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KINETICS AND MECHANISM OF *cis*-2-PENTENE ISOMERIZATION BY A CATALYST FORMED FROM TRIS(TRIPHENYLPHOSPHINE)DINITROGENCOBALT HYDRIDE

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SUMMARY

It has been shown that tris(triphenylphosphine)dinitrogencobalt hydride etherate (I) is the direct precursor of the catalyst of isomerization of *cis*-2-pentene to the *trans*-isomer. The isomerization is second order with respect to pentene and first order with respect to the cobalt complex. It is inhibited by excess of the substrate. The structures of complexes present in the reaction mixture are discussed.

INTRODUCTION

The mechanism of olefin isomerization catalyzed by transition metal complexes has not yet been elucidated. Three mechanisms of this reaction have been proposed, *viz.*: 1,3 internal hydride shift[1]; external 1,3 allylic exchange[2]; 1,2 addition/elimination[3].

The catalytic systems causing olefin dimerization frequently have the property of isomerizing 1-olefin to 2-olefin. This isomerization is undesirable since α-olefins are of greater importance than their β-isomers, so it is of interest to devise a system in which oligomerisation is not accompanied by such isomerization.

The question of the mobility of the transition metal–hydrogen bond seems to be of importance in this kind of study. Tris(triphenylphosphine)dinitrogencobalt hydride (I) is a particularly suitable compound for studying the factors influencing the Co–H bond.

Kovács *et al.*[4] described the kinetics and the mechanism of 1-hexene isomerization under the influence of complexes for which the $(PPh)_3CoN_2$ was the direct precursor. Yamamoto[14] reported that tris(triphenylphosphine)dinitrogencobalt hydride or its derivatives causes isomerization of 1-butene to a mixture of *cis*- and *trans*-2-butenes, but there were no kinetic studies of this reaction and its mechanism was not established.

KINETICS OF *cis*-2-PENTENE ISOMERIZATION WITH $(PPh_3)_3CoN_2H$ AND ANALOGOUS COMPLEXES AS CATALYSTS

The formation of the *trans*-stereoisomer starts immediately when *cis*-2-pentene is added to the benzene solution of (I). After the addition of the olefin the evolution of nitrogen takes place. Its amount is considerable when the olefin is added in high molar ratio of 1/8 to 1/10. For the molar ratio (I)/olefin = 1/1 to 1/2 nitrogen evolution is slight. The isomerization is first order in cobalt on the basis of eqn. (1)[5]:

$$n=\frac{\log\left[-\left(\frac{\Delta C_5}{\Delta t}\right)_1\right]-\log\left[-\left(\frac{\Delta C_5}{\Delta t}\right)_2\right]}{\log[\text{cat}]_1-\log[\text{cat}]_2} \tag{1}$$

When the data obtained for the initial stages of the reaction are substituted in eqn. (1) it is found that $n=1.1$ and 1.3 for two series of experiments. Within one experiment the reaction is second order in *cis*-2-pentene as shown in Fig. 1.

Under our conditions the presence of 1-pentene was not been detected. The influence of different reagents on the isomerization rate is shown in Table 1. The PPh_3 ligands of (I) are readily displaced by various phosphines according to eqn. (2).

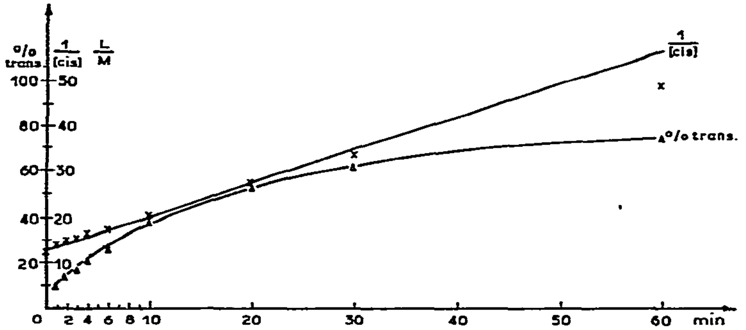


Fig. 1. Isomerization of *cis*-2-pentene → *trans*-2-pentene $c_{Co}=0.03\ M$; 25°; benzene solution; molar ratio (I)/*cis* = 1/2.

