ALKYL COMPLEXES OF COBALT IN CATALYTIC CYCLES FOR HYDROGENATION OF ALKENES

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Summary

The potential of several alkylcobalt complexes as catalysts for hydrogenation and isomerization of alkenes has been investigated. The complexes $CH_3Co(CO)_2$(Pom-Pom) (Pom-Pom = 1,2 bis(dimethoxyphosphino)ethane), $CH_3Co(CO)_3P(OMe)_3$ and $C_6H_5CH_2Co(CO)_3PPh_3$ are compared to $CH_3Co(CO)_2(P(OMe)_3)_2$ for their ability to function in catalytic cycles. Each is active for hydrogenation and isomerization of alkenes under conditions where the carbonylation–decarbonylation equilibrium is readily established. The lifetime for the complexes is much shorter than for $CH_3Co(CO)_2(P(OMe)_3)_2$ suggesting that two phosphorus donors in *trans* positions in an intermediate is a requirement for catalyst stability in these alkylcobalt complexes.

Homogeneous catalysis has occupied a central position in and provided much of the impetus for organometallic chemistry [1–3]. The majority of catalytic systems have centered on square planar complexes, transition metal hydrides and transition metal clusters, although some novel approaches to opening catalytic sites have recently been reported [4–6].

We previously reported the catalytic hydrogenation and isomerization of 1-alkenes by $CH_3Co(CO)_2(P(OMe)_3)_2$ [4]. This compound shows a marked activity (450 turnovers/h) at ambient conditions. This complex, $CH_3Co(CO)_2(P(OMe)_3)_2$, showed very little activity for hydrogenation or isomerization of more hindered alkenes. Catalysis of 1-alkenes was inhibited by the presence of CO and $P(OMe)_3$ and was not affected by the presence of *p*-dinitrobenzene [4]. A mechanism for the hydrogenation and isomerization of 1-alkenes by $CH_3Co(CO)_2(P(OMe)_3)_2$ was suggested which incorporated a series of carbonylation–decarbonylation cycles to open coordination sites for catalytic reactions [4]. This is shown in Fig. 1. Based on the very slow elimination of CH_4 and $CH_3C(O)H$ from the catalyst system the geometry of two intermediates was assigned [4]. This is shown in Fig. 2.

We now report the results of several alkylcobalt complexes in homogeneous hydrogenation cycles which provide additional support for the suggested mechanism.
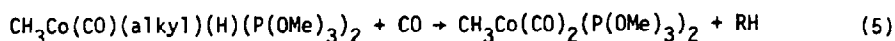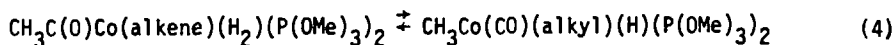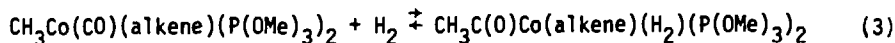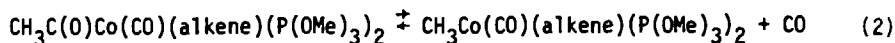
$$CH_3Co(CO)_2(P(OMe)_3)_2 + alkene \rightleftharpoons CH_3C(O)Co(CO)(alkene)(P(OMe)_3)_2 \qquad (1)$$

$$CH_3C(O)Co(CO)(alkene)(P(OMe)_3)_2 \rightleftharpoons CH_3Co(CO)(alkene)(P(OMe)_3)_2 + CO \qquad (2)$$

$$CH_3Co(CO)(alkene)(P(OMe)_3)_2 + H_2 \rightleftharpoons CH_3C(O)Co(alkene)(H_2)(P(OMe)_3)_2 \qquad (3)$$

$$CH_3C(O)Co(alkene)(H_2)(P(OMe)_3)_2 \rightleftharpoons CH_3Co(CO)(alkyl)(H)(P(OMe)_3)_2 \qquad (4)$$

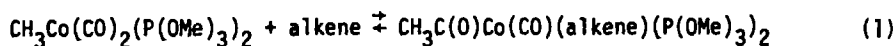$$CH_3Co(CO)(alkyl)(H)(P(OMe)_3)_2 + CO \rightarrow CH_3Co(CO)_2(P(OMe)_3)_2 + RH \qquad (5)$$

Fig. 1. Scheme for the catalytic hydrogenation of 1-alkenes by $CH_3Co(CO)_2(P(OMe)_3)_2$ [4].

Further these results show the potential of carbonylation–decarbonylation cycles in opening coordination sites for catalytic reactions.

