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Comparison of $-Sn\phi_3$ and $-SnCl_3$ as Cocatalyst Groups for $[Pt(P\phi_3)_2ClQ]$ in the Isomerization of 1,5-Cyclooctadiene

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The effect of Ph_3SnX (X = H, Cl, Br, and NO_3) on the catalytic isomerization of 1,5-cyclooctadiene (COD) by some platinum complexes was investigated. The results were compared with those using $SnCl_2 \cdot 2H_2O$ as the cocatalyst. It was observed that PPh_3SnCl is an active cocatalyst in these systems, especially for isomerization. A mechanism is proposed for the isomerization process.

Earlier papers in this series have described the isomerization and selective hydrogenation of poly-olefinic compounds under the catalytic influence of dihalo-di-phosphine complexes of platinum(II) or palladium(II) and related compounds, with the addition of tin(II) chloride as a cocatalyst. A considerable number of compounds containing a variety of ligands has been studied, but little attention has been paid to the role of the cocatalyst. It was shown (*1*, *2*) that lead(II) chloride and germanium(IV) chloride can play this role, but are much inferior to tin(II) chloride; no detailed study of their behavior was made. Their inferiority is attributed to the lesser tendency of lead and germanium to form bonds to platinum and palladium. This raises the question as to whether compounds of tin, other than the halides and pseudohalides, might serve as cocatalysts. In the study reported in this paper, we have replaced the $SnCl_3^-$ group which has been used before by the $-Sn(C_6H_5)_3$ group. In the former, the tin is in the +2 oxidation state, and in the latter, in the +4 state, but the platinum–tin bond is formed in both cases.

EXPERMENTAL

Syntheses. Most of the compounds used were synthesized by published methods: *cis*-$[Pt(P\phi_3)_2Cl_2]$ (*3*), *trans*-$[Pt(P\phi_3)_2HCl]$ (*3*), *trans*-$[Pt(P\phi_3)_2HSnCl_3]$ (*3*), *cis*-$[Pt(P\phi_3)_2Br_2]$ (*2*), *cis*-$[Pt(P(O\phi)_3)_2Cl_2]$ (*2*), *cis*-$[Pt(As\phi_3)_2Cl_2]$ (*4*), *cis*-$[Pt(Sb\phi_3)_2Cl_2]$ (*5*) *cis*-$[Pt(S\phi_2)_2Cl_2]$ (*6*), *cis*-$[Pt(Se\phi_2)_2Cl_2]$ (*6*), $[Pt(\phi_2PCH_2CH_2)Cl_2]$ (*7*), $[Pt(P\phi_3)_4]$ (*4*), $Sn\phi_3NO_3$ (*8*), and *trans*-$[Pt(P\phi_3)_2Cl(Sn\phi_3)]$ (*9*). Triphenyltin bromide, $Sn\phi_3Br$, was prepared by refluxing a mixture of 2.0 g of $Sn\phi_3Cl$ and 5.0 g of LiBr in 50 ml of acetone for 90 min. The acetone was removed under reduced pressure and the white solid was extracted with benzene. Evaporation of the benzene gave the desired product. *Anal.* Calcd for $C_{18}H_{15}SnBr$: C, 50.29; H, 3.52; Br, 18.59. Found: C, 51.26; H, 3.67; Br, 17.81.

Attempts to prepare *trans*-$[Pt(P\phi_3)_2Cl(Sn\phi_3)]$ by treating $Pt(P\phi_3)_4$ with $Sn\phi_3Cl$, as described in the literature (*10*), resulted in the formation of $[Pt(P\phi_3)_2Cl_2]$.

Substrate and catalyst analysis. High-pressure hydrogenation reactions were carried out using a 300-ml stainless steel Magne-Drive autoclave, fitted with a temperature regulator, a sampling valve, and an air-driven motor. Samples were with-

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drawn at specific intervals and analyzed by gas chromatography using a 10 ft × $\frac{1}{8}$ in. copper column, packed with 20% diethylene glycol adipate on Chromosorb P (60/80 mesh). A thermal conductivity detector was employed and the flow rate and the temperature were varied to give optimum separation of the hydrogenation products.

