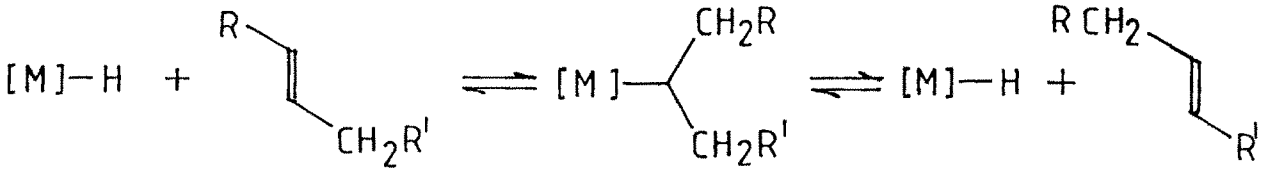
CHAPTER 6
Isomerization Reaction

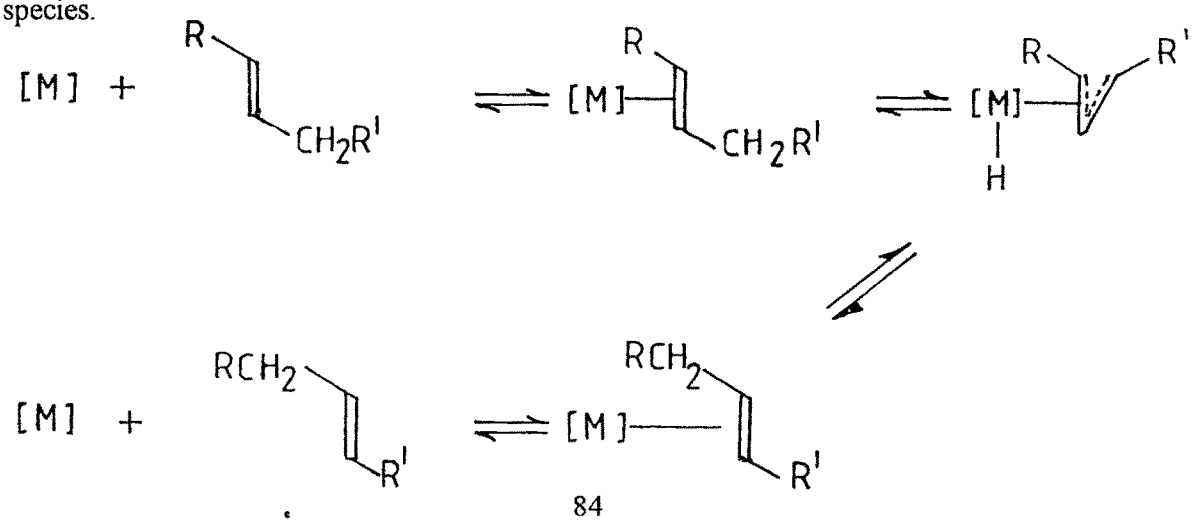
Besides epoxidation, another important reaction, catalyzed by metal complexes is isomerization of olefins. Isomerization of olefins has been carried out using $[MX_2(PR_3)_2]$ - $NaBH_4$ (Where M=Co, Ni; X=halide, SCN, PR_3=PPh_nEt_{3-n}) [1]; $Co(N_2)(PPh_3)_3$, $H_3Co(PPh_3)$ [2] and nickel [3] and palladium [4] dithio-β-diketonates with alkylaluminium co-catalysts in homogeneous conditions.

Isomerization of olefins by transition metal complexes follow two general mechanisms [5].

1 The first mechanism involves the reversible addition of a metal-hydride (a stable species or generated in situ) across a double bond to generate a transition metal σ-alkyl species.

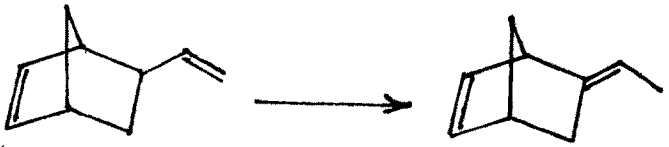


2 The second mechanism involves coordination of the olefin to the transition metal followed by insertion of the metal into an allylic C-H bond to generate π-allyl metal-hydride species.



The chemistry of reduction of cobalt has received great attention after Sloan's report of active hydrogenation catalyst system composed of Co(III) acetylacetonate and organoaluminium compounds [6]. These systems were later reported to be active as catalysts for oligomerization of olefins. Cobalt(II), cobalt(III) and nickel(II) acetylacetonates in conjunction with alkylaluminiums have been used for co-dimerization of 2,5-norbornadiene with ethylene [7], and dimerization of ethylene [8]. Reaction between Co(II) and Co(III) acetylacetonates and alkylaluminium or $Mg(n\text{-butyl})_2$ has been studied [9,10] and the mechanism is understood upto certain extent. It is known that reduction of $Co(acac)_3$ with $AlEt_3$ gives $EtAl(acac)_2$ or $Al(acac)_3$ species in solution and low valent Co(acac) or Co-hydride species and Co^0 metal particles The precise active site in these systems is, however, not known with certainty due to complicated nature of the system It was thought worthwhile, therefore, to study reaction of Co(salen) type of complexes with triethylaluminium and to use the catalyst system for isomerization of olefins. 5-Ethylidene-8,9,10-trinorborn-2-ene (**2**) was chosen as substrate due to its industrial importance.