Experimental

Previously reported experimental procedures were used for preparation of $CH_3Co(CO)_2(P(OMe)_3)_2$ and for the catalytic hydrogenation studies [4].

Infrared spectra were recorded on a Beckman 4240 spectrophotometer; NMR spectra were recorded on a Varian EM 390 spectrometer. The data from the deuterium labeling were collected by GC-Mass spectrometry (12' carbowax column) with the aid of Dr. Tim Wachs of the Cornell Mass Spectral Facility.

The mono substituted methyl complex, $CH_3Co(CO)_3P(OMe)_3$, was prepared from the acetyl derivative in a procedure previously described for CH_3Co-$(CO)_2(P(OMe)_3)_2$ [7]. The acyl complex [7], $CH_3C(O)Co(CO)_3P(OMe)_3$, was treated with a slight excess of NaOMe in THF for 20 h. Excess CH_3I was added and the solution was stirred for 2 h. The solution was filtered and the solvent removed by reduced pressure. Washing with hexane led to the product, $CH_3Co(CO)_3P(OMe)_3$, in 27% yield (IR 2020(M), 1960(vs) cm^{-1}).

$CH_3Co(CO)_3PPh_3$ and $C_6H_5CH_2Co(CO)_3PPh_3$ were prepared by literature procedures [8,9]. The methyl complex, $CH_3Co(CO)_3PPh_3$, was isolated as yellow crystals and the infrared spectrum (2055(m), 1975(sh) and 1955(vs) cm^{-1}) was in good agreement with the reported spectrum [8]. The benzyl complex also produced yellow crystals with the infrared spectrum (2036(w) and 1956(s) cm^{-1}) in agreement with previous work [9].

1,2-Bis(dimethoxyphosphino)ethane (Pom-Pom) was prepared by the literature procedure [10]. Purification was achieved by vacuum distillation and column chro-
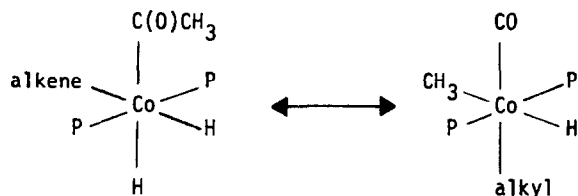

Fig. 2. Required stereochemistry of reaction 3 leading to *cis*-alkyl and H, but *trans*-CH$_3$ and -H [4] (P = P(OMe)$_3$).

matography (alumina/Et$_2$O). The NMR spectrum (τ 6.4(m), 8.5(m)) was as reported [10].

The preparation of CH$_3$Co(CO)$_2$(Pom-Pom) was similar to that of CH$_3$Co-(CO)$_2$(P(OMe)$_3$)$_2$ [4]. A solution of 1.3 g (6.4 mmol) of KCo(CO)$_4$ in 200 ml of toluene was stirred while 0.90 g (6.4 mmol, 0.40 ml) of CH$_3$I was slowly added. After the CH$_3$I addition, 1.4 g (6.4. mmol) of Pom-Pom was added and the mixture stirred overnight. The resulting yellow solution was filtered and reduced in volume. Column chromatography (alumina/hexane) yielded a yellow oil. Recrystallization (toluene/hexane) at $-20\,^\circ$C gave pale yellow crystals which showed the expected infrared absorptions (toluene) in the carbonyl region at 1991(s), 1935(vs) and 1645 cm^{-1} for CH$_3$C(O)Co(CO)$_2$(Pom-Pom). This species could be decarbonylated under a stream of N$_2$ at room temperature.

Results and discussion

Two reactions of CH$_3$Co(CO)$_2$(P(OMe)$_3$)$_2$ were examined to further investigate the catalytic hydrogenation and isomerization of 1-alkenes. The effect of hydrogen pressure was examined by increasing the pressure of hydrogen from 2 to 60 atm in the hydrogenation of 1-octene by CH$_3$Co(CO)$_2$(P(OMe)$_3$)$_2$ which led to an increase of 100 in the rate of formation of octane and isomerization of 1-octene. At room temperature and 60 atm of H$_2$ 30 ml of 1-octene were converted to 23 ml octane, 3 ml trans-2-octene, 0.6 ml cis-2-octene and 3 ml of 1-octene in 1 h. Deuterium incorporation into the hydrogenated and isomerized alkene was also investigated:

