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OXIDATIVE ADDITION, REDUCTIVE ELIMINATION, AND ISOMERIZATION REACTIONS OF ORGANOPLATINUM COMPLEXES

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Summary

The investigation of a variety of oxidative addition reactions of I_2, CH_3I, and CF_3I with *trans*-$PtRI[P(CH_3)_2(C_6H_5)]_2$ ($R = C_6H_5, CH_3$) and the stereochemistry of the resulting platinum(IV) compounds are discussed. The additions of CH_3I, and CF_3I to *cis*-PtR_2L_2 [where $R = C_6H_5, CH_3$; $L = CNC_6H_4$-CH_3, $As(CH_3)_3$ or $P(CH_3)_2(C_6H_5)$] have been investigated and the stereochemistry of the platinum(IV) compounds was found to be dependent on both R and L. Stereochemical rearrangements can be facilitated by the formation of Pt^{IV} cations. In several instances reductive elimination occurred to give Pt^{II} compounds. Factors governing the isomerization and reductive elimination reactions are discussed. Kinetic data for the oxidative addition of methyl iodide and acetyl chloride to *cis*-$Pt(CH_3)_2(CNC_6H_4CH_3)_2$ are given.

Introduction

Oxidative addition and reductive elimination reactions of transition metal complexes form the basis of many catalytic systems [1 - 3]. The addition of a molecule X—Y to a square planar d^8 platinum(II) complex to give an octahedral d^6 platinum(IV) complex represents one of the classic examples of such reactions. In particular, methylplatinum(II) complexes of the types *trans*-$Pt(CH_3)XL_2$ and *cis*-$Pt(CH_3)_2L_2$ (where L = tertiary phosphine or arsine [4]) have been shown to undergo a variety of oxidative addition reactions although no kinetic data have yet been obtained. Little is known about oxidative addition reactions of other organoplatinum(II) complexes such as *trans*-$PtRXL_2$

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and *cis*-PtR_2L_2 (where R = CF_3, C_6H_5). Such reactions have been studied in the present work.

Complexes of the type $PtIR_2R'L_2$ formed by oxidation of PtR_2L_2 by R′I undergo a variety of reductive elimination and isomerization reactions, especially if the coordinated iodide is removed by silver ion. The course of the reaction is discussed in terms of the natures of R, R′ and L.

Results and discussion

Analytical and physical data for the new platinum complexes that have been isolated are listed in Table 1, and spectroscopic data are given in Table 2. Stereochemistries were assigned from various NMR spin—spin coupling constants such as $^2J(Pt—CF_3)$, $^2J(Pt—CH_3)$ and $^3J(Pt—P—CH_3)$ since the magnitude of these coupling constants is very dependent upon the nature of the *trans*-ligand and on the oxidation state of platinum [5 - 10]. Also, in the phosphine complexes, the coupling patterns of the methyl groups in the $P(CH_3)_2(C_6H_5)$ ligand give valuable stereochemical information. For example, a doublet pattern for the phosphine methyl resonances usually indicates that the phosphines are in a *cis*-configuration whereas a triplet pattern usually is characteristic of mutually *trans*-phosphines [11]. One must be careful however, since slight distortions from 180° of the *trans*-^{31}P nuclei [6] may collapse the virtual coupling pattern to a doublet which could be mistakenly interpreted as indicating a *cis*-configuration.

TABLE 1

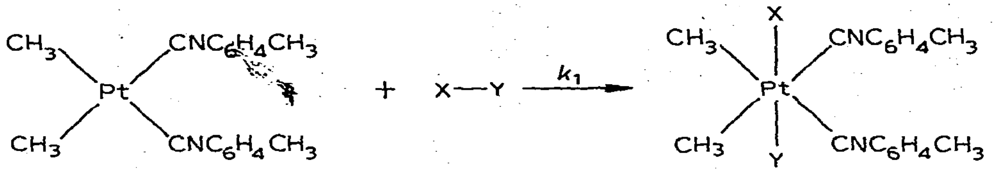
PHYSICAL AND ANALYTICAL DATA FOR NEW COMPLEXES

Complex[a] and colour	Isomer	Analyses found (calcd.) (%)				Melting point (°C)
		Carbon	Hydrogen	Fluorine	Iodine	
$PtCl(CH_3)_2(COCH_3)A_2$ white	(X)	22.41 (22.09)	4.86 (5.01)			117—120[c]
$PtI(CF_3)(CH_3)_2A_2$ white	(III)	16.60 (16.35)	3.83 (3.66)	8.91 (8.62)		163—165[d]
$PtI(CF_3)(CH_3)_2(CNC_6H_4CH_3)_2$ yellow	(IV)	34.50 (34.70)	3.15 (3.37)	9.03 (8.67)		113[d]
$PtI(CH_3)_2(CF_3)Q_2$ white	(IV)	32.82 (32.73)	4.32 (4.05)	8.50 (8.18)		144[d]
trans-$Pt(C_6H_5)IQ_2$ white		39.31 (39.11)	4.08 (4.03)			127—129
$Pt(CH_3)I_3Q_2$ dark brown	(Ia)	23.55 (23.55)	2.87 (2.91)		43.97 (43.90)	120—126
$Pt(CF_3)I_3Q_2$ dark brown	(Ib)	22.35 (22.17)	2.51 (2.41)	6.42 (6.19)	41.50 (41.33)	120 dec.
$Pt(CF_3)(CH_3)_2IQ_2$ white	(V)[b]	32.01 (32.73)	3.82 (4.05)	8.58 (8.18)		116[d]
$Pt(CF_3)(C_5H_5)_2IQ_2$ white	(V)	42.14 (42.40)	4.02 (3.93)	7.01 (6.94)		188—190
$Pt(C_6H_5)_2I_2Q_2$ orange	(XIV)	38.32 (38.23)	3.80 (3.67)		28.80 (28.86)	85—100[d]
$Pt(CH_3)_2(CF_3)ClQ_2$ white	(IV)	37.61 (37.66)	4.60 (4.66)	10.32 (9.41)		160[d]
$Pt(CF_3)I(CNC_6H_4CH_3)_2$ white		32.41 (32.67)	1.24 (1.13)	8.91 (9.14)		> 200

[a] A = $As(CH_3)_2$, Q = $P(CH_3)_2C_6H_5$. [b] Containing some (IV) and $PtCF_3IQ_2$. [c] Loses C_2H_6. [d] Loses $(CH_3)_2CO$.

(i). Kinetic study of the addition of methyl iodide and acetyl chloride to cis-$Pt(CH_3)_2(p\text{-}CN{-}C_6H_4{-}CH_3)_2$

The oxidative addition of X—Y (where X—Y is CH_3I or CH_3COCl) to *cis*-$Pt(CH_3)_2(p\text{-}CN{-}C_6H_4{-}CH_3)_2$, in chloroform, gave exclusively the *trans*-adduct (eqn. 1) and the reaction rates were found to obey second-order kinetics.



(1)

$-d[Pt(CH_3)_2(CNC_6H_4CH_3)_2]/dt = k_1\cdot[X{-}Y]\cdot[Pt(