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Reaction of Secondary Alkyl Halides with Platinum(0) Complexes. Some New Five-Coordinate Platinum(II) Complexes

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The reactions of various secondary alkyl and benzyl halides with complexes of the type PtL_n (where $n = 3$ or 4 and L is a phosphine) have been studied. Instead of the expected product of oxidative addition, only complexes of the type PtX_2L_2 ($X = Cl$, Br or I) are isolated. A possible mechanism has been proposed and the order of reactivity for the alkyl halides and the various platinum(O) complexes used, is given. Moreover, the formation of some new five-coordinate complexes, PtX_2L_3 is observed and their importance in the mechanism of phosphine catalyzed isomerization of square-planar complexes PtX_2L_2 is discussed.

Introduction

There is great interest in the mechanism of oxidative addition of alkyl halides to complexes of metals in a low oxidation state. In particular the stereochemistry at the carbon center of the alkyl halide after addition is in doubt.[1,2] Most studies have focussed on the versatile $IrX(CO)[PR_3]_2$ system of complexes. The reactive Pt(O) complexes of the type PtL_n (where $n = 3$ or 4 and L is a phosphine) have not received much study, though oxidative additions are known.[3,4]

$$PtL_n + RX \rightarrow PtRXL_2 + (n-2)L \qquad (1)$$

Since the Pt(II) products that are formed could be reasonably stable, we have studied the reaction of various secondary alkyl halides in reaction (1). The hope was that optically active halides could eventually be used to probe the question of stereochemistry. As it happens, the rapidity of the β-elimination reaction[5] makes the initial products of the reaction, $PtRXL_2$, very unstable. Nevertheless the products that were finally formed were rather surprising, and we wish to report them.

Results and Discussion

We examined the reactions of 2-bromobutane, 2-iodobutane, 1-bromoethylbenzene and 2-bromoethylpropionate with PtL_n, where L is $P(C_6H_5)_3$, $P(CH_3)_2C_6H_5$, or $P(C_2H_5)_3$. The solvent was normally benzene, but dichloromethane was used as well.

When L is triphenylphosphine and $n = 3$ or 4, the alkyl halides gave good yields of products of the type $PtX_2[P(C_6H_5)_3]_2$. An exception was 2-bromobutane, which reacts extremely slowly. The other halides reacted at room temperature, or more rapidly upon refluxing. In the case of 1-bromoethylbenzene, monitoring the ir spectrum while reaction was in progress showed the formation of bands that could be attributed to styrene (1590 cm^{-1} and 1570 cm^{-1}).

When $L = P(CH_3)_2C_6H_5$ and $n = 4$, the reactions with 2-iodobutane and 1-bromoethylbenzene gave yellow–orange, microcrystalline products which analyzed well for the composition PtX_2L_3, where $X = I$ or Br. Both of the above alkyl halides react much more rapidly with the $P(CH_3)_2C_6H_5$ complex than with the $P(C_6H_5)_3$ complex. The reaction of 2-bromobutane was again found to be very slow.

When the reaction of 1-bromoethylbenzene with $Pt[P(CH_3)_2C_6H_5]_4$ was followed spectrophotometrically in the visible region between 500 and 350 nm, an initial rapid decrease in absorbance was observed followed by the growth of a band at 400 nm. The overall reaction is complete in 5 min when the concentrations of $Pt[P(CH_3)_2C_6H_5]_4$ and $CH_3CH(Br)C_6H_5$ are about $10^{-3}M$ and 0.05–0.1*M*, respectively, in benzene solutions. When the reaction of $Pt[P(C_6H_4CH_3)_3]_3$ with 1-bromoethylbenzene in $CDCl_3$ was followed by nmr, the formation of two doublets at 5.20 ppm (δ, J_{H-H} *cis* = 10.4 Hz) and 5.54 ppm (δ, J_{H-H} *trans* = 17.3 Hz) characteristic of styrene, is observed. Moreover, the reaction was studied using optically active D-(–) 1-bromoethylbenzene ($[\alpha]_D^{25} = -60°C$ in benzene solution). Extremely rapid and complete disappearance of optical activity was observed. The reaction of $P(CH_3)_2C_6H_5$ with $CH_3CH(Br)C_6H_5$ in benzene was found to be extremely slow, and could therefore not influence the result in the above experiments. When optically active D-(+)-2-bromobutane was used in the reaction, the activity decreased gradually and dropped to zero in about 4 days.