$$1\text{-octene} + D_2 \text{ (1 atm)} \xrightarrow{\text{CH}_3\text{Co(CO)}_2(\text{P(OMe)}_3)_2} \text{deuterium incorporation}$$
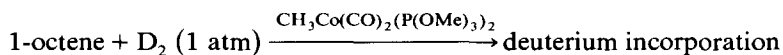
Up to three deuterium atoms were incorporated into the 1-octene, up to two were incorporated into trans-2-octene and up to two were incorporated into cis-2-octene under an atmosphere of D$_2$. The relative amounts are shown in Table 1. The incorporation into 1-octene indicates that the equilibria 1–4 (Fig. 1) may occur without progressing to the hydrogenated product. The incorporation into the 2-octenes is substantial but less than into 1-octene, consistent with deuterium incorporation before and/or during isomerization. The isomerized alkene (2-octene) would probably be lost from the coordination sphere and not recomplexed, as expected from the lack of 3-octene, the failure of CH$_3$Co(CO)$_2$(P(OMe)$_3$)$_2$ to catalyze hydrogenation of 2-octene, and the lower deuterium incorporation in 2-octene than in 1-octene. The incorporation into octane also indicates the equilibria exchanging hydrogen and deuterium occur readily since the primary octane formed contained

TABLE 1

THE RELATIVE AMOUNTS OF DEUTERIUM INCORPORATION INTO OCTENES DURING ISOMERIZATION

Alkene	C$_8$H$_{16}$	C$_8$H$_{15}$D	C$_8$H$_{14}$D$_2$	C$_8$H$_{13}$D$_3$
1-Octene	1	0.9	0.24	0.04
trans-2-Octene	1	0.62	0.12	–
cis-2-Octene	1	0.57	0.03	–

only one deuterium (about 3 times the amount of $C_8H_{16}D_2$). No non-deuterated octane was formed.

In catalytic hydrogenation of alkenes by $CH_3Co(CO)_2(P(OMe)_3)_2$ hydrogenated alkene is produced at greater than 10^6 rate of formation of CH_4 [4]. This was ascribed to the geometry of the proposed intermediates as shown in Fig. 2. To maintain the methyl *trans* to the hydride, avoiding CH_4 elimination in the inter- mediate, $CH_3Co(R)(H)(CO)(P(OMe)_3)_2$, the $P(OMe)_3$ ligands must be *trans* as previously discussed [4]. To test this hypothesis we prepared the bidentate analogue of the catalyst, $CH_3Co(CO)_2(Pom-Pom)$ (Pom-Pom $= (OMe)_2PCH_2CH_2P(OMe)_2$) where the phosphorus donors must be *cis* and investigated its ability to catalyze the hydrogenation and isomerization of alkenes. This complex functioned very similarly to the monodentate analogue as a catalyst, only slower with a rate of 20 turnovers/h. A portion of the lowered activity may be due to the decomposition of the catalyst which is greatly enhanced in comparison to the $P(OMe)_3$ complex. The amount of CH_4 and CH_3CHO formed during hydrogenation by $CH_3Co(CO)_2(Pom-Pom)$ was 33% after 2 h which can be compared to 5% after 24 h for $CH_3Co(CO)_2(P(OMe)_3)_2$. The structures which may lead to enhanced decomposition are shown in Fig. 3. The top reaction leads to a facial arrangement of CH_3, H and R while the lower reaction leads to *cis* H and R, but *trans* CH_3 and H. These possibilities are consistent with the production of CH_4 in lower rates than RH for hydrogenations by $CH_3Co(CO)_2(Pom-Pom)$ but at a more rapid rate than for hydrogenation by $CH_3Co(CO)_2(P(OMe)_3)_2$. The rate of elimination of CH_4 from $CH_3Co(CO)_2(Pom-Pom)$ in comparison to the production of RH suggests a 100 fold preference for the path shown in the lower part of Fig. 3. A preference for alkene *trans* to H would be expected from the more favorable distribution of ligands with π bonding capability.

The monophosphite complex, $CH_3Co(CO)_3P(OMe)_3$, shows no catalytic activity at ambient conditions, however when $CH_3Co(CO)_3P(OMe)_3$ is placed in the pres-
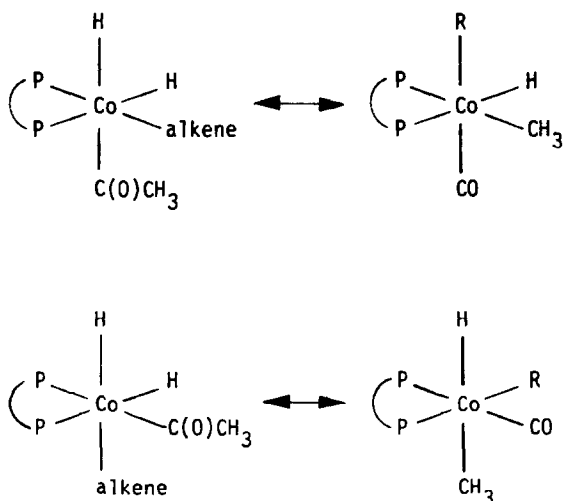

