABLE 4

PHYSICAL DATA OF COMPLEX (A), $C_{17}H_9O_9Co_3$

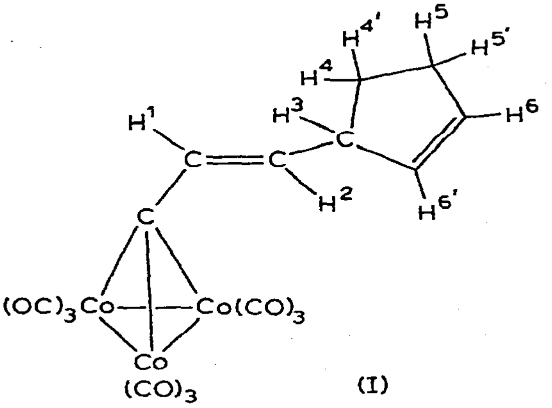
M.p.	62–63°C	
Mass spectrum	$(C_7H_9)CCo_3(CO)_n^+$ $m/e = 534 - n \times 28$ $(n = 0 \approx 9)$	
IR spectrum	$\nu(C{\equiv}O)$ 2100 w, 2055 vs, 2038 vs, 2025 m $cm^{-1\,a}$	
	$\nu(C{=}C)$ 1595 m $cm^{-1\,b}$	assigned to *trans* olefin
	$\delta(CH)$ 945 m $cm^{-1\,b}$	
NMR spectrum[c]	δ 7.38 (d, $J(H^1{-}H^2) = 15$ Hz)	1H olefinic proton (H^1)
	δ 5.99 (d,d, $J(H^2{-}H^3) = 8$ Hz)	1H olefinic proton (H^2)
	δ 5.65 (s)	2H olefinic protons (H^6 and $H^{6'}$)
	δ 2.0–3.0 (c)	5H methine and methylene protons (H^3, H^4, $H^{4'}$, H^5, and $H^{5'}$)

[a] Hexane solution. [b] Nujol. [c] Solvent, $CCl_4 + DMSO\text{-}d_6$; TMS as internal standard. (c), Complex.

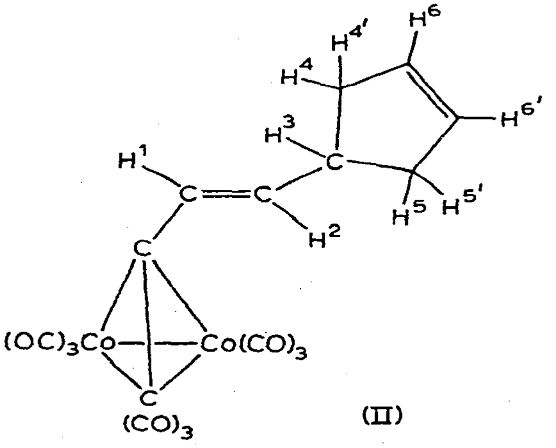
$DCCo_3(CO)_9$, complexes $C_{17}H_8DO_9Co_3$ (A′) and $C_{18}H_8DO_{10}Co_3$ (B′) could be isolated.

Physical data of complex (A) are shown in Table 4. The mass spectrum of this complex shows stepwise loss of nine molecules of carbon monoxide and it is recognized that the C≡O stretching region in the IR spectrum of complex (A) is consistent with a $CCo_3(CO)_9$ moiety (C_{3v}). Therefore, it is reasonable to consider that complex (A) has the structure $(C_7H_9)CCo_3(CO)_9$. It can be seen from the NMR data that complex (A) contains two *trans* olefin protons and two equivalent olefin protons. The IR spectrum also shows the presence of a *trans* olefinic bond in the complex. From these observations, we assigned either of structures (I) or (II) to complex (A).

The mass spectrum of the deuterated complex (A′) shows peaks at $m/e = 535 - (n \times 28)$ $(n = 0 \approx 9)$. IR and NMR spectra of the complex (A′) are same as those of the complex (A), except for a decrease in the number of protons from five to four in the δ 2.0–3.0 region of its NMR spectrum. This suggests that the deuterium atom is attached to the methylene carbon atom of the cyclopentenyl ring of (I) or (II).