5-Ethylidene-8,9,10-trinorborn-2-ene (**2**) is used as a diene comonomer for the production of ethylene-propylene-rubber Industrially, **2** is prepared by isomerization of 5-vinyl-8,9,10-trinorborn-2-ene (**1**) using heterogeneous catalysts (Eq.1) [11,12]. Use of super-bases [13], organometallic complexes [14,15], metal carbonyls [16] and a combination of β-diketonates of Co(II) and Co(III) with alkylaluminium halides [17] have also been reported for this isomerization reaction.



1 2

The present chapter reports a study of the isomerization of 1 using a combination of Co^{II}(salen) or related complexes (containing ligands with NO coordinating sites) and $AlEt_3$ as catalyst.

Experimental

Materials

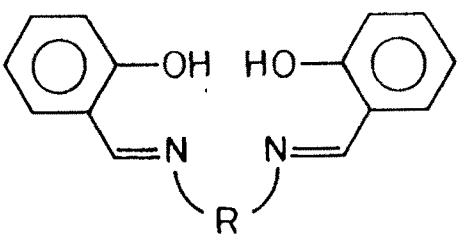
1,2 and PPh_3 were obtained from Aldrich, USA. $AlEt_3$ was supplied by Polyolefin Industries Ltd.,Thane, India. All other chemicals were of AR grade. Toluene and benzene were distilled over sodium prior to use for each reaction. Dichloromethane was distilled over P_2O_5. All other reagents were used, as supplied, without further purification. $(C_2H_5)_4N.BF_4$ for electrochemical studies was purchased from Aldrich, USA and used as such.

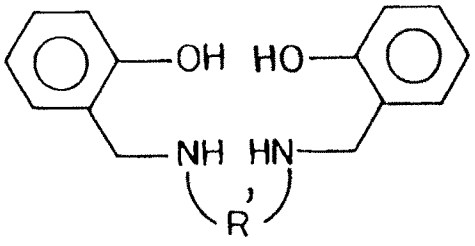
Instrumentation

GC-Mass spectra were recorded on a HP-5985 instrument using a capillary column (50 m, i d.. 0.2 mm) loaded with cross-linked methyl silicone (film thickness 0.5 μm). Cobalt was estimated by a GBC 902 atomic absorption spectrometer. EPR Spectra were recorded on a Bruker ESP-300 X-band spectrometer using a 100 KHz field modulation. Low temperature measurements were performed using a quartz Dewar flask. Spectral parameters were determined using DPPH as marker. Details of the C,H,N analysis, UV-vis, IR, GC and CV methods are given in the previous chapters.

Synthesis of Complexes

The ligands L^1 to L^3, with the following structures, were synthesized using known methods.

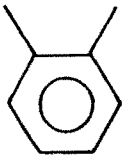




L^1 : R = $(CH_2)_2$

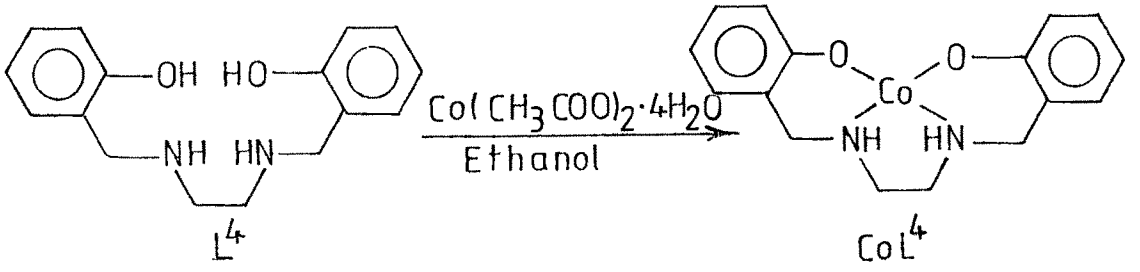
L^4 : R' = $(CH_2)_2$

L^2 : R =



L^3 : R = $(CH_2)_2$ NH $(CH_2)_2$

The salicylideneamine (L^4) was prepared by hydrogenation of L^1 [18]. CoL^1, CoL^2, CoL^3 and CoL^1X (X= Im, Py) were prepared using literature methods [19-21]. CoL^4 was synthesized as follows : 2.72 g (0 01 M) of the ligand L^4 in 50 ml absolute alcohol was mixed with 2.49 gm (0.01 M) of $Co(CH_3COO)_2$. $4H_2O$ in 50 ml absolute alcohol with stirring. This mixture was then refluxed under N_2 for 4 hours The dark solution obtained was reduced to about 50 ml and left overnight at about 10 °C. Yellowish-brown solid precipitated was suction filtered under N_2, recrystalized in EtOH-MeOH (1.1) solvent mixture and dried at room temperature under vacuum for 4h Found · Co,17 7; C,58 1; H,5.6; N,8.2 % Calcd for $CoC_{16}H_{18}N_2O_2Cl$ (CoL^4) Co,17 9; C,58.3; H,5.5; N,8.5 %.