The band observed at 400 nm in the reaction of *sec*-alkyl bromides with $Pt[P(CH_3)_2C_6H_5]_4$ is due to the compound $PtBr_2[P(CH_3)_2C_6H_5]_3$. A benzene solution of the isolated compound shows the same band at 400 nm. The growth of this band is probably due to the reaction of either $PtBr_2[P(CH_3)_2C_6H_5]_2$ or $PtHBr[P(CH_3)_2C_6H_5]_2$ with excess phosphine liberated during reaction (1).

This was confirmed by showing that both *cis*-$PtBr_2[P(CH_3)_2C_6H_5]_2$ and *trans*-$PtHBr[P(CH_3)_2C_6H_5]_2$ reacted rapidly with excess phosphine to give yellow solutions with an absorption band at 400 nm. In the case of the dibromide complex, good yields of the product could be isolated. This was not possible in the case of the bromohydride complex, however.

$PtBr_2[P(CH_3)_2C_6H_5]_3$ dissolves in ethanol to give a colorless solution from which a white solid can be isolated. This analyzes for $[PtH(P(CH_3)_2C_6H_5)_3]^+Br^-$, and has a weak band at 2000 cm^{-1} which could be assigned to a Pt–H stretch. The nmr spectrum in $CDCl_3$, however, revealed no hydride resonance and hence the exact nature of this solid is in doubt.

$PtBr_2[P(CH_3)_2C_6H_5]_3$ could either be ionic $[PtBr(P(CH_3)_2C_6H_5)_3]^+Br^-$ or $PtBr_2[P(CH_3)_2C_6H_5]_3$, a five-coordinate complex. On adding $NaClO_4$ to a yellow acetone solution of $PtBr_2[P(CH_3)_2C_6H_5]_3$, (band at 380 nm (sh)), a white solid, $[PtBr(P(CH_3)_2C_6H_5)_3]^+ ClO_4^-$ is isolated. This shows no characteristic band in the visible region in acetone solution (it is insoluble in benzene). Hence it appears that $[PtBr(P(CH_3)_2C_6H_5)_3]^+$ is not the species responsible for the 400 nm band in the visible spectrum. In solution, there should exist the following equilibria

$$PtBr_2[P(CH_3)_2C_6H_5]_2 + P(CH_3)_2C_6H_5 \rightleftharpoons \qquad (2)$$
$$PtBr_2[P(CH_3)_2C_6H_5]_3 \rightleftharpoons [PtBr(P(CH_3)_2C_6H_5)_3]^+Br^-$$

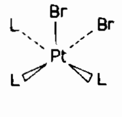
In benzene solutions the five-coordinate complex appears to be the only species since benzene solutions of this complex obey Beer's law down to concentrations of $10^{-5}M$. The extinction coefficient of the 400 nm band is $1400 M^{-1}$ cm^{-1}, and is sensitive to the addition of small amounts of added $P(CH_3)_2C_6H_5$ which increases the intensity of the band. It is possible that this results from the addition of another mole of phosphine to the sixth coordination site. In one case a solid with the composition PtX_2L_4 was isolated (see Experimental).

Five-coordinate complexes of the type PtX_2L_3 and PdX_2L_3 have been reported earlier by Mann and coworkers,[6] though this paper appears to have been largely overlooked. These authors used 2-phenylphosphindoline as L. Dimethylphenylphosphine is very closely related to this ligand and should behave in a similar fashion. Moreover, the cone angle and basicity of $P(CH_3)_2C_6H_5$ make it very suitable for the formation of five-coordinate complexes. Both $P(C_2H_5)_3$ and $P(C_6H_5)_3$ have larger cone angles, which agrees with our failure to observe PtX_2L_3 complexes.

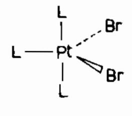
Five-coordinate complexes of Pt(II) while rare, are not unknown. Closely related to our examples are some cationic isocyanide complexes reported recently.[8]

The ^{1}H nmr spectrum of $PtBr_2[P(CH_3)_2C_6H_5]_3$ reveals some interesting aspects of the stereochemistry and lability of this complex. In $CDCl_3$ or CH_2Cl_2 solution, at 34° C, only a broad featureless spectrum is obtained at $\tau \sim 8$ ppm for the methyl protons of the ligand. But when cooled to –30° C, three doublets (in the ratio 1:4:1) and three triplets (in the ratio 1:4:1) are observed. The lower intensity resonances are the ^{195}Pt satellites. The triplet, arising from virtual coupling of *trans*-phosphines, is twice as intense as the doublet.