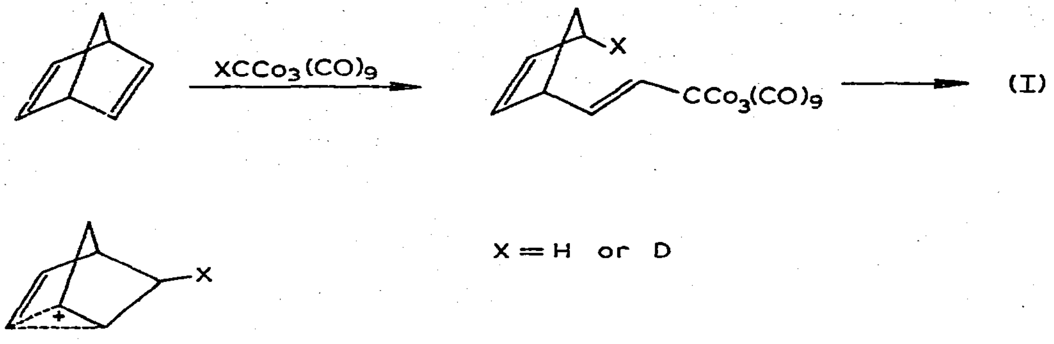


(I)



(II)

From the results described above, the direct insertion of norbornadiene to the C–X bond of $XCCo_3(CO)_9$ (X = H or D) to produce the complex with structure (I) can be speculated. As an alternative route, it can also be considered that the reaction proceeds via an intermediate such as (III) to produce the complex with structure (II). As the NMR spectrum of $HCCo_3(CO)_9$ shows a peak at δ 11.36 in a hexadeuteriobenzene solution, it is acceptable to consider that $HCCo_3(CO)_9$ can act as an acid.



(III)

The physical properties of complex (B) are summarized in Table 5. The C≡O stretching frequency region in the IR spectrum of complex (B) suggests that it contains a $CCo_3(CO)_9$ moiety (C_{3v}). It is also recognized from IR and NMR data that an aldehyde group is included in complex (B). This is supported by the observation that the mass spectrum of this complex shows peaks corresponding to $(C_8H_9O)CCo_3(CO)_n^+$ ($m/e = 562 - n \times 28$, $n = 0 \approx 9$) and $(C_7H_9)CCo_3^+$ ($m/e = 282$). Further, observation of the peak corresponding to $Co_3CCH{=}CHCHO^+$ ($m/e = 244$) in the mass spectrum suggests that the complex (B) has the norbornene structure, since loss of cyclopentadiene from norbornene by a retro Diels–Alder reaction is a common reaction, taking place easily under the conditions of measurement. Such a peak was