TABLE 1

SECOND ORDER RATE CONSTANTS FOR THE ISOMERIZATION *cis*-2-PENTENE → *trans*-2-PENTENE; INFLUENCE OF DIFFERENT REAGENTS

([Co] 0.03 *M*; molar ratio (I)/*cis*-2-pentene 1/2; benzene solution; 25°.)

Catalytic system	$k_{obs}\times 10^{-2}$ ($l\cdot mol^{-1}\cdot s^{-1}$)
(I)	1.06
(I) + 3 PPh_3	0.26
(I) + 3 PPh_2Et	0.07
(I) + 3 $PPhEt_2$	0.00
(I) + 3 PEt_3	0.00
(I) + 3 $P(OMe)_3$	0.00
(I) + 3 $P(OPh)_3$	0.00
(I) + CH_3CN	0.07
(I) + C_2H_5CN	0.07
(I) + PhCN	0.36
(I) heated[a] 80–90°	1.30

[a] Co concentration 0.05 *M*

$$(I)+3\ PR_3 \rightarrow (PR_3)_3CoN_2H+3\ PPh_3 \qquad (2)$$

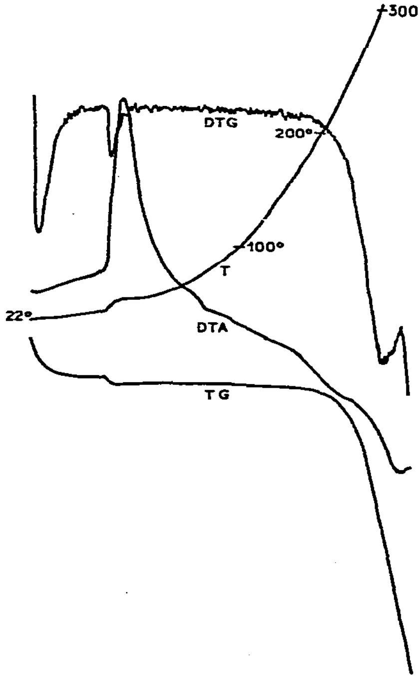
The exchange is very rapid. This can be seen from the immediate disappearance of the N_2 frequency of the parent compound (I) and the simultaneous appearance of new N_2 frequencies associated with the newly formed complex. For the complexes with $PR_3=PEt_3$, PEt_2Ph, $PEtPh_2$, $\nu(N_2)$ were as follows: 2024, 2050, 2085 cm^{-1}. Similar observations for $(PPh_3)_3CoN_2$ have been made by Ötvös *et al.*[6].

The exchange of coordinated nitrogen with nitriles takes place according to eqn. (3).

$$(I)+RCN \rightarrow (PPh_3)_3Co(RCN)H+N_2 \qquad (3)$$

This has been reported to be reversible for $R=CH_3$ or C_2H_5 and irreversible for PhCN[7].

Pyrolysis of (I) has been studied by derivatography (Fig. 2). It is evident from Fig. 2 that nitrogen is no longer present after compound (I) has been pyrolyzed. Nitrogen is lost even at ~35°, and this dissociation is exothermic. Within the temperature range 35–90° no significant mass nor enthalpy change has been observed. The PPh_3 ligands start to separate at about 240°, this is an endothermic process. We conclude that after pyrolysis of complex (I) at 80–90° no nitrogen remains, but the