After each experiment, the reaction mixture was concentrated to about 5 ml under reduced pressure; the catalyst residue was precipitated by addition of low boiling petroleum ether and analyzed by ir, NMR, and elemental analysis.

RESULTS

The most striking difference between the behavior of $[Pt(P\phi_3)_2ClSnCl_3]$ and $[Pt(P\phi_3)_2Cl(Sn\phi_3)]$ is that with an excess of cocatalyst, the former gives both isomerization and hydrogenation, whereas the latter gives isomerization almost exclusively. Table 1 gives some typical results with the $-Sn\phi_3$ group as the cocatalyst. Two observations stand out: (1) No isomerization takes place in the absence of the cocatalyst, and (2) the phosphorus-containing ligands give much more active isomerization catalysts than those containing arsenic, antimony, sulfur, or selenium. With the $-SnCl_3$ group as the cocatalyst, the arsine gives a more efficient catalyst than the phosphine, and the sulfide and selenide less efficient ones (*6*).

TABLE 1

Isomerization of 1,5-Cyclooctadiene (4.0 g) Using 0.25 mmole of Pt-Complex and 0.25 mmole of Triphenyltin Chloride[a]

Experiment	Catalyst	Cocatalyst	Time (hr)	Percentage 1,5-COD isomerized
0	$(Ph_3P)_2PtCl_2$	None	2.0	0
1	$(Pt_3P)_2PtCl_2$	Ph_3SnCl	2.0	100
2	*trans*-$(Ph_3P)_2PtHCl$	Ph_3SnCl	2.0	98.2
3	$(Diphos)PtCl_2$	Ph_3SnCl	3.5	100
4	$[(Pho)_3P]_2PtCl_2$	Ph_3SnCl	2.0	100
5	$(Ph_3As)_2PtCl_2$[b]	Ph_3SnCl	5.5	55
6	$(Ph_3Sb)_2PtCl_2$[b]	Ph_3SnCl	2.0	48
7	$(Ph_2S)_2PtCl_2$[b]	Ph_3SnCl	4.0	57
8	$(Ph_2Se)_2PtCl_2$[b]	Ph_3SnCl	3.0	30

[a] Under 500 psi of H_2 pressure at 120°C in 50 ml CH_2Cl_2.

[b] The complex showed decomposition.

TABLE 2

Effect of Variation of the Cocatalyst on the Isomerization of 1,5-Cyclooctadiene[a]

Experiment	Catalyst	Cocatalyst	Time (hr)	Percentage 1,5-COD isomerized
9	$(Ph_3P)_2PtCl_2$	Ph_3SnH	2	98.0
10	$(Ph_3P)_2PtCl_2$	Ph_3SnNO_3	2	43.6
11	$(Ph_3P)PtCl_2$	$SnCl_2 \cdot 2H_2O$	2	94.3
12	$(Ph_3P)_2PtBr_2$	Ph_3SnBr	2	100

[a] In 50 ml CH_2Cl_2 under 500 psi of H_2 pressure at 120°C, using 0.25 mmole of each catalyst and cocatalyst.

Table 2 further compares, the behavior of some cocatalysts containing the $-Sn\phi_3$ group with that containing the $-SnCl_3$ group. It is evident that the $-Sn\phi_3$ group is an effective cocatalyst, but that the inclusion of the nitrate group greatly decreases the catalytic activity.

Experiments 1 and 11, performed under exactly the same conditions, indicate that $(Ph_3P)_2PtCl(SnPh_3)$ is at least as good a catalyst for the isomerization of 1,5-cyclooctadiene (COD) as $(Ph_3P)_2PtCl(SnCl_3)$. Figure 1 illustrates the rate of isomerization under the conditions of Experiment 1. Similar experiments, using the $-SnCl_3$ group, give similar results, but the reaction is somewhat slower. Increasing the amount of cocatalyst, in the case of $-SnPh_3$, has little effect, but in the case of $-SnCl_3$, it increases the amount of hydrogenation.