The spectrum shown in Table I is quite different from that of *cis*-$PtBr_2[P(CH_3)_2C_6H_5]_2$.[9] The nmr spectrum is consistent with both structures A and B,



A



B

providing the conditions for virtual coupling hold for the axial phosphines in B. It is also consistent with the simple ion $PtBrL_3^+$, either free or as an ion pair with Br^-. However, the complex $PtBr[P(CH_3)_2C_6H_5]_3^+ ClO_4^-$ in $CDCl_3$ shows three doublets and three triplets, well resolved even at 30° C. The structure A has been found by Mann and coworkers by X-ray diffraction for the related palladium complex with L = 2-phenylphosphindoline.

The featureless broad nmr spectrum at 34° C indicates a rapid exchange of the non-equivalent ligand positions. This could occur via rearrangement of the five-coordinate complex, or by dissociation of a phosphine ligand, followed by reattachment at a different position. Adding $0.002M$ free $P(CH_3)_2C_6H_5$ to a $0.2M$ solution of $PtBr_2[P(CH_3)_2C_6H_5]_3$ speeds up the exchange reaction, since a well resolved spectrum is not attained until –50° C.

A semi-log plot of the line widths of the low temperature spectra of $PtBr_2L_3$ ($L = P(CH_3)_2C_6H_5$) *vs* 1/T gave a good straight line. The activation energy is

TABLE I. ^{1}H NMR Spectrum of $PtBr_2[P(CH_3)_2C_6H_5]_3$.

τ-value[a]	Multiplicity and J value(s) in Hz		
8.57 d	Three doublets	J(P–H)	11
		J(Pt–H)	42
7.84 t	Three triplets	J(P–H)	4
		J(Pt–H)	23

[a] τ values in ppm relative to internal TMS (τ = 10.00). Spectrum taken at –30° C in $CDCl_3$.

23 kcal/mol, and the apparent rate constant at 25° C is $9.1 \times 10^3\ sec^{-1}$. The most significant observation is that the ^{195}Pt satellites disappear during line broadening. This suggests a dissociation process, rather than an intramolecular rearrangement.

It may be recalled that *cis* and *trans* PtX_2L_2 isomerize rapidly in the presence of excess L.[10] Haake and Pfeiffer have attributed the isomerization to a peculiar rearrangement of a five-coordinate PtX_2L_3.[11a] However a recent detailed study by Cooper and Powell[11b] shows rather convincingly that a double exchange mechanism is operating. That is, X^- is displaced by L, and L is then displaced by X^-. In non-polar solvents a stable intermediate is formed, with the composition PtX_2L_3.

In $CDCl_3$ the intermediate formed from *cis*-$PtCl_2[P(CH_3)_3C_6H_5]_2$ + $P(CH_3)_2C_6H_5$ has an nmr spectrum very similar to that reported in Table I. Powell and Cooper have formulated this intermediate as the contact ion-pair $[PtCl(P(CH_3)_2C_6H_5)_3]^+Cl^-$, which they postulate to have a square pyramidal structure with Cl^- occupying the axial position.

It is most interesting that in the structural work on PdL_3Br_2 reported by Mann,[6] the axial Pd–Br bond distance is 0.4 Å longer than the equatorial bond distance. It appears therefore to be a matter of taste whether one chooses to call PtX_2L_3 a five-coordinate complex or an ion-pair. Our results are otherwise in complete agreement with those of Cooper and Powell, including the immediate formation of $[PtBr(P(CH_3)_2C_6H_5)_3]^+$ and free halide ion in polar solvents.

Phosphine exchange in the related complexes, NiX_2L_3, has been studied by nmr.[12] The mechanism, is a dissociative one, and the activation energies are of the order of 12–15 kcal/mol. The role of further added phosphine in the case of $PtBr_2L_3$ is not clear. Possibly another mechanism is operating, in which a six-coordinate complex is involved. This was not observed for NiX_2L_3.

Addition of $P(CH_3)_2C_6H_5$ to benzene suspensions of *cis*-$PtCl_2[P(CH_3)_2C_6H_5]_2$ gave yellow solutions which showed a band at 350 nm, attributable to $PtCl_2[P(CH_3)_2C_6H_5]_3$. However the compound could not be isolated. The corresponding $PtI_2[P(CH_3)_2C_6H_5]_3$ could be isolated as a bright orange solid which has a band in the visible region at 457 nm in benzene solution. $Pt(SCN)_2[P(CH_3)_2C_6H_5]_3$, made in a similar manner, appears to be ionic even in the solid state, $[Pt(NCS)(P(CH_3)_2C_6H_5)_3]^+SCN^-$, since the ir spectrum in Nujol mull shows two ν_{CN} bands at 2095 cm^{-1} (coordinated NCS) and 2052 cm^{-1} (ionic SCN^-). Moreover, the ^1H nmr spectrum shows a broad doublet at $\tau = 8.2$ ppm (40° C) and does not resemble the spectra obtained for the other $PtX_2[P(CH_3)_2C_6H_5]_3$ complexes.