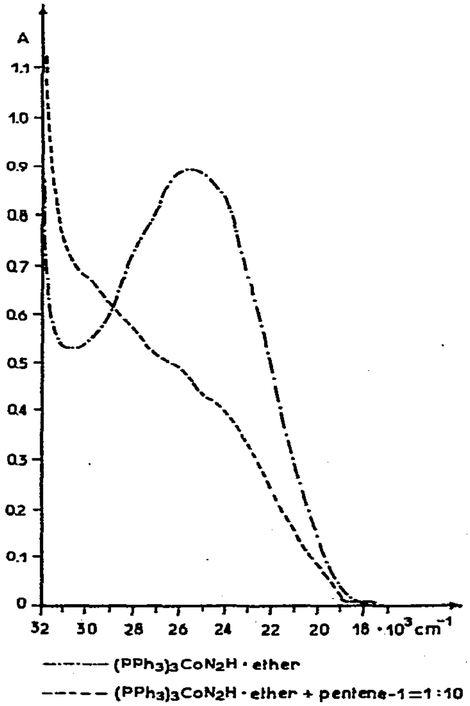


Fig. 2. Derivatograph of $(PPh_3)_3CoN_2H$·ether in an argon atmosphere. Temperature range 22–300°. Rate of heating 6°/min.

Fig. 3. Electronic spectrum of $(PPh_3)_3CoN_2H$·ether and of the product of the reaction of this complex with 1-pentene.

TABLE 2

INFLUENCE OF THE INITIAL *cis*-2-PENTENE CONCENTRATION c_0 ON THE RATE OF ISOMERIZATION

c_0 (M)	$\frac{k_{obs}}{[Co]}$ $(l^2 \cdot mol^{-2} \cdot s^{-1})$
0.167	0.0752
0.127	0.144
0.078	0.272
0.071	0.324

TABLE 3

ELECTRONIC SPECTRA OF THE COMPLEXES $(PR_3)_3CoN_2H$ AND $(PPh_3)_3Co(RCN)H$

Complex	ν $(cm^{-1} \times 10^{-3})$	ε
(I)	25.7	1390
(I)+MeCN	22.0	576
(I)+EtCN	22.2	643
(I)+PhCN	23.2	910
(I)+PPh_2Et	25.7	1460
(I)+$PPhEt_2$	25.6	1460

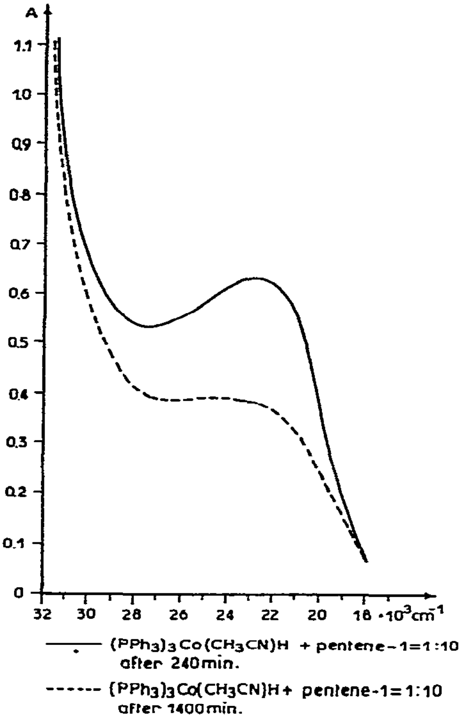
Co–H bond is still present. The benzene solution of the pyrolyzed complex at temperatures below 90° does not exhibit EPR absorption. The complex obtained in this way still catalyses the pentene isomerization.

We have found that the rate of isomerization decreases with increasing initial concentration of the substrate (Table 2). For a molar ratio of (I)/*cis*-2-pentene = 1/10 and c_0Co 0.03 *M*, after 60 min the solution no longer contains (I), as can be seen from the complete disappearance of $\nu(N_2)$ in the IR spectrum and from the evolution of about 95% of N_2 present in (I). Under these conditions the reaction takes the following path:

$$\text{(I)} + cis\text{-2-pentene} \rightarrow \text{(II)} + trans\text{-2-pentene} + N_2 \qquad (4)$$

(II) denotes a complex (or complexes) which does not contain the N_2 ligand, and which probably contains more than one coordinated olefin. All attempts to isolate (II) failed. The electronic spectrum of the reaction mixture (4) is presented in Fig. 3. The same type of absorption curve was observed when 2-pentene or 1-pentene was used. The disappearance of the 25700 cm^{-1} band also indicates that the parent compound (I) is not present. The 25700 cm^{-1} band is probably a charge transfer band connected with the presence of the ligand containing a triple bond in the complex (I). The electronic spectra of complexes formed after ligand exchange reactions (2) and (3) with PR_3 and RC≡N present essentially the same type of absorption curve. Absorption maxima and extinction coefficients are reported in Table 3.