The importance of a chloro group on the tin and the necessity for gaseous hydrogen are indicated in Table 3. There is almost no rearrangement of the 1,5-cyclooctadiene unless there is a source of hydrogen from the atmosphere or from the catalyst.

Subjecting Ph_3SnCl to the reaction conditions of Expt 1, but in the absence of both the catalyst and 1,5-COD, resulted in the recovery of the original compound. No Ph_3SnH was formed. However, $(Ph_3P)_2PtCl_2$ in the absence of the cocatalyst and 1,5-COD yielded a mixture of both

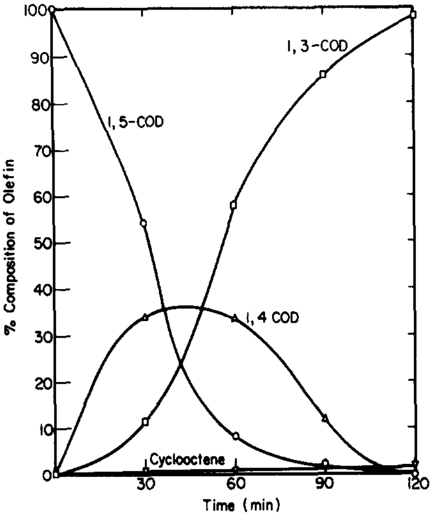


FIG. 1. Rate of isomerization using [Pt(Pϕ_3)$_2$-ClSnϕ_3].

cis- and *trans*-$(Ph_3P)_2PtHCl$, as indicated by a triplet in the ν_{Pt-H} region (*3*).

Elemental analysis of the used catalyst from the various runs gave quite unexpected, but interesting, results. NMR and ir analyses indicated the absence of both olefin and a metal hydride in the compounds isolated. A purified sample of the product from Experiment 1 analyzed to: C, 47.54; H, 3.84; Cl, 10.81; Sn, 11.90; and P, 6.23, which corresponds closely to the formula $C_{42}H_{35}P_2SnCl_3Pt \cdot 2H_2O$, which has the following calculated analyses: C, 47.69; H, 3.72; Cl, 10.05; Sn, 11.22; and P, 5.86. The following structure is proposed:

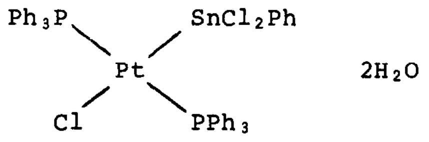


TABLE 3

Effect of the Nature of the Ambient Gas on the Catalytic Isomerization of 1,5-Cyclooxtadiene[a]

Experiment	Catalyst	Cocatalyst	Gas	Percentage 1,5-COD isomerized
13	$(Ph_3P)_2PtCl_2$	Ph_3SnCl	N_2	3
14		Ph_3SnH	N_2	13
15		Ph_3SnCl	H_2	98
16	$(Ph_3P)_2PtHCl$	Ph_3SnCl	H_2	28
17		Ph_3SnH	H_2	33
18		—	H_2	13

[a] Under 500 psi of N_2 or H_2 pressure, using 0.25 mmole of each catalyst and cocatalyst, at 120°C in a mixture of 40 ml CH_2Cl_2 and 30 ml i-PrOH for 4 hr.

Such a compound could result from the reaction of HCl (generated during the course of the formulation of the catalyst) and *trans*-$(Ph_3P)_2PtClSnPh_3$, as shown below:

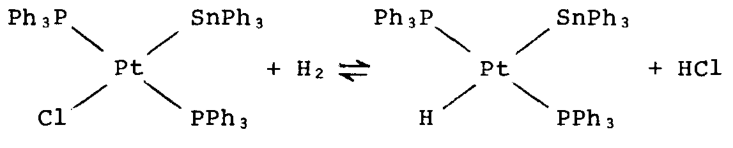
$$trans\text{-}(Ph_3P)_2PtClSnPh_3 + 2HCl \rightarrow trans\text{-}(Ph_3P)_2PtClSnCl_2Ph + 2C_6H_6.$$

Gorsich has reported a similar reaction involving Ph–Sn bond breaking (*11*):

$$Ph_3Sn\text{–}Mn(CO)_5 \xrightarrow{HCl} PhCl_2SnMn(CO)_5.$$

The catalysts containing Ph_2S, Ph_2Se, and Ph_3Sb all showed some decomposition as evidenced by the formation of a platinum mirror on the walls of the reaction flask.