Procedure for Isomerization of 1

All the operations were performed in a glove box under nitrogen atmosphere. For a typical reaction, catalyst (0.24 mmol) and 5 ml of freshly distilled toluene were mixed in a two-necked 100 ml round bottom flask **1** (24 mmol), 5 ml solvent and $AlEt_3$ (0 96 mmol) were added in sequence. The reaction mixture was then stirred magnetically in an oil-bath under nitrogen atmosphere at the specified temperature The reaction was terminated after 4h by addition of 1 ml ethanol The contents were cooled and a known amount of chlorobenzene was added as internal standard The resulting solution was analyzed by GC to determine the quantity of **2** and side products, if any, using a 6 m x 3 mm column packed with 10% Apiezon Grease L on Chromosorb W The relations used to calculate different reaction parameters are given under respective tables

GC Analysis conditions · As in Chapter 2, except that the injection port was maintained at 150°C and the column temperature programming was as follows :

Initial Temperature		40 °C
Initial Time	:	8 min
Heating Rate	.	2 °C/min
Final Temperature	:	110 °C
Final Time	:	20 min

Retention times for various components under these conditions were :

Chlorobenzene	.	51.4 min
1	:	55.9 min
2	·	61 1 min
3	.	65 3 min

EPR Studies

CoL^1 in CH_2Cl_2 was frozen to -196 °C and its EPR spectrum recorded. It was then warmed to 25 °C and 4 equivalents of $AlEt_3$ were added under N_2. The contents were frozen immediately and the EPR spectrum recorded. Again it was warmed, allowed to age at 25 °C for 30 minutes and then the EPR spectrum was recorded at -196 °C.

Results and Discussion

CoL^1-$AlEt_3$ forms an active catalyst system for the isomerization of **1** under ambient conditions. The kinetics of the reaction using this catalyst system at 80 °C (Figure 1) show that the optimum reaction time is 4h. Beyond this period the yield of **2** remains unchanged

Independently CoL^1 or $AlEt_3$ does not isomerize **1**, demonstrating that the isomerization of **1** to **2** occurs only in the presence of the CoL^1-$AlEt_3$ combination.

Various catalyst to substrate (**1**) molar ratios were used for the isomerization studies (Table 1) At a catalyst to **1** ratio of 1:100 the conversion of **1** was 40% and the selectivity to **2** was high. Hence this ratio was chosen for further studies. The reaction temperature has a pronounced effect over the isomerization of **1** (Table 2). At 25 °C there was no reaction whereas at 50 °C conversion of **1** was 40% and selectivity to **2** was 100%. On increasing the temperature the conversion improved but the selectivity to **2** fell due to the formation of by products.

The influence of the CoL^1 - $AlEt_3$ molar ratios on the yield of **2** is shown in Table 3. A CoL^1- $AlEt_3$ ratio of 1:4 was optimum, though a minimum CoL^1 - $AlEt_3$ ratio of 1·2 was required to initiate the reaction. At lower molar ratios the turnover of the catalyst for formation of **2** was low and at higher ratios side products were dominant. When the reaction mixture containing a CoL^1 - $AlEt_3$ ratio of 1:10 (last entry in Table 3) was analyzed by GC-MS, a molecular ion peak with m/z = 122, having base peak of m/z = 93 was observed.

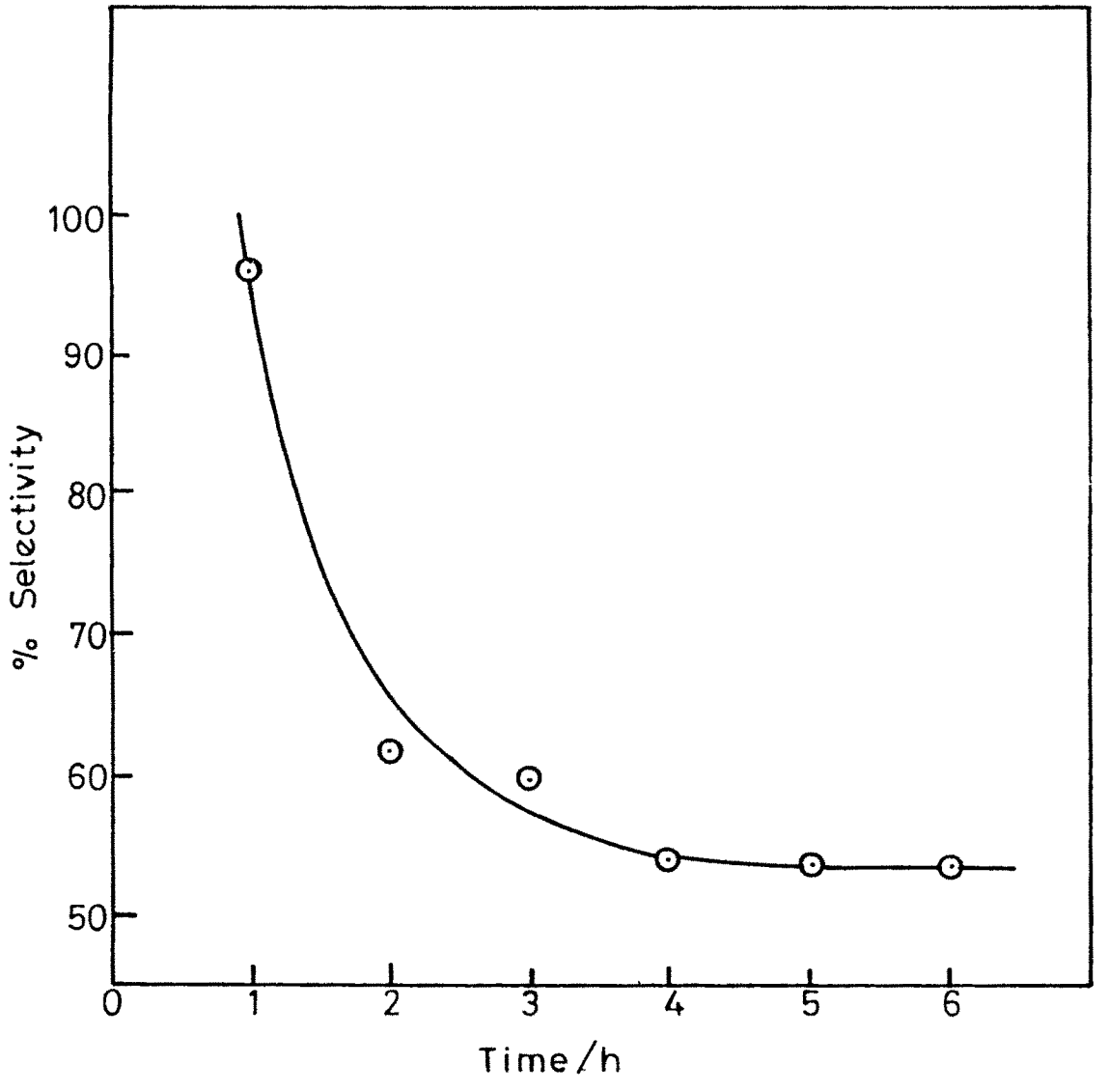
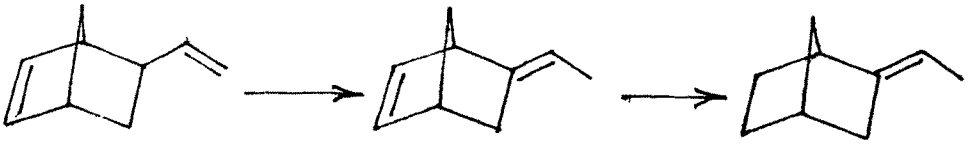


