CHEMISTRY LETTERS, pp. 1273-1276, 1978. Published by the Chemical Society of Japan

PREPARATION AND THERMAL DECOMPOSITION OF UNSYMMETRICAL DIALKYL PLATINUM(II) COMPLEXES. ELUCIDATION OF A FACTOR CONTROLLING THE EASE OF β-ELIMINATION

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Unsymmetrical dialkylbis(triphenylphosphine)platinum(II), $Pt(R_a)(R_b)(PPh_3)_2$, has been prepared by the reaction of $Pt(R_a)X(PPh_3)_2$ with alkylating reagents such as $(R_b)MgX$ and $(R_b)Li$. The distribution of the gaseous products on thermolysis of these compounds reveals that the relative ease of β-eliminaiton concerning R_a and R_b is controlled by the numbers of β-hydrogens in these alkyl groups.

β-Elimination of alkenes from transition metal alkyls is considered as one of the most important elemental reactions in organometallic and catalytic chemistry.[1)] Recent investigations concerning the thermal decomposition of isolated transition metal alkyls have shed light on an understanding of the detailed process of the β-elimination.[2)] Dialkyl platinum(II) complexes, especially, serve as good models for the investigation, since they generally undergo thermal degradation giving alkane and alkene through a clean β-elimination.[3)] Now, if one employs an unsymmetrical dialkyl platinum(II) $Pt(R_a)(R_b)L_2$ for the thermolysis, the abstraction of the β-hydrogen of an alkyl group will compete with that of another alkyl group to give a mixture of $R_a(-H)$, R_bH, R_aH, and $R_b(-H)$:

$$Pt(R_a)(R_b)L_2 \xrightarrow[\text{β-elimination concerning } R_a]{} R_a(-H) + R_bH \qquad (1a)$$

$$Pt(R_a)(R_b)L_2 \xrightarrow[\text{β-elimination concerning } R_b]{} R_aH + R_b(-H) \qquad (1b)$$

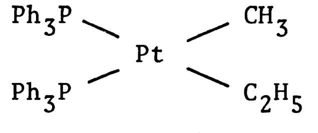
The analysis of the thermolysis products informs which alkyl group is preferentially amenable to the abstraction of the β-hydrogen by platinum and therefore may give informations about the factors which control the β-elimination. In this paper, we describe the preparation of unsymmetrical dialkylbis(triphenylphosphine)platinum(II), $Pt(R_a)(R_b)(PPh_3)_2$, as well as the thermal decomposition of these complexes.

The unsymmetrical dialkyl platinum(II) complexes were prepared by the reaction of monoalkylchlorobis(triphenylphosphine)platinum(II), $Pt(R_a)Cl(PPh_3)_2$[4)], with alkylating reagents such as alkyl lithium and Grignard reagents in diethyl ether at ambient conditions:

$$cis\text{-}Pt(R_a)Cl(PPh_3)_2 + R_bM \longrightarrow cis\text{-}Pt(R_a)(R_b)(PPh_3)_2 + MCl \qquad (2)$$

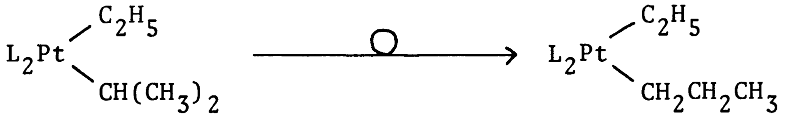
R_a = C_2H_5, n-C_3H_7; R_b = CH_3, C_2H_5, n-C_3H_7, i-C_3H_7, n-C_4H_9, i-C_4H_9;
M = Li, MgBr.

These unsymmetrical dialkyl platinum(II) complexes were stable in air at room temperature and easily recrystallized from a mixture of benzene and pentane. Table 1 summarizes the elemental analyses, decomposition points, and IR spectra of these compounds. Acidolysis of these complexes gave alkanes R_aH and R_bH in a 1/1 ratio. ^{1}H-NMR spectra of these unsymmetrical dialkyl platinum(II) complexes generally showed complex patterns in a region of alkyl group (δ 0.5-2.0 ppm in CD_2Cl_2), since α- and β-protons are coupled with ^{195}Pt as well as ^{31}P nuclei. Among them ^{1}H-NMR spectrum of methyl ethyl platinum(II) complex $\underset{\sim}{1}$ showed relatively simple pattern. The methyl protons give rise to a double doublet due to the coupling with two different types of ^{31}P's(J_{P-H}=7Hz, $J_{P'-H}$=8Hz) indicating that the complex has a cis-configuration. Satellites of the double doublet due to the coupling with ^{195}Pt were also observed (J_{Pt-H}=70Hz).