It was of interest to find out whether pentene would react with complexes of the formula $(PPh_3)_3Co(RCN)H$ with loss of the ligand containing the triple bond. We found that this displacement, like that of the N_2 ligand, does take place but it is much slower (Figs. 4 and 5).



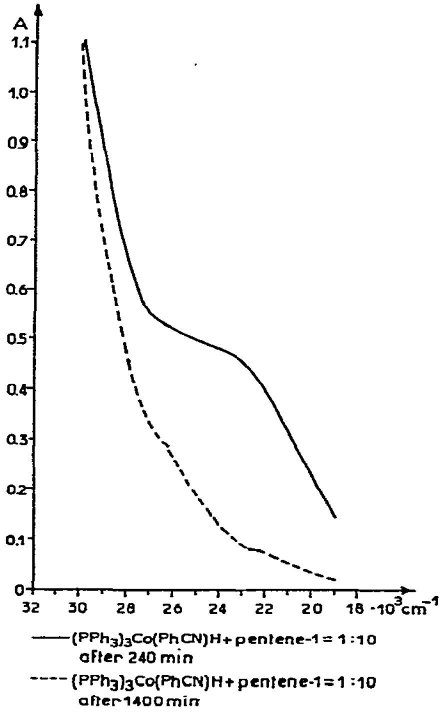


Fig. 4. Changes in the electronic spectrum of $(PPh_3)_3Co(CH_3CN)H$ during the reaction with 1-pentene.

Fig. 5. Changes in the electronic spectrum of $(PPh_3)_3Co(PhCN)H$ during the reaction with 1-pentene.

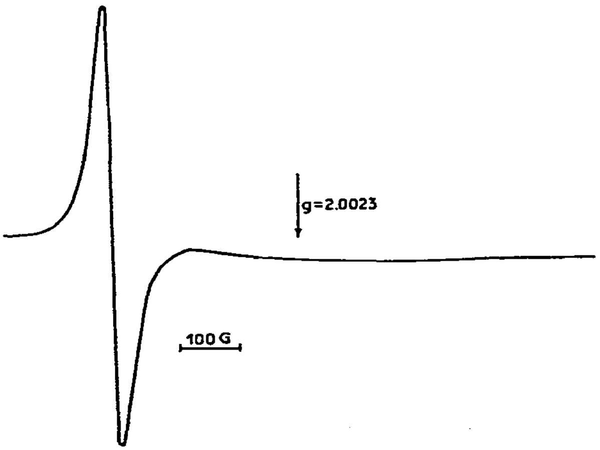


Fig. 6. EPR spectrum of the reaction product of (II) with styrene. Molar ratio (II)/styrene = 1/10; temperature of the reaction and of the cavity 25°; $c_{Co}=0.01$ *M*.

The reaction mixture (4) does not exhibit EPR absorption. By contrast, it is known[8] that the reaction of (I) with styrene gives a paramagnetic cobalt complex and ethylbenzene. The EPR spectrum of this complex consists of an asymmetric curve containing 13 lines[8].