Figure 1 Kinetics of the isomerization of 1
$CoL^1 : AlEt_3 : 1 = 1 . 4 \quad 100$, $CoL^1 = 0.24$ mmol, Temp = 80 °C

This byproduct was identified as 2-ethylidene-8,9,10-trinorbornane (**3**). This was further confirmed by comparison with an authentic sample of **3**. In this reaction, besides the hydrogenated product **3** , oligomers of **1** were also formed.

The effect of variation of concentration of CoL^1 at a constant ratio of **1** : $AlEt_3$ was also studied (Table 4). This study indicates that both conversion of **1** and yield of **2** increase proportional to the concentration of CoL^1 complex suggesting that cobalt metal centre is involved in the active species and not the Al centre.

The CoL^1-$AlEt_3$-**2** (1:4:50) system when heated in benzene at 50 °C did not give **3**, whereas at 80 °C there was a moderate yield of **3**. Further, the yield of **3** increased with an increase in the CoL^1-$AlEt_3$ ratio. These observations suggest that **3** is formed by the isomerization of **1** followed by the hydrogenation of **2** (Eq. 2). The cobalt species with a Co-H bond might be responsible for this hydrogenation step and $AlEt_3$ provides the hydrogen for the reduction of the trinorbornenic double bond.



1 **2** **3**

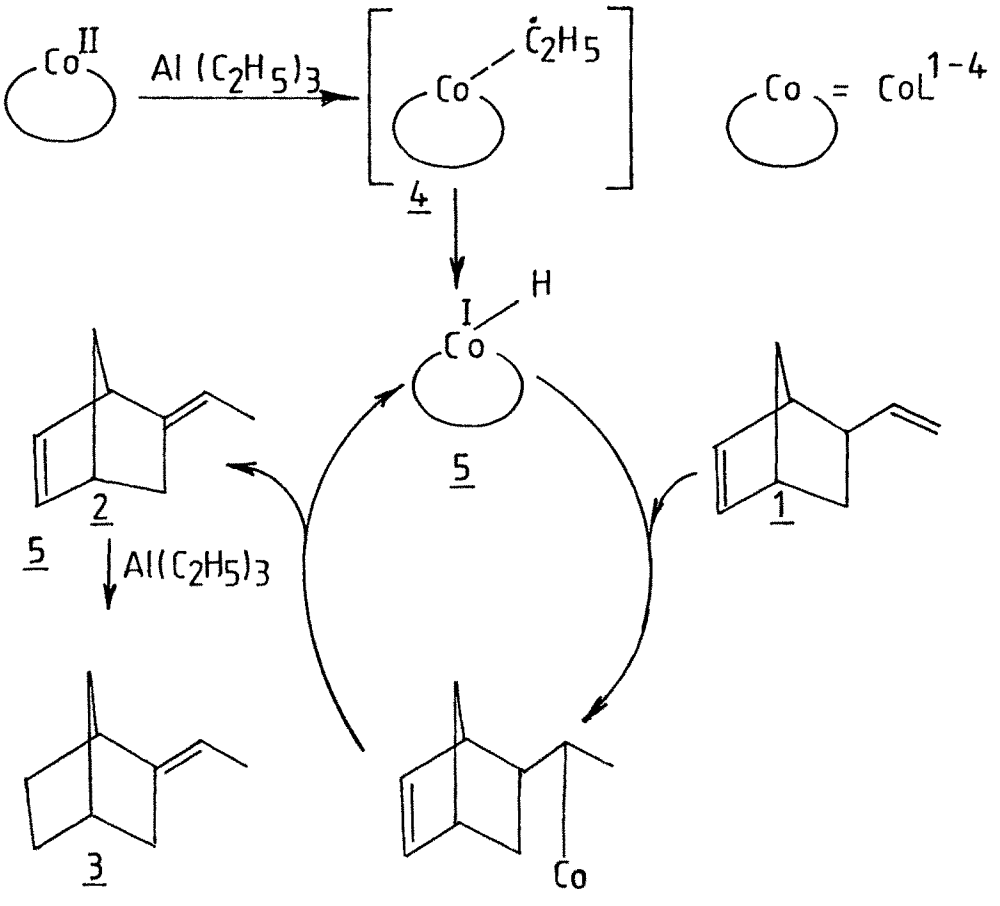
The hydrogenation of the trinorbornenic double bond takes place at a temperature relatively higher than the isomerization of the vinyl double bond. This is in agreement with literature reports [22] that isomerization is relatively faster than hydrogenation.