The reaction of trans-$Pt(C_2H_5)I(PPh_3)_2$[5)] with CH_3Li also gave the same product. These results indicate that the unsymmetrical dialkyl platinum(II) complexes with two triphenylphosphine ligands take cis-configuration similar to the symmetrical dialkyl platinum(II) complexes[4-6)].

The complex $\underset{\sim}{3}$ was readily converted into its stable isomer $\underset{\sim}{2}$ at room temperature as followed by NMR in CD_2Cl_2.



$\underset{\sim}{3}$ $\underset{\sim}{2}$ (3)

The rearrangement of s-C_4H_9 group was more facile and attempt to prepare a s-butyl ethyl platinum complex according to eq. (2) was unsuccessful to give a pure n-butyl

Table 1 Analytical Data and IR Spectra of Unsymmetrical Dialkyl Platinum(II) Complexes

Compounds[a)]		Yield(%)[c)]	C%(calcd)	H%(calcd)	d.p.(°C)	IR spectra(cm^{-1})[b)]
$Pt(C_2H_5)(CH_3)(PPh_3)_2$	1	58	61.0(61.3)	5.0(5.0)	160-163	2920m,2900sh,2840m,2970sh,1190s
$Pt(C_2H_5)(n-C_3H_7)(PPh_3)_2$	2	52	62.7(62.2)	5.5(5.4)	148-150	2940m,2900w,2830m,2800sh,1185m
$Pt(C_2H_5)(i-C_3H_7)(PPh_3)_2$	3	35[d)]	63.5(62.2)	5.5(5.4)	135-138	2890-1950br,2840m,1190m
$Pt(C_2H_5)(n-C_4H_9)(PPh_3)_2$	4	51	62.2(62.3)	5.5(5.5)	140-143	1940m,2880w,2850m,2800sh,1190m
$Pt(C_2H_5)(i-C_4H_9)(PPh_3)_2$	5	23	62.4(62.3)	5.7(5.5)	136-137	2930,2890br,2830m,1190m
$Pt(C_2H_5)(C_6H_5)(PPh_3)_2$	6	50	63.9(64.0)	4.9(4.9)	163-165	3040m,2950w,2880m,2840w,1190m
$Pt(n-C_3H_7)(n-C_4H_9)(PPh_3)_2$	7	40	63.3(63.0)	5.8(5.7)	132-135	2940sh,2900m,2850m,2800sh,1185m

a) n, normal; i, iso; acac, 2,4-pentadionato.

b) KBr disc. s, strong; m, medium; w, weak; sh, shoulder.

c) after recrystallization.

d) crude product.

ethyl platinum complex. Similar conversion of secondary alkyl gold and -iron complexes into their stable isomers has been reported.[7)]

Table 2 summarizes the results of thermolysis of unsymmetrical dialkyl platinum(II) complexes in solid state. Similar results were also obtained in toluene (R_a = C_2H_5; R_b = CH_3, C_2H_5, n-C_3H_7 at 60°C). Mass balance showed that almost all the alkyl groups bonded to Pt were incorporated into the gaseous product. The fact that the amounts of R_aH and $R_a(-H)$ are roughly equal to those of $R_b(-H)$ and R_bH respectively indicates that the thermolysis proceeds through clean β-elimination (reactions 1a and 1b).

Examination of the distribution of the products reveals that the relative ease of the occurrence of β-elimination concerning the R_a group (reaction 1a) to that concerning the R_b group (reaction 1b) is equal to the ratio of the number of the β-hydrogens of R_a to that of R_b. Figure 1 demonstrates a linear relationship with a slope of 1 between $N_\beta(R_b)/N_\beta(R_a)$ ($N_\beta(R)$ = number of β-hydrogen of R group) and $R_aH/R_a(-H)$, the latter value being able to be taken as the measure for the relative ease of the abstraction of β-hydrogen of R_b to that of R_a. However, the result on thermolysis of i-propyl ethyl platinum(II) complex **3**, as an exception, did not fall on this line. This may have arisen from the fast alkyl isomerization of i-propyl to n-propyl group during the decomposition.