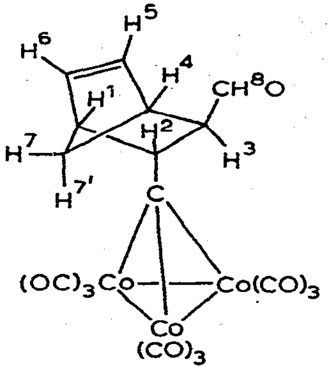
TABLE 5

PHYSICAL DATA OF COMPLEX (B), $C_{18}H_9O_{10}Co_3$

M.p.	65–66°C	
Mass spectrum	$(C_8H_9O)CCo_3(CO)_n^+$ $m/e = 562 - n \times 28$ ($n = 0 \approx 9$)	
	$(C_7H_9)CCo_3^+$ $m/e = 282$	
	$Co_3CCH{=}CHCHO^+$ $m/e = 244$	
IR spectrum	ν(C≡O) 2110 m, 2068 (sh), 2058 vs, 2047 vs, 2025 m cm$^{-1\,a}$	
	ν(C=O) 1728 cm$^{-1\,b}$	assigned to aldehyde group
	ν(CH) 2730 w, 2820 w cm$^{-1\,b}$	
NMR spectrum[c]	δ 9.22 (s)	1 H aldehyde proton (H^8)
	δ 6.06 (m)	1 H olefinic protons (H^5, H^6)
	δ 5.73 (m)	1 H
	δ 3.95 (d, $J(H^2–H^3)$ 5.2 Hz)	1 H methine proton (H^2)
	δ 2.88 (m)	1 H methine proton (H^3)
	δ 2.74 (s)	2 H bridge-head protons (H^1, H^4)
	δ 1.87 (d, $J(H^7–H^{7'})$ 9 Hz)	1 H methylene protons (H^7, $H^{7'}$)
	δ 1.41 (d, $J(H^7–H^{7'})$ 9 Hz)	1 H

[a] Hexane solution. [b] CCl_4 solution. [c] Solvent, C_6D_6; TMS as internal standard. (s), Singlet; (m), multiplet; (d), doublet.

not observed in the mass spectrum of complex (A). We assigned structure (IV) to complex (B) on the basis of these observations, with a consideration of minimizing its steric requirements.



(IV)

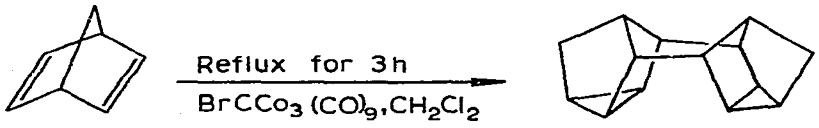
The mass spectrum of the deuterated complex (B') shows peaks corresponding to $(C_8H_8DO)CCo_3(CO)_n^+$ ($m/e = 563 - n \times 28$, $n = 0 \approx 9$), $(C_7H_8D)CCo_3^+$ ($m/e = 283$) and $Co_3CCH{=}CHCDO^+$ ($m/e = 245$). The IR spectrum of the complex (B') shows a strong band at 1712 cm^{-1} but bands which are attributable to C–H stretching frequencies of the aldehyde group are not observed. The signal at δ 9.22 is not observed in the NMR spectrum of complex (B'), although the other signals which appeared in the spectrum of the complex (B) are observed unchanged.

These results confirmed that the deuterium atom of $DCCo_3(CO)_9$ was incorporated into the aldehyde group. Therefore, it is considered that complexes (B) and (B') were formed by the insertion of carbon monoxide and norbornadiene into the C–X bond of $XCCo_3(CO)_9$ (X = H or D).

We found that insertion reactions of olefins into the C–H bond of $HCCo_3(CO)_9$ take place readily. For example, $C_2H_5CCo_3(CO)_9$ was formed from the reaction of ethylene and $HCCo_3(CO)_9$. Details of these reactions will be reported in the near future.

Dimerization of norbornadiene

Although no norbornadiene complexes were obtained in the reactions of $BrCCo_3(CO)_9$ and $ClCCo_3(CO)_9$ with norbornadiene, it was found that dimerization of norbornadiene took place in the presence of a catalytic amount of $BrCCo_3(CO)_9$. Thus, the reaction took place to produce only one product, in high yield, when a solution of norbornadiene in methylene dichloride was heated for 3 h under reflux in the presence of $BrCCo_3(CO)_9$. It was confirmed that the product was Binor S from



Binor S

its elemental analysis, molecular weight measurement, and IR and NMR data. As it was shown that norbornadiene dimerized selectively under mild conditions, the dimerization reaction of norbornadiene by $XCCo_3(CO)_9$ was investigated in more detail.

The dependence of the yield of Binor S and of the selectively of the reaction on the variation of the apical substituent, X, of $XCCo_3(CO)_9$ was examined in refluxing methylene dichloride. The results are summarized in Table 6. $BrCCo_3(CO)_9$ and $ClCCo_3(CO)_9$ were found to be effective catalysts for the selective dimerization of norbornadiene. The former was more effective than the latter. Other substituted methinyltricobalt enneacarbonyls used in the reactions were found to be almost inactive.