The isomerization reaction of 1 to 2 was also studied using CoL^2, CoL^3 and CoL^4 complexes in association with $AlEt_3$. The results (Table 5) show that changes in the ligand bound to the Co(II) metal ions did not affect the yield of 2 or turnover number of the catalyst either at 50 or 80 °C. It was observed that the use of cobalt complexes with an axial ligand like imidazole or pyridine inhibited hydrogenation of the trinorbornenic double bond at 80 °C and the selectivity for 2 was greater. However, when PPh_3 was used, the yield of 2 was greater. There was also simultaneous formation of 3 at temperatures higher than 50 °C (Table 6)

From the study of the effect of temperature and Arrhenius plot, E_a and $\Delta H^{\#}$ values for the isomerization of 1 were calculated using CoL^1 and CoL^1-PPh_3 catalyst systems (Table 7). These values show that addition of the PPh_3 accelerates the activation of 1 and the formation of the active cobalt species by reducing the activation energy and thus facilitating the formation of 2.

A tentative mechanism (Scheme I) may be suggested considering that in the isomerization of 1, there is formation of a cobalt species with a Co-H bond and that this might be responsible for the transformation of 1. This is supported by electronic and EPR spectral studies and CV measurements.

All the cobalt complexes studied were sparingly soluble in toluene and benzene However, addition of $AlEt_3$ to the catalyst-1 mixture in the solvent immediately turned the reddish brown heterogeneous mixture into a green coloured homogeneous solution. The electronic spectral study (Figure 2) shows three absorption bands at 409, 344 and 244 nm for CoL^1-1 in CH_2Cl_2 On addition of $AlEt_3$, the absorption at 409 nm disappeared and a weak



Scheme I

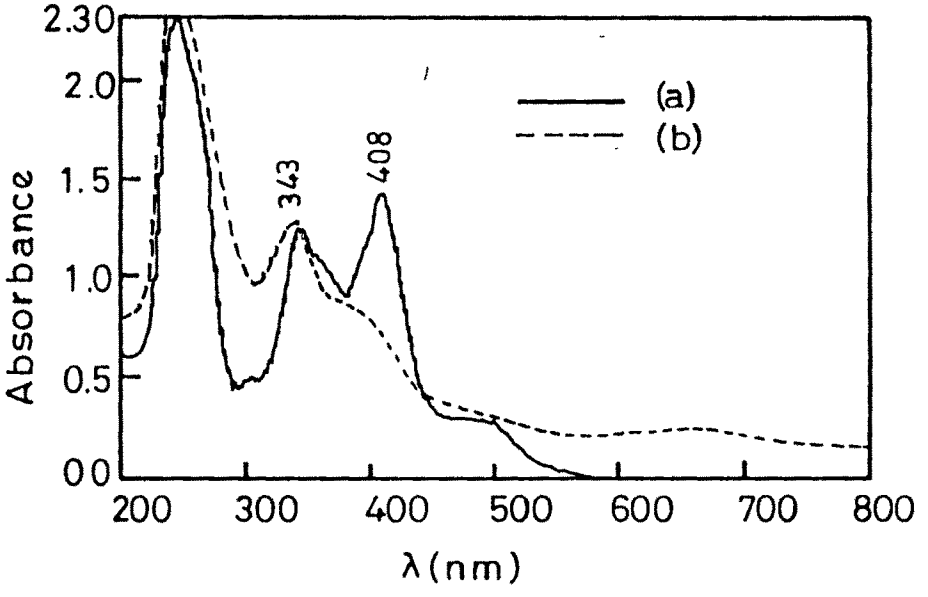


Figure 2 Uv-vis absorption spectra in CH_2Cl_2
(a) $CoL^1 \cdot \underline{1} = 1 : 100$, $CoL^1 = 0.24$ mmol
(c) $CoL^1 : AlEt_3 . \underline{1} = 1 : 4 : 100$, $CoL^1 = 0.24$ mmol

broad band appeared at 645 nm for the Co^{I} species, as observed by Calderazzo [23]. This shows the formation of a soluble complex with a cobalt centre in an oxidation state different from that in the starting complex. Calderazzo also reported that on reduction of CoL^{1} with sodium metal in THF a green coloured solution was obtained [23].

EPR studies of the CoL^{1}-$AlEt_3$ system at -196 °C threw some light on the nature of the active species. On addition of $AlEt_3$ to CoL^{1} the characteristic EPR signal of the paramagnetic Co(II) species (reddish brown solution) disappeared and there was a new signal with a g value 2.07 The EPR active species were short lived and on warming to room temperature rapidly converted into the ultimate EPR silent species (Figure 3). The signal at -196 °C with g = 2 07 (spectrum b) might be due to the ethyl radical which is transferred from $AlEt_3$ to Co(II), reducing it to Co(I). Generally the Co-C_2H_5 bond is unstable at elevated temperatures and hence **4** might lead to formation of **5**. Thus the active cobalt species in the reaction is the EPR silent low spin Co(I) complex bonded to a hydride ligand.