Fig. 3. Possible stereochemistries of the intermediates in catalytic hydrogenation of alkenes by $CH_3Co(CO)_2(Pom-Pom)$ (R = alkyl, P⌢P = Pom-Pom). The first reaction leads to the isomer with R, H and CH_3 on the same face of the octahedron which should lose RH and CH_4 at comparable rates.

ence of 1-hexene and H_2 at 60 °C, hydrogenation and isomerization were observed (100 turnovers/h) although the catalyst had a short lifetime with CH_4 elimination greatly enhanced in comparison to $CH_3Co(CO)_2(P(OMe)_3)_2$. In contrast to $CH_3Co(CO)_2(P(OMe)_3)_2$, the monophosphite species functions as a catalyst for hydrogenation of cyclohexene with little difference in rate from hydrogenation of 1-hexene. This may indicate that the selectivity in hydrogenation observed for $CH_3Co(CO)_2(P(OMe)_3)_2$ is steric in nature.

The analogous triphenylphosphine complex, $CH_3Co(CO)_3PPh_3$, shows only slight activity for hydrogenation and isomerization of 1-hexene at 60 °C. The benzyl complex, $C_6H_5CH_2Co(CO)_3PPh_3$, was of considerable interest because the carbonylation–decarbonylation equilibrium is established at 30 °C [9]. The complex, $C_6H_5CH_2Co(CO)_3PPh_3$, was active at 30 °C for hydrogenation of 1-octene (10 turnovers/h) and isomerization to cis-2-octene (16 turnovers/h) and trans-2-octene (56 turnovers/h) in the presence of H_2. The lifetime was short, with dimer, $Co_2(CO)_6(PPh_3)_2$, formation. Isomerization of 1-octene occurred in the absence of H_2 at a much reduced rate (2 turnovers/h). The dimer, $Co_2(CO)_6(PPh_3)_2$, showed no reaction with 1-octene, in the presence or absence of H_2, up to 60 °C, which was the highest temperature investigated. To determine if a seventeen electron species could be the active catalyst, a solution of $Co_2(CO)_6(PPh_3)_2$ was photolyzed in 1-octene under an atmosphere of H_2; no reaction was observed. The dimer is evidently formed in a termination step for the catalytic cycle. Photolysis of $Co_2(CO)_6(P(OMe)_3)_2$ and $Co_2(CO)_4(P(OMe)_3)_4$ in the presence of H_2 and 1-octene also gave no evidence of reaction.

These investigations into the potential of alkyl complexes of cobalt as catalysts for the hydrogenation and isomerization of alkenes have shown that opening two coordination sites by carbonylation–decarbonylation reactions allow catalytic cycles. Both the pressure dependence and the deuterium labeling indicate a mechanism involving several equilibria, with increased hydrogen pressure shifting the equilibria toward product. The enhanced catalyst decomposition for $CH_3Co(CO)_2(Pom-Pom)$ in comparison to $CH_3Co(CO)_2(P(OMe)_3)_2$ suggests the stereochemistries for intermediates as shown in Fig. 2–4. All evidence is consistent with the originally proposed mechanism (Fig. 1) while substantial portions of the data are inconsistent with other mechanisms. A radical mechanism can be ruled out by the following data: (1) p-dinitrobenzene has no effect on the rate of hydrogenation, (2) hydrocarbon coupling products (i.e. C_2H_6) are not observed and a metal carbonyl dimer is only observed for the benzyl complex, (3) the analogous hydrides are not active in catalytic reactions, (4) the analogous dimers are not catalysts, even under photolysis, and (5) the alkyl complex, $CH_3Co(CO)_2(P(OMe)_3)_2$, can be quantitatively recovered after short (2 h) reaction times [13].