The results shown in Table 7 were obtained when the reactions were carried out at 45°C for 40 min in the presence of $BrCCo_3(CO)_9$ in various solvents. The reactions did not take place in solvents other than halogenated solvents under these reaction conditions. Methylene dichloride was found to be the best of the halogenated

TABLE 6

EFFECT OF X OF $XCCo_3(CO)_9$[a]

Catalyst	*Conversion (%)*	*Yield of dimers (%)*	
		Binor S	*Other dimers*
$BrCCo_3(CO)_9$	84	100	—
$ClCCo_3(CO)_9$	37	100	—
$FCCo_3(CO)_9$	6	100	—
$HCCo_3(CO)_9$	2	100	—
$CH_3CCo_3(CO)_9$	1	100	—
$C_6H_5CCo_3(CO)_9$	2	100	—
$C_2H_5OOCCCo_3(CO)_9$	3	100	—

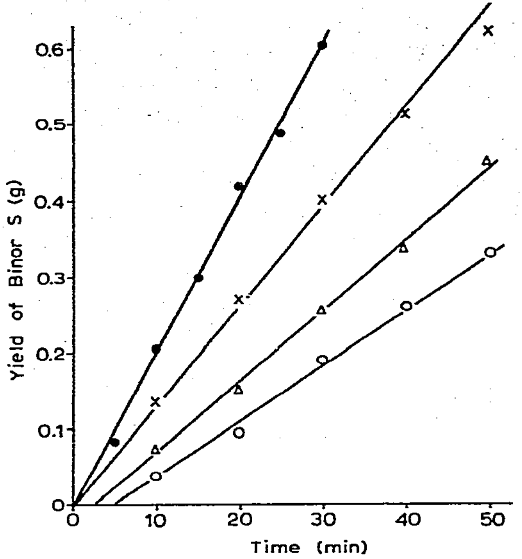
[a] For $XCCo_3(CO)_9$, 0.1 g; norbornadiene, 1 g; CH_2Cl_2, 5 ml; reflux for 3 h.

TABLE 7

EFFECT OF SOLVENT[a]

Solvent	*Conversion (%)*	*Selectivity to Binor S formation (%)*	*Yield of catalyst recovered (%)*
Benzene	0	—	85
Hexane	0	—	75
THF	0	—	86
CH_2BrCH_2Br	2	100	86
CH_2ClCH_2Cl	4	100	86
CH_2Br_2	3	100	86
CH_2Cl_2	57	100	85

[a] For $BrCCo_3(CO)_9$, 200 mg; norbornadiene, 1 g; solvent, 5 ml; reaction temp., 45°C; reaction time, 40 min.



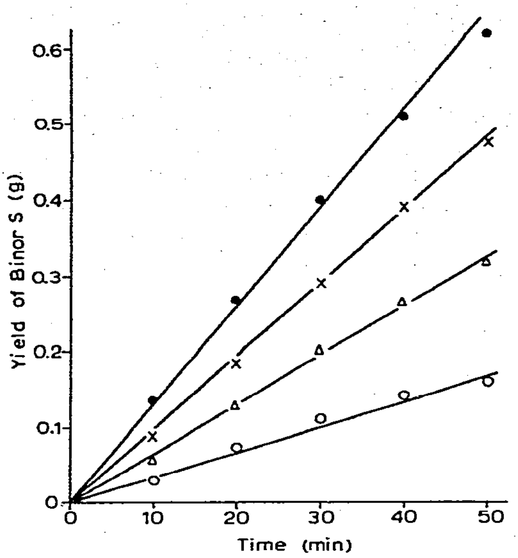
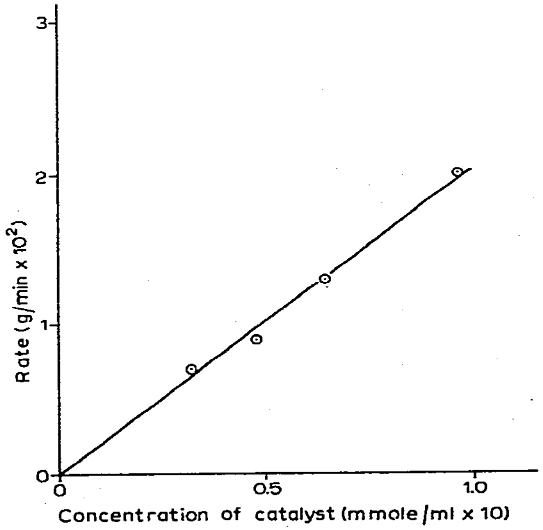