To see whether a metal hydride was involved, as indicated by the reaction below, a separate reaction was carried out in the presence of triethylamine (Et_3N). A white compound was isolated which elemental analysis and sublimation point showed to be Et_3NHCl.



That the catalyst can be recovered and reused was shown by an experiment in which 0.025 mmole of catalyst residue (10% of the original amount) was employed un-

TABLE 4

Isomerization of 1,5-Cyclooctadiene Using 0.25 mmole of *trans*-$(Ph_3P)_2PtClSnPh_3$[a]

Experiment	Catalyst	Solvent	Time (hr)	*T* (°C)	Percentage 1,5-COD isomerized
19	$(Ph_3P)_2PtClSnPh_3$	CH_2Cl_2	2	120	95.5
20	$(Ph_3P)_2PtClSnPh_3$	CH_2Cl_2	3	120	100
21	$(Ph_3P)_2PtClSnPh_3$	CH_2Cl_2	2	120	87.4[b]
22	$(Ph_3P)_2PtClSnPh_3$	CH_2Cl_2	2	120	61.5[c]
23	$(Ph_3P)_2PtClSnPh_3$	CH_2Cl_2 + i-PrOH (1:1)	6	100	83.0
24	$(Ph_3P)_2PtClSnPh_3$	i-PrOH	5.5	120	56.0
25	$(Ph_3P)_2PtClSnPh_3$	Ethyl acetate	6	120	0
26	$(Ph_3P)_2PtClSnPh_3$	MeOH + benzene (2:3)	2	120	50.0
27	*trans*-$(Ph_3P)_2PtClSnCl_3$	CH_2Cl_2 + i-PrOH (1:1)	3	100	93.0

[a] Under 500 psi of H_2 pressure.
[b] Plus 0.25 mmole of Ph_3P.
[c] Plus 0.50 mmole of Ph_3P.

der the usual conditions. After 4 hr, 86% of the 1,5-COD had been isomerized. A sample of fresh catalyst (0.025 mmole), under the same conditions, isomerized only 30% of the COD in the same length of time. Thus, a recovered catalyst is more effective than a fresh one.

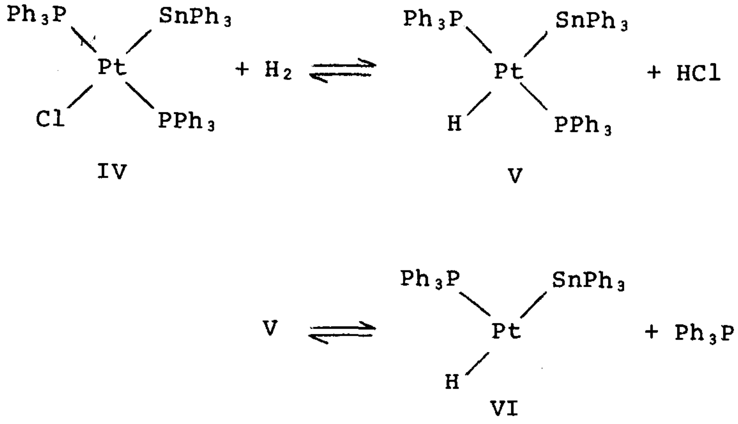
DISCUSSION

When tin(II) chloride is used as the cocatalyst, an excess of $SnCl_2$ must be added because the reaction