The formation of Co(I) species has been further confirmed by cyclic voltammetric studies. The cyclic voltammogram of CoL^{1} (Fig.4(a)) shows a cathodic peak at -1.4 V corresponding to Co(II)/Co(I) reduction. The corresponding anodic peak is not distinct showing that the reduction is not reversible in CH_2Cl_2. On addition of $AlEt_3$ to CoL^{1} solution no redox couple is observed in the CV. Thus, it is observed that the peak due to Co(II)/Co(I) disappears on addition of $AlEt_3$ (b) (Figure 4). There is no peak at higher potential [24] of +0.38 V corresponding to Co(III)/Co(II) reduction, showing that Co(III) is not generated on addition of $AlEt_3$. This supports that Co(II) is reduced to Co(I) on reaction with $AlEt_3$. The

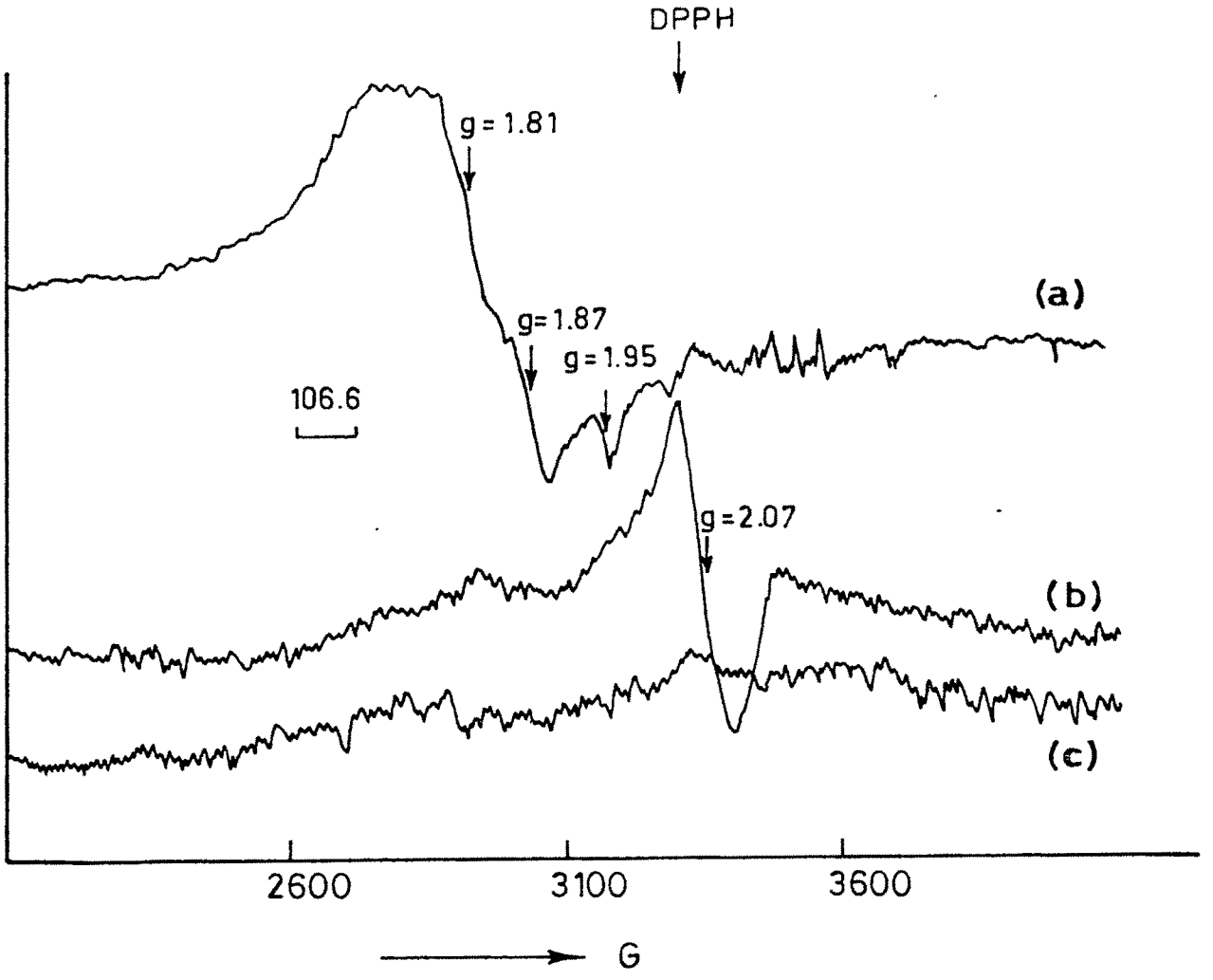


Figure 3 EPR spectra at -196 °C of (a) CoL^1 in CH_2Cl_2, (b) CoL^1 : $AlEt_3$ (1 : 4) in CH_2Cl_2 and (c) CoL^1 . $AlEt_3$ in CH_2Cl_2 after standing at 25 °C for 30 min