Fig. 1. Rates of product formation in the reaction of norbornadiene (1 g) in the presence of $BrCCo_3(CO)_9$ in CH_2Cl_2 (5 ml) under reflux. ○ 0.032 mmole/ml of catalyst, △ 0.048 mmole/ml of catalyst, × 0.064 mmole/ml of catalyst, ● 0.096 mmole/ml of catalyst.

Fig. 2. Rates of product formation in the reaction of norbornadiene in the presence of $BrCCo_3(CO)_9$ (200 mg) in CH_2Cl_2 (5 ml) under reflux. ○ 0.45 mmole/ml of Norb, △ 0.90 mmole/ml of Norb, × 1.35 mmole/mol of Norb, ● 1.80 mmole/ml of Norb.



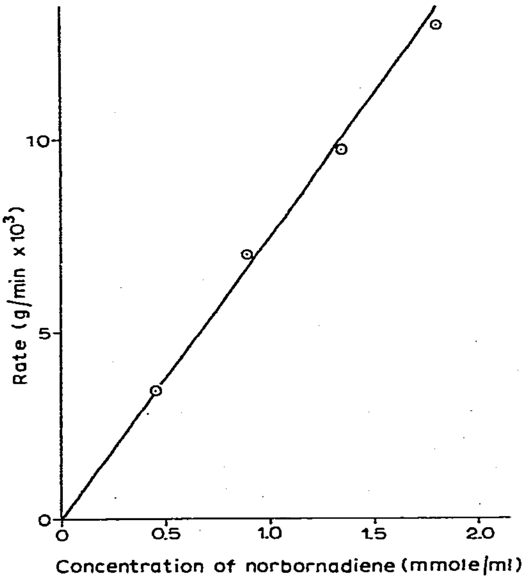


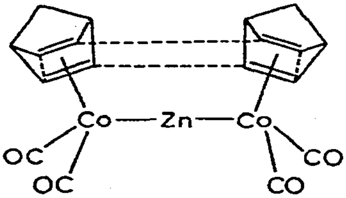
Fig. 3. Rate *vs.* concentration of catalyst in dimerization of norbornadiene.

Fig. 4. Rate *vs.* concentration of norbornadiene in dimerization reaction.

solvents. When the reactions were stopped, the reaction solutions appeared to be homogeneous and the catalyst was recovered in about 85% yield in all cases.

Since the reaction appears to proceed in an homogeneous system we examined the dependence of the reaction rates on the concentration of norbornadiene and catalyst. As shown in Figs. 1 and 2, the yields of Binor S increased linearly with the reaction time, although some induction period was observed at lower concentrations of catalyst. It is recognized that the dimerization rates obtained from the slopes of these linear plots were directly proportional to the concentrations of both norbornadiene and catalyst (Figs. 3 and 4).

From these observations, the reaction appears to proceed with retention of the skeletal structure of the cluster catalyst; the mode of action of the catalyst has remained obscure. Our results suggest a different mode of action of $BrCCo_3(CO)_9$ from that proposed by Schrauzer *et al.*[14] who proposed a mechanism in which norbornadiene is dimerized through an intermediate such as (V) to Binor S via a multicenter π-complex process. They also reported that the rates of reaction depended on the amount of catalyst used and the square of the concentration of norbornadiene in the reaction when $Zn[Co(CO)_4]_2/BF_3 \cdot O(C_2H_5)_2$ is the catalyst[15].



(V)

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