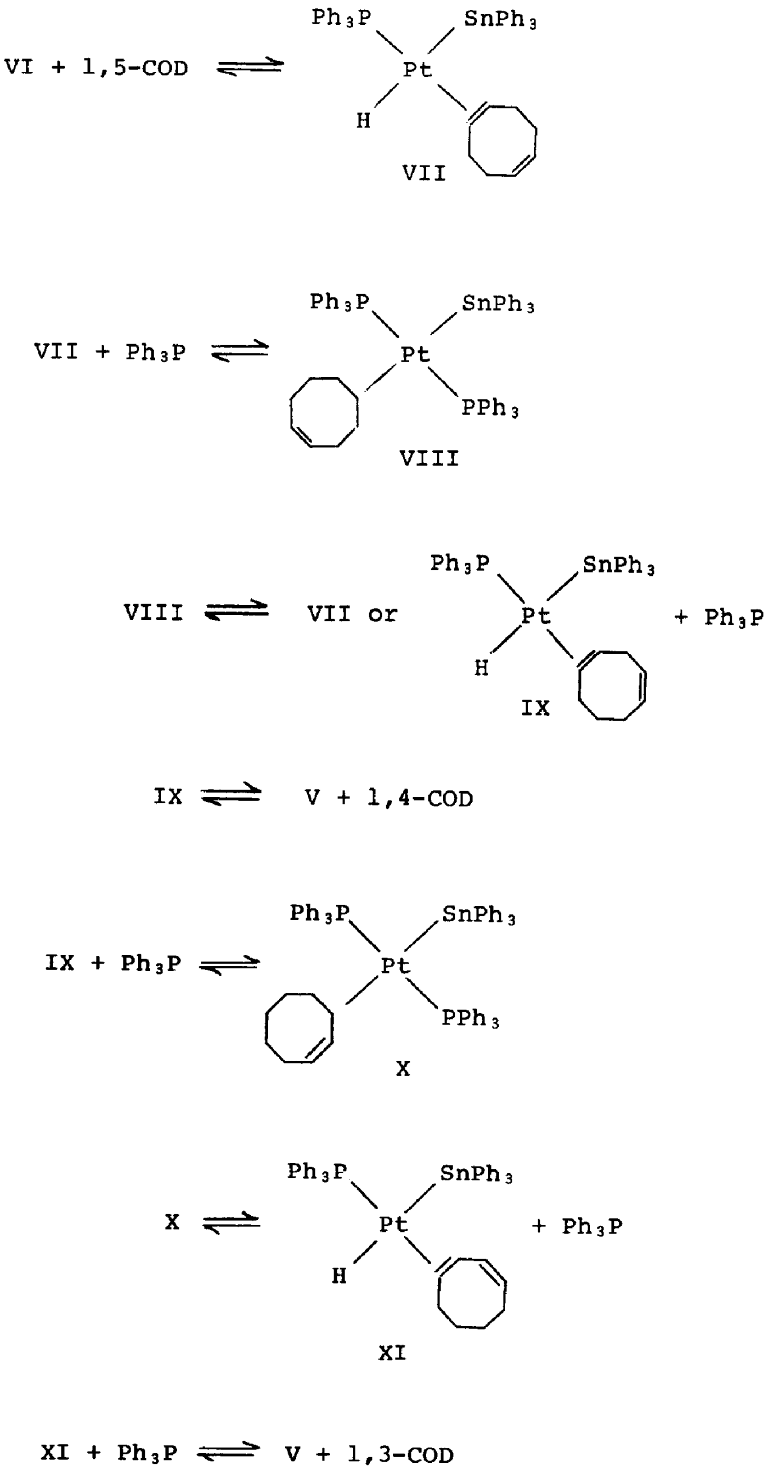
$$[Pt(P\phi_3)_2Cl_2] + SnCl_2 \rightleftarrows [Pt(P\phi_3)_2Cl(SnCl_3)]$$

reaches equilibrium. The optimum ratio of tin to platinum is about 10:1.

Experiments 20, 21, and 22 (Table 4) show that the addition of an excess of triphenylphosphine greatly reduces the catalytic activity. This may be due to the addition of a molecule of triphenylphosphine to the coordination sphere of the platinum, thus making it impossible for the olefin to coordinate. Alternatively, it may be due to the replacement of the chloro group by a molecule of the more strongly coordinating phosphine. Table 4 also shows that the choice of solvent is clearly of great



SCHEME 1



SCHEME 1—*Continued*

importance, as it is when [$Pt(P\phi_3)_2Cl(SnCl_3)$] is used (*6*).