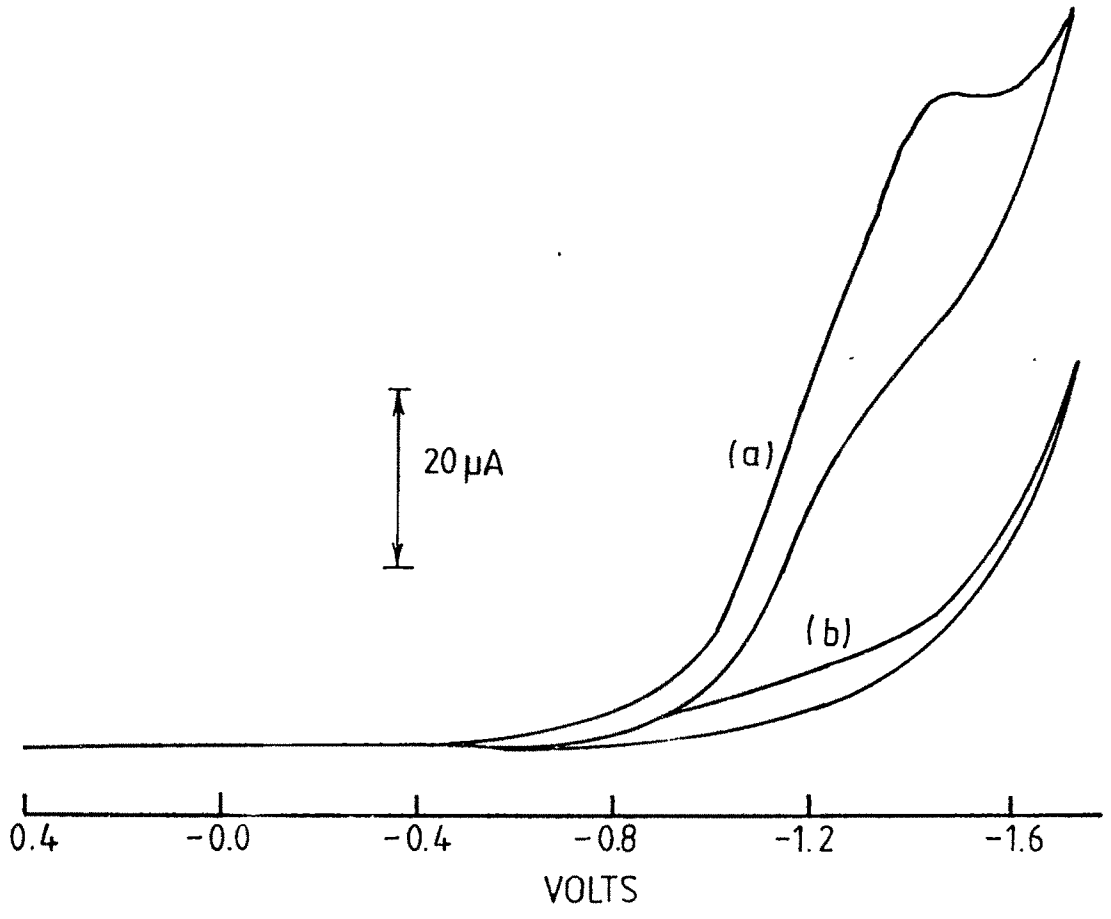


Figure 4 Cyclic Voltammograms of CoL^1 (1.5×10^{-3} M) in CH_2Cl_2, $[Et_4N][BF_4]$ 0.1 M, $v = 0.1$ Vs^{-1}
(a) before addition of $AlEt_3$
(b) after addition of $AlEt_3$

reduction of Co(I)/Co(0) is not observed as it occurs at highly negative potential, not attainable electrochemically in CH_2Cl_2.

The increase in the yield of formation of **2** on addition of PPh_3 to Co^I-$AlEt_3$ further supports that the isomerization of **1** proceeds through initial formation of the metal- hydride species, because it is known that metal hydrides are stabilized by PPh_3 [25]. At higher temperature the metal-hydrides would hydrogenate the trinorbornenic double bond of **2** to yield **3**. All these studies indicate that isomerization of **1** to **2** would be via Co-H bond formation and that **2** is further hydrogenated to **3**, as shown in scheme I. However, detailed kinetic studies are necessary to fully establish the proposed mechanism.

References

1 H Kanai, S Sakaki, T Sakatani, *Bull Chem Soc Jpn*, 1987, **60**, 1589.

2 F K Shmidt, L O Nindakova, S M Krasnopolskaya, N G Devyatko, T V Dmitrieva, G V Ratovskii, *Kinet Katal*, 1978, 19, 143 (Russ), CA 88 : 189720 r.

3 R Abeywickrema, M A Bennett, K J Cavell, M Kony, A F Masters, A G Webb, *J Chem Soc, Dalton Trans*, 1993, 59.

4 K J Cavell, K Y Chan, E J Peacock, M J Ridd, N W Davies, *Aust J Chem*, 1991, **44**, 171.

5 S G Davies, Ed., *Organotransition Metal Chemistry : Applications to Organic Synthesis*, Vol.2, Pergamon Press, 1990, p. 266.

6 M F Sloan, A S Matlack, D S Breslow, *J Am Chem Soc*, 1963, **85**, 4014.

7 S M Pillai, G L Tembe, M Ravindranathan, *J Mol Catal*, 1993, **84**, 77.

8 S M Pillai, G L Tembe, M Ravindranathan, *J Mol Catal*, 1990, **58**, 171.

9 S Pasynkiewicz, A Pietrzykowski, K Dowbor, *J Organomet Chem*, 1974, **78**, 55.

10 K Luhder, W H Bohmer, I Stoldt, K Madeja, *React Kinet Catal Lett*, 1992, **48**, 9, and references therein.

11 G. Suzukamo, M.Fukao, F.Masuko, M.Usui and K.Kimura, European Patent 230,025 (1987); CA, **107**, 200 104

12 G. Suzukamo and M. Fukao, European Patent 219,637,1987; CA, **107**, 97971

13 Yu. G. Osokin, V. Sh. Fel'dblyum, A. F. Plate, N. A. Belikova, D. M. Lisitsin, T. I. Bogolepova, L. M. Chashnik, E. K. Kuzmin, Yu. V. Sh Orlov and A I. Shantenshtein, U.S.S.R Patent 591, 447, 1978; CA, **89**, 6014.