The reaction of $Pt[P(C_2H_5)_3]_3$ was studied only with 2-iodobutane, owing to difficulty in handling this Pt(O) complex (which is obtained as an orange oil). Rapid formation of quantitative yields of yellow, crystalline $PtI_2[P(C_2H_5)_3]_2$ was observed.

Conclusions

While we have little direct evidence, we assume that the following reactions are occurring:

$$PtL_3 + RX \xrightarrow{-L} PtXRL_2 \xrightarrow{-olefin} PtHXL_2 \quad (3)$$

$$PtHXL_2 \rightarrow PtX_2L_2 + ? \quad (4)$$

$$PtX_2L_2 + L \rightleftharpoons PtX_2L_3 \rightleftharpoons [PtXL_3]^+X^- \quad (5)$$

Olefin elimination from Pt(II) alkyls is a well known reaction.[5,13] Another possibility is that secondary halides form ion-pairs in solution, R^+X^-, and that the hydride $PtHXL_2$, is formed directly by proton abstraction from R^+.[14] It is not clear how PtX_2L_2 is formed in reaction (4), but similar disproportionations of Pt(II) have been observed before.[13] We have no evidence on the mechanism of the oxidative-addition step. It is quite possible that free radicals are involved since Osborn has shown that galvinoxyl, a free radical trap, inhibits many reactions of alkyl halides with Pt(O) complexes.[15] We did, however, carefully exclude oxygen from our systems.

The reactivities of the complexes decreased in the order $Pt[P(C_2H_5)_3]_3 > Pt[P(CH_3)_2C_6H_5]_3 > Pt[P(C_6H_5)_3]_{3\ or\ 4}$. For the alkyl halides the order was $CH_3CHBrC_6H_5 \sim CH_3CHBrCOOC_2H_5 > CH_3I > CH_3CHIC_2H_5 \gg CH_3CHBrC_2H_5$.

Experimental

Melting points are not corrected. All operations involving Pt(O) complexes and free phosphines were carried out in an atmosphere of nitrogen. All the solvents and liquid phosphines were refluxed and distilled under nitrogen or under a vacuum. Secondary alkyl halides were degassed before use. Tetrakis(triphenylphosphine)platinum(O) was prepared according to the method of Ugo *et al.*[16] The complexes $PtX_2[P(CH_3)_2C_6H_5]_2$ (X = Cl, Br, I, SCN) were prepared according to literature methods.[9]

Infrared spectra were recorded on a Perkin–Elmer 33 F Grating Spectrophotometer, and absorption spectra on a Cary 14 recording spectrophotometer. Studies on optical activity were made using a Cary 60 ORD–CD spectrophotometer. Nmr spectra were recorded on either a Varian T60 or a Perkin–Elmer R–20B spectrometer.

Preparation of tetrakis(dimethylphenylphosphine) platinum(O)

This complex was prepared according to the reported method,[17] but bright yellow, crystalline product was obtained in 90% yields only when the quantities of $P(CH_3)_2C_6H_5$ and KOH were changed to 2.4 grams and 0.8 grams respectively. M.p. 84°–85° C (in a sealed, evacuated tube). Found: C, 51.5; H, 5.8. $C_{32}H_{40}P_4Pt$ requires C, 51.4; H, 5.9%.

Preparation of tris(triethylphosphine)platinum(O)

K_2PtCl_4 (1.5 g) dissolved in 10 ml of water is added dropwise with stirring to a 30:1 $EtOH/H_2O$ (31 ml) mixture containing 3 ml of triethylphosphine and 0.7 g of KOH. White solid is formed immediately and the pink color of the solution is discharged after stirring for one hour. The solvent is removed under vacuum down to 10 ml; 30 ml of acetone is added and the precipitated KCl is filtered off. The filtrate is stripped of solvent under vacuum and $Pt[P(C_2H_5)_3]_3$ is obtained as an orange oil.