It was of interest to find out whether styrenes would also give the paramagnetic cobalt species from (II). The reaction of (II) with $PhCH{=}CH_2$ did indeed, give the paramagnetic cobalt complex, the EPR spectrum of which is shown in Fig. 6. (Ethylbenzene is also formed in this reaction.) The spectrum, shown in Fig. 6, is completely different from that of the substance produced in the reaction of (I) with styrene[8]. The appearance of 13 lines in the spectrum of the reaction product of (I) with styrene is due to the interaction of the unpaired electron with two cobalt nuclei of the binuclear complex. This is not the case when the paramagnetic complex is produced from (II) and $PhCH{=}CH_2$, which indicates the presence of the same hindrance in the dimerization reaction leading to binuclear paramagnetic species. Obviously it is the coordination of pentene which inhibits the dimerization for electronic or steric reasons. The fact that we have not observed any hyperfine coupling for the paramagnetic product of the reaction of (II) with $PhCH{=}CH_2$ indicates that the unpaired electron is in an orbital having no density at the Co nucleus.

DISCUSSION AND CONCLUSIONS

Mechanism of the catalytic isomerization

The kinetic data can be rationalized by the following scheme:

$$(PPh_3)_3CoN_2H + \textit{cis}\text{-2-pentene} \rightleftarrows \pi\text{-}(\textit{cis}\text{-2-pentene})(PPh_3)_2CoN_2H + PPh_3 \qquad (5)$$

$$\pi\text{-}(\textit{cis}\text{-2-pentene})(PPh_3)_2CoN_2H \rightleftarrows A \rightleftarrows \pi\text{-}(\textit{trans}\text{-2-pentene})(PPh_3)_2CoN_2H \qquad (6)$$

$$\pi\text{-}(\textit{trans}\text{-2-pentene})(PPh_3)_2CoN_2H + \textit{cis}\text{-2-pentene} \rightleftarrows$$
$$\rightleftarrows \pi\text{-}(\textit{cis}\text{-2-pentene})(PPh_3)_2CoN_2H + \textit{trans}\text{-2-pentene} \qquad (7)$$

$$\pi\text{-}(\textit{cis}\text{-2-pentene})(PPh_3)_2CoN_2H + \textit{cis}\text{-2-pentene} \rightarrow II + N_2 \qquad (8)$$

For high molar ratios of (I)/*cis*-2-pentene reaction (8) predominates. This scheme can be rewritten using the following abbreviations:

cis-2-pentene = *cis*

trans-2-pentene = *trans*

π-(*cis*-2-pentene)$(PPh_3)_2CoN_2H$ = C

π-(*trans*-2-pentene)$(PPh_3)_2CoN_2H$ = D

$$(I) + \textit{cis} \rightleftarrows C + PPh_3 \qquad (9)$$

$$C \rightleftarrows A \rightleftarrows D \qquad (10)$$

$$D + \textit{cis} \rightleftarrows C + \textit{trans} \qquad (11)$$

It follows from the stationary state hypothesis that:

$$\frac{d[C]}{dt} = k_9\cdot[I]\cdot[\textit{cis}] + k_{11}\cdot[D]\cdot[\textit{cis}] + k_{-10}\cdot[D] - k_{-9}\cdot[C]\cdot[PPh_3] - k_{10}\cdot[C] = 0$$

and,

$$\frac{\mathrm{d}[\mathrm{D}]}{\mathrm{d}t} = k_{10}\cdot[\mathrm{C}]-k_{-10}\cdot[\mathrm{D}]-k_{11}\cdot[\mathrm{D}]\cdot[cis]=0$$

$$[\mathrm{C}] = \frac{k_{-10}\cdot[\mathrm{D}]+k_{11}\cdot[cis]\cdot[\mathrm{D}]}{k_{10}}$$

$$[\mathrm{D}] = \frac{k_9\cdot k_{10}\cdot[\mathrm{I}]\cdot[cis]}{k_{-9}\cdot[\mathrm{PPh_3}]\cdot(k_{-10}+k_{11}\cdot[\mathrm{I}])}$$

The rate determining step is the reaction (11)

$$\frac{\mathrm{d}[trans]}{\mathrm{d}t} = k_{11}\cdot[\mathrm{D}]\cdot[cis] \tag{12}$$

We consider here only the reaction proceeding from left to right since we are concerned experimentally only with the early stages of the reaction. Introducing [D] into (12) we obtain:

$$\frac{\mathrm{d}[trans]}{\mathrm{d}t} = \frac{k_9\cdot k_{10}\cdot k_{11}\cdot[cis]^2\cdot[\mathrm{I}]}{k_{-9}\cdot[\mathrm{PPh_3}]\cdot(k_{-10}+k_{11}\cdot[cis])}$$

when $k_{-10}\gg k_{11}$ this equation reduces to:

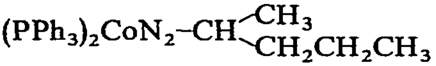
$$\frac{\mathrm{d}[trans]}{\mathrm{d}t} = \frac{k_9}{k_{-9}}\cdot\frac{k_{10}}{k_{-10}}\cdot k_{11}\,\frac{[cis]^2\cdot[\mathrm{I}]}{[\mathrm{PPh_3}]}$$

$$\frac{\mathrm{d}[trans]}{\mathrm{d}t} = K_9\cdot K_{10}\cdot k_{11}\,\frac{[cis]^2\cdot[\mathrm{I}]}{[\mathrm{PPh_3}]} \tag{13}$$

which is in good agreement with experimental data, so that the hypothesis that for this type of catalysis the rate determining step is the ligand exchange reaction (11) seems to be justified.

A and (II) complexes; mechanism of inhibition

The transient species A seems to be a conventional σ-organometallic product:



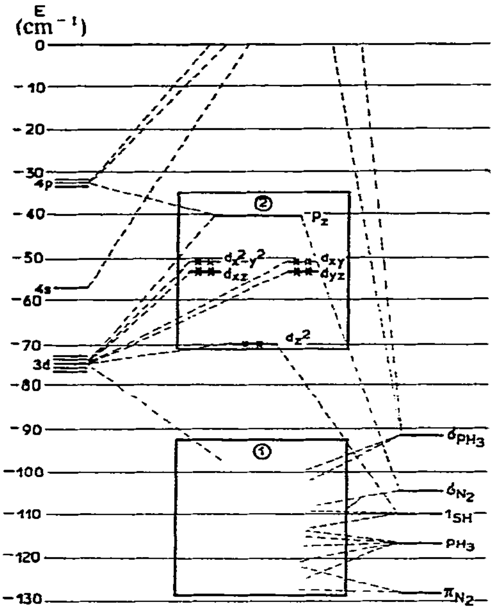
$$\mathrm{(PPh_3)_2CoN_2{-}CH}\begin{cases}\mathrm{CH_3}\\\mathrm{CH_2CH_2CH_3}\end{cases}$$

so the scheme presented is an addition–elimination sequence.

Undoubtedly the inhibition of catalysis is connected with the ligand exchange reaction (8). The complex (II) has such a structure that an isomerization is no longer possible. This could be rationalized in two ways:

1. Formation of a σ-organometallic intermediate (in which free rotation is possible) cannot take place on electronic grounds. The hydrogen in (II) has lost its hydridic nature, and does not add to π complexed olefin.
2. A σ-organometallic compound is formed, but the ligand exchange (11) is hindered.

It is possible to construct a qualitative energy level diagram for (I). Energies for 3*d*, 4*s* and 4*p* levels of Co are taken from Richardson *et al.*[10,11], energies for N_2 from Ransil[12], and the energy for H is taken as $110\times10^3\,\mathrm{cm}^{-1}$. Energy levels for



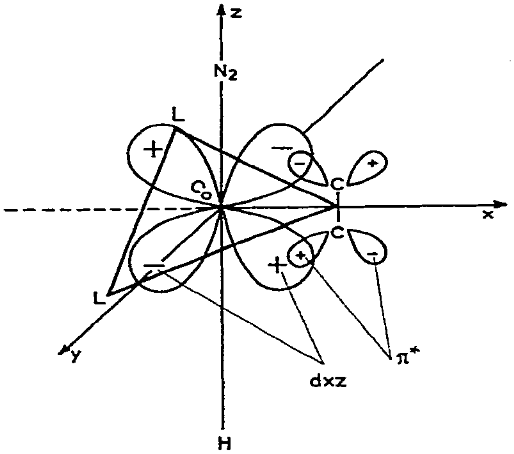


Fig. 7. Qualitative energy level diagram for $(PPh_3)_3CoN_2H$.

Fig. 8. Complex formed in the first stage of interaction of an olefin with $(PPh_3)_3CoN_2H$.

triphenylphosphine were approximated by those for PPh_3[13]. Energy levels for the molecular orbitals of complex (I) were obtained by SCCC calculations[13]. The energy level diagram is presented in Fig. 7. This diagram is not quantitative, but the sequence of orbitals seems to be correct.

It is seen from Fig. 7 that two groups of orbitals exist: bonding ① and non-bonding ② . The reactivity of the complex is mainly dependent on the latter group. All four orbitals: d_{xz}, d_{yz}, d_{xy} and $d_{x^2-y^2}$ are occupied, and as a result complex (I) will act primarily as a Lewis base.

The observed dependence of the rate on PPh_3 concentration suggests that the π-complexed olefin occupies a place formerly taken by triphenylphosphine (Fig. 8). In this structure the bond between cobalt and the olefin is formed first of all by the charge donation $Co \rightarrow \pi^*$. (Some interaction of the type $\pi \rightarrow Co$ should also exist but it is believed to be much less important.) It is reasonable to assume that any interaction of (I) with olefinic substrates starts by formation of this type of complex.

The rate of isomerization changes when nitrogen is exchanged for RCN or completely expelled from the coordination sphere. The rate decreases in the sequence: pyrolyzed complex $> N_2 > PhCN > CH_3CN$, which is the sequence of increasing basicity of the nitrogen lone pair. The charge on the cobalt atom should also increase in the same order. This will in turn raise the level of the d_{xz}, d_{yz} orbitals making more difficult the dissociation of a π-complexed olefin in D (the $Co \rightarrow \pi^*$ bond is stronger). The complex involved in catalysis is substance C.

The increased basicity of nitrogen in N_2, PhCN, CH_3CN sequence is also responsible for the decrease of the rate of the ligand exchange:

$$(PPh_3)_3Co(X{\equiv}X)H + {>}C{=}C{<} \rightarrow (PPh_3)_2CoH({>}C{=}C{<})X + X{\equiv}X \qquad (15)$$

EXPERIMENTAL

All operations were performed under N_2 purified over BTS catalyst. Solvents were distilled over sodium wire and deoxygenated before use. IR spectra were measured on a Unicam SP 200, ESR spectra on a JEOL ESR JM 3X and electronic spectra on a Unicam SP 700 instrument. Derivatography of complex (I) was studied on the Derivatograph Model MOM 1950 system F. Paulik, J. Paulik and L. Erdey.

Synthesis of $(PPh_3)_3CoN_2H$

Tris(triphenylphosphine)dinitrogencobalt hydride etherate (I) was prepared by the Yamamoto method[14]:

$$Co(Acac)_3 + Al(i\text{-}Bu)_3 + PPh_3 + N_2 \xrightarrow{\text{ether}} (PPh_3)_3CoN_2H\cdot\text{ether}$$

Triphenylphosphine and triisobutylaluminium were Reagent Grade, and were used without further purification. Cobalt(III) acetylacetonate $Co(Acac)_3$ was synthezized by Bryant and Fernelius's method[9].

Kinetic measurements and analysis

Samples of (I) were introduced under nitrogen into the reactor, and deoxygenated benzene was added. The reactor was placed in the thermostat (±1°) and a benzene solution of *cis*-2-pentene was added. Samples were taken at different time intervals. The reaction was quenched by adding benzoic acid. Samples were distilled before analysis, and were analyzed by GLC on a 3 m column of 30% 3,3-oxydipropionitrile on Chromosorb P 60/80 mesh at 55° using Ar as carrier gas in conjunction with a flame ionization detector.

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