14 Y. Ishii, A. Saitoh, S Hamanaka and M.Ogawa, *Sekiyu Gakkaishi*, 1986, **29**, 20

15 Japan Kokai 7588,059 (1975); CA **86**, 55075.

16 Y. Osokyn, Y. Grinberg, V. Sh. Fel'dblyum, I. Toeitlin, N Belikoba and A. Plate, *Neftekhimiya*, 1980, **20**, 354.

17 S. Muthukumaru Pillai, *React Kinet Catal Lett*, 1994, **52**, 35.

18 K. V. Patel and P. K Bhattacharya, *Indian J Chem*, 1984, **23A**, 527.

19 R. H. Bailes and M. Calvin, *J Am Chem Soc*, 1947, **69**, 1986.

20 L. G. Marzilli, P. A. Marzilli and J. Halpern, *J Am Chem Soc*, 1971, **93**, 1374.

21 R. S. Drago, P. J. Cannady and K. A. Leslie, *J Am Chem Soc*, 1980, **102**, 6014.

22 M. Hudlicky, *Reductions in Organic Chemistry, Ellis Hor Word Limited, Chichester*, 1984, p 4.

23 F. Calderazzo and C. Floriani, *J Chem. Soc, Chem Commun*, 1967,139.

24 D. J. Brockway and B. O. West, *J Chem. Soc, Dalton Trans*, 1979, 1891

25 M. L. H. Green and D. J. Jones, *Adv Inorg Chem Radiochem*, 1965, 7, 115.

Table 1 Influence of CoL^1 molar ratio on isomerization of **1** [a]

CoL^1 : **1**	**1** converted mmol	Conversion[b]/%	Selectivity[c]/%	Turnover[d]
1:25	4.56	76	42	19
1:50	7.44	62	57	31
1:100	9.84	41	78	41
1:200	15.36	32	78	64

a CoL^1 = 0.24 mmol, CoL^1: $AlEt_3$ = 1:4, 4h, 80 °C.

b % Conversion = $\frac{\text{mmol of } \mathbf{1} \text{ converted to products}}{\text{mmol of } \mathbf{1} \text{ initially taken}} \times 100$

c % Selectivity = $\frac{\text{mmol of } \mathbf{2} \text{ formed}}{\text{mmol of } \mathbf{1} \text{ converted to products}} \times 100$

d Turnover = $\frac{\text{mmol of } \mathbf{2} \text{ formed}}{\text{mmol of catalyst used}}$

Table 2 Effect of temperature on isomerization of **1** [a]

Temperature / °C	Conversion / %	Selectivity / %	Turnover
25	-	-	-
50	14	100	14
80	42	78	41
100	73	68	73

a CoL^1 = 0.24 mmol, $CoL^1 \cdot AlEt_3$: **1** = 1 . 4 : 100, 4h.

Table 3 Influence of CoL^1 : $AlEt_3$ molar ratio on yield of **2** [a]

CoL^1 : $AlEt_3$	Conversion / %	Selectivity / %	Turnover
1:1	-	-	-
1:2	8	100	8
1:4	14	100	14
1:6	21	41	21
1:10	46	9	46

a CoL^1 : **1** = 1 · 100, 4h, 50 °C, CoL^1 = 0.24 mmol.

Table 4 Influence of CoL^1 concentration on isomerization of **1** at constant $AlEt_3$: **1** molar ratio[a]

CoL^1 / mmol	CoL^1:$AlEt_3$:**1**	Conversion / %	**2** / mmol	Turnover
0.12	1:8:200	5.8	1.3	10
0.16	1:6:150	8.3	109	12
0.24	1:4:100	14	3.6	14

a 4h, 50 °C

Table 5 Activity of various cobalt complexes for isomerization of **1** [a]

Run	Complex	Temp/°C	Conversion of **1** / %	Selectivity /%	Turnover
1	CoL^1	50	14	100	14
2	CoL^1 Im[b]	50	15	100	15
3	CoL^1 PPh_3[c]	50	16	98	16
4	CoL^4	50	15	100	15
5	CoL^1	80	41	78	41
6	CoL^1 Im[b]	80	40	100	40
7	CoL^1 Py[d]	80	38	100	38
8	CoL^2	80	30	98	30
9	CoL^3	80	33	100	33
10	CoL^4	80	30	94	30

a Co : $AlEt_3$ · **1** = 1 · 4 : 100.
b Im = imidazole
c CoL^1 : PPh_3 = 1 · 1
d Py = pyridine

Table 6 Influence of temperature on isomerization of **1** with CoL^1-PPH_3-$AlEt_3$ system[a]

Temperature / °C	Conversion / %	Selectivity / %	Turnover
50	16	98	16
80	59	84	59
100	64	86	64

a Conditions are same as given in the previous table

Table 7 E_a and $\Delta H^{\#}$ for formation of **2**[a]

Catalyst	E_a / (Kcal / mol)	$\Delta H^{\#}$ / (Kcal / mol)
CoL^1-$AlEt_3$	7 27	6.63[a]
CoL^1-PPH_3-$AlEt_3$	5.88	5.24[a]

a 50 °C