When one of the alkyl group (R_b) had no β-hydrogen atom (for example, CH_3 and C_6H_5), only R_bH and $R_a(-H)$ were formed. (The origin in Fig. 1 shows the case.)

$$Pt(R_b)(C_2H_5)(PPh_3)_2 \longrightarrow R_bH + C_2H_4$$

$$R_b = CH_3,\ C_6H_5$$

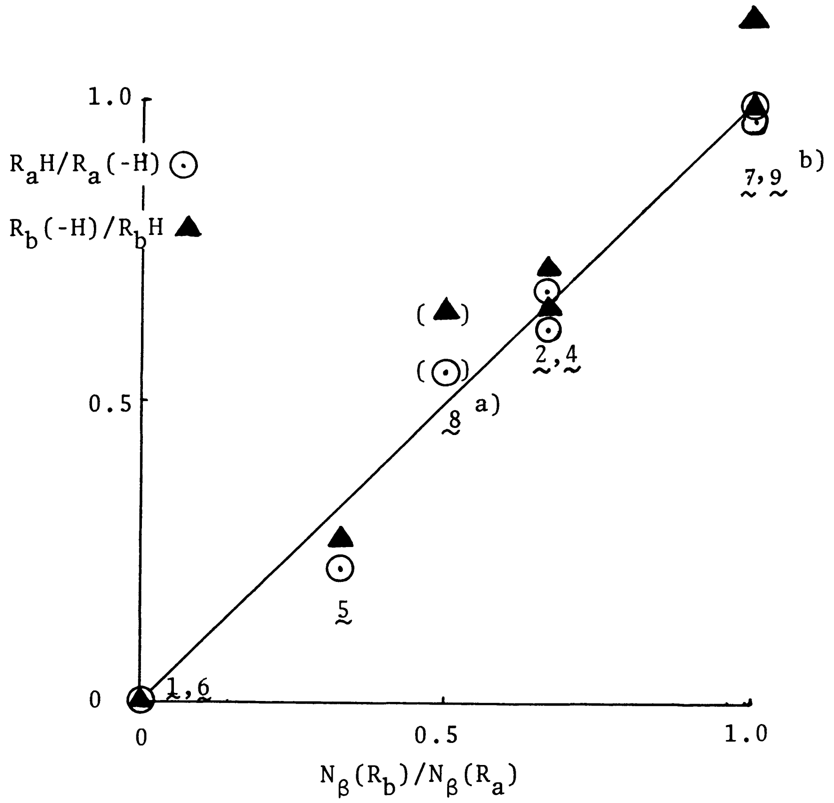
Further study in this line is under investigation.

Table 2 Thermal Decomposition of $Pt(R_a)(R_b)(PPh_3)_2$ in Solid State[a)]

Compounds(mmol)			Geses evolved(mmol)						
No.	R_a	R_b	R_aH	$R_a(-H)$	R_bH	$R_b(-H)$	Yield(%)	$R_aH/R_a(-H)$	$R_b(-H)/R_bH$
1	C_2H_5	CH_3 (0.078)	0	0.076	0.077	0	0.153(98)	0	0
2	C_2H_5	n-C_3H_7 (0.060)	0.022	0.036	0.034	0.023	0.115(96)	0.62	0.67
3	C_2H_5	i-C_3H_7 (0.031)	0.012	0.016	0.016	0.014	0.058(93)	0.73	0.88
4	C_2H_5	n-C_4H_9 (0.088)	0.029	0.043	0.048	0.034	0.154(87)	0.69	0.72
5	C_2H_5	i-C_4H_9 (0.039)	0.007	0.030	0.024	0.007	0.068(86)	0.22	0.28
6	C_2H_5	C_6H_5 (0.051)	0	0.043	0.056	0	0.099(96)	0	0
7	n-C_3H_7	n-C_4H_9 (0.043)	0.018	0.019	0.011	0.012	0.060(70)	0.98	1.1

a) Up to 180°C *in vacuo*.

Fig. 1 Relation between $N_\beta(R_b)/N_\beta(R_a)$ and $R_aH/R_a(\text{-H})$ (or $R_b(\text{-H})/R_bH$)



a) The results were obtained from the thermolysis of crude material of $Pt(i\text{-}C_4H_9)(n\text{-}C_5H_{11})(PPh_3)_2$, 8.

b) The values for symmetrical dialkyl platinum complex. (see ref. 3) 9=$Pt(n\text{-}Bu)_2(PPh_3)_2$

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(Received July 20, 1978)