This convenient preparation starting with K_2PtCl_4 is outlined in the following reaction sequence:

$$K_2PtCl_4 + 2\,P(C_2H_5)_3 \xrightarrow{EtOH/H_2O} PtCl_2[P(C_2H_5)_3]_2 + 2\,KCl \quad (6)$$

$$PtCl_2[P(C_2H_5)_3]_2 + KOH + C_2H_5OH \rightarrow PtHCl[P(C_2H_5)_3]_2 + CH_3CHO + KCl + H_2O \quad (7)$$

$$PtHCl[P(C_2H_5)_3]_2 + P(C_2H_5)_3 + KOH \xrightarrow{acetone} [PtH(P(C_2H_5)_3)_3]^+OH^- + KCl \quad (8)$$

$$[PtH(P(C_2H_5)_3)_3]^+OH^- \xrightleftharpoons{vacuum} Pt[P(C_2H_5)_3]_3 + H_2O \quad (9)$$

The addition of acetone in reaction (8) precipitates KCl and drives the reaction towards the ionic product.[18] Reaction (9) is reversible and differs from that of the triphenylphosphine complex which does not react with water.

Reaction of PtL_n with Secondary Alkyl Halides

These reactions were usually conducted in benzene (dichloromethane was also used in some cases). Usually, about 0.2 g of Platinum(O) complex was taken in 10–15 ml of benzene and about a five-fold excess of alkyl halide added and stirred. Times of reaction and approximate yields of PtX_2L_2 or PtX_2L_3 are shown in Table II. The yields are based on Pt, and are independent of whether PtL_3 or PtL_4 is used.

Preparation of the Complexes $PtX_2[P(CH_3)_2C_6H_5]_3$ (X = Br, I and SCN

To 0.8 g of $PtX_2[P(CH_3)_2C_6H_5]_2$ suspended in 15 ml of benzene, is added dropwise $P(CH_3)_2C_6H_5$ (0.18 g for X = Br, 0.15 g for X = I and 0.2 g for X = SCN) in 5 ml of benzene. After stirring for 0.5 to 1 hour, the solid is filtered, washed with pentane and dried in air. (For X = I and SCN, the benzene is removed under vacuum and the solid obtained washed with pentane.) The solids are recrystallized from benzene/pentane solutions. (i) $PtBr_2[P(CH_3)_2C_6H_5]_3$: m.p. 90–95° C. Found: C, 37.9; H, 4.6; Br, 20.0; P, 11.8; Pt, 25.6; $C_{24}H_{33}Br_2P_3Pt$ requires: C, 37.5; H, 4.3; Br, 20.7; P, 12.0; Pt, 25.3% (Same analysis is obtained for the yellow product obtained from the reaction of $CH_3CH(Br)C_6H_5$ with $Pt[P(CH_3)_2C_6H_5]_4$. (ii) $PtI_2[P(CH_3)_2C_6H_5]_3$: m.p. 115–130° C (turns red around 85° C). Found: C, 33.9; H, 4.0; $C_{24}H_{33}I_2P_3Pt$ requires C, 33.5; H, 3.7%. (iii) $[Pt(NCS)(PMe_2Ph)_3]^+SCN^-$: m.p. 150–160° C. Found: C, 43.3; H, 4.7; N, 3.6; $C_{26}H_{33}S_2N_2P_3Pt$ requires C, 43.6; H, 4.6; N, 3.9%.

When excess phosphine is used for any of the above syntheses, solids with variable composition are obtained. With a four-fold excess of phosphine in the case of $PtI_2[P(CH_3)_2C_6H_5]_2$, a creamy, white solid of composition $PtI_2[P(CH_3)_2C_6H_5]_4$ is isolated. This dissolves in benzene rapidly to give an orange solution of $PtI_2[P(CH_3)_2C_6H_5]_3$.

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TABLE II.[a]

RX	$CH_3CH(Br)C_2H_5$		$CH_3CH(I)C_2H_5$		$CH_3CH(Br)C_6H_5$		$CH_3CH(Br)COOEt$	
L	Time of Reaction	Yield	Time of Reaction	Yield	Time of Reaction	Yield	Time of Reaction	Yield
$P(C_2H_5)_3$	slow	–	3 hours	80%				
$P(CH_3)_2C_6H_5$	slow	–	5 hours	75%	2 hours	90%		
$P(C_6H_5)_3$	very slow	–	3 days	75%	15 hours	85%	12 hours	80%

[a] All reactions are at room temperature (25° C). PtX_2L_3 is isolated when L = $P(CH_3)_2C_6H_5$.

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