The unique properties of $SnCl_2$ are attributed to the formation of $SnCl_3^-$ which, due to its high *trans* effect, labilizes the group *trans* to it in *trans*-$(Ph_3P)_2PtHSnCl_3$ for the isomerization process to occur. The $-Sn\phi_3$ group has an even stronger *trans*-directing influence than the $-SnCl_3$ group (*9*) so it might be expected to give a more active catalyst. This is not borne out by the results of Experiments 23 and 27, but this may be due to the lack of stability of [$Pt(P\phi_3)_2Cl(Sn\phi_3)$] in polar solvents (*9*). In methylene chloride, it is a highly efficient isomerization catalyst (Experiments 19 and 20). Unlike $SnCl_2$, which can insert itself into the Pt–Cl bond, Ph_3SnCl follows a different path(s) to form the Pt–Sn complex. Either of the following mechanistic approaches could account for the formation of the actual catalyst:

I. (1) $$\textit{cis}\text{-}(Ph_3P)_2PtCl_2 + H_2 \rightleftharpoons \textit{cis-}\text{ or }\textit{trans}\text{-}(Ph_3P)_2PtHCl + HCl,$$

(2) $$(Ph_3P)_2PtHCl + Ph_3SnCl \underset{\text{addition}}{\overset{\text{oxidative}}{\rightleftharpoons}} (Ph_3P)_2PtHCl_2SnPh_3,$$

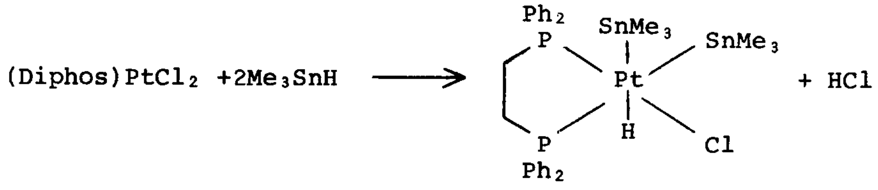
(3) $$(Ph_3P)_2PtHCl_2SnPh_3 \rightleftharpoons (Ph_3P)_2PtClSnPh_3 + HCl,$$

or

II. $$(Ph_3P)_2PtHCl + Ph_3SnCl \underset{\text{substitution}}{\overset{\text{direct}}{\rightleftharpoons}} (Ph_3P)_2PtClSnPh_3 + HCl.$$

Formation of the platinum–hydrido complex in step 1 is imperative if the subsequent reactions are to occur. Thus, a mixture of $(Ph_3P)_2PtCl_2$ plus Ph_3SnCl under N_2 atmosphere brought about only 3% isomerization of 1,5-COD (Experiment 13). Hence, it can be concluded that H_2 is necessary for the isomerization to occur (Experiments 13–18).

Step 2 in mechanism I involves a Pt(IV) complex. Although such an octahedral Pt(IV) complex was not isolated from the reaction mixture, a hexacoordinate Pt(IV) complex, involving hydrido, chloro, and trimethylstannato groups, was isolated by Clemmit and Glockling (*12, 13*) by oxidative addition of Me_3SnH to $(diphos)PtCl_2$:



Experiments 20, 21, and 22 show the effect of excess Ph_3P on the rate of isomerization of 1,5-COD. A decrease in the rate of the isomerization process is observed. This suggests that a pentacoordinate species involving *trans*-$(Ph_3P)_2PtHSnPh_3$ and the olefin is not a likely intermediate as was suggested for the case *trans*-$(Pt_3P)_2PtHSnCl_3$ (14). Although Pt(II), a d^8 system, could expand its coordination sphere, the presence of the bulky triphenylphosphine and triphenyltin groups would sterically hinder such an expansion. The mechanism, illustrated in Scheme 1, is more likely to take place for the isomerization process.

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