The presence of the alkyl group serves as a probe of the possible geometries of the intermediates, which cannot be directly observed, by comparison of the rates of elimination. The fact that CH_4 is eliminated during the catalysis by $CH_3Co(CO)_2(P(OMe)_3)_2$ at $1/10^6$ of the rate of hydrogenated alkane is quite informative regarding the required geometry, and provides strong evidence for the reaction shown in Fig. 2. That the rate of CH_4 elimination is enhanced relative to hydrogenated product for either $CH_3Co(CO)_2(Pom-Pom)$ or $CH_3Co(CO)_3P(OMe)_3$ indicates other geometric possibilities for these complexes. Such possibilities are shown in Fig. 3 and 4.
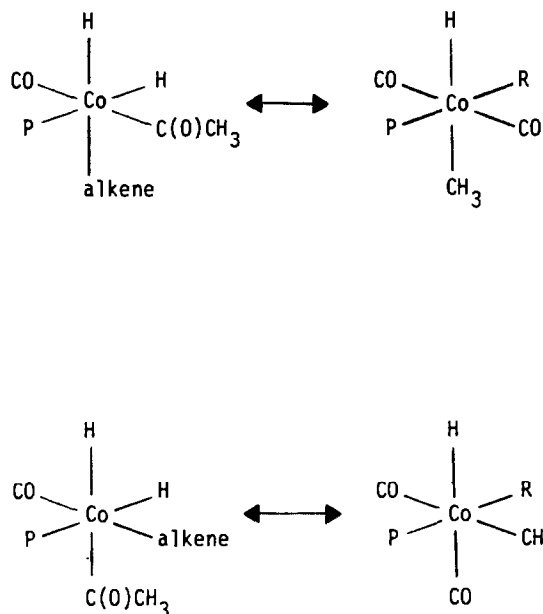
Fig. 4. Possible stereochemistries in the catalytic hydrogenation of alkenes by $CH_3Co(CO)_3P(OMe)_3$ (R = alkyl, P = P(OMe)$_3$). The second reaction should lead to loss of CH_4.

This ability to define the stereochemistry of intermediates allows more mechanistic interpretation than is usually possible for a catalytic cycle. Reaction 4 requires that the alkene insert into the *cis* Co–H bond as opposed to a hydride migration and further that this reaction occur orders of magnitude more rapidly than elimination of CH_3CHO which would be a competing reaction. Alkyl migration to the open coordination site occurs. Reductive elimination only occurs from a *cis* geometry in this scheme which indicates some rigidity in the six-coordinate complex and rules
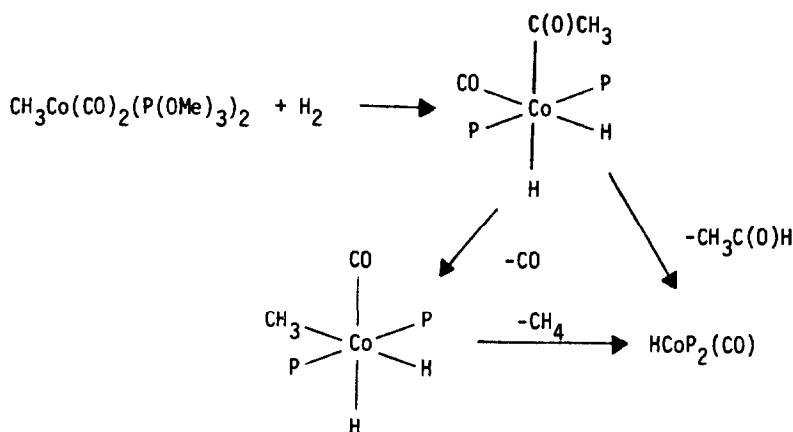

Fig. 5. Illustration of the addition of H_2 to the cobalt center prior to alkene complexation. This would result in enhanced reductive elimination of CH_4 and $CH_3C(O)H$.

out bimolecular elimination in this cycle. The data suggest that the alkene adds prior to H_2 since the addition of H_2 would almost certainly lead to loss of CH_4 and $CH_3C(O)H$ as shown in Fig. 5. Addition of H_2 to a very similar rhodium complex led to aldehyde elimination in the hydroformylation reaction [12].

The ligand environment affects the capability of these alkylcobalt complexes to function as catalysts both in the rate and in catalyst lifetime. Our data suggest that two phosphorus donors which may occupy *trans* positions in the six-coordinate intermediates are required for reasonable catalyst lifetime.

This research has shown that: (1) alkyl complexes can be active in catalytic cycles for hydrogenation and isomerization of alkenes, (2) this activity is seen at conditions where carbonylation and decarbonylation occur readily, (3) similar hydrido complexes are not active, (4) metal dimers are not active, even under photolysis, (5) *p*-dinitrobenzene has no effect on the rate of hydrogenation but CO or $P(OMe)_3$ inhibit catalytic activity, (6) the most reasonable mechanism involves alkyl migration, and (7) the presence of the alkyl group as a mechanistic probe provides unique information on the catalytic cycle.

Acknowledgement

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13 A mechanism in which the radical pair $[CH_3, Co(CO)_2(P(OMe)_3)_2]$ is trapped in a solvent cage and never become free in solution cannot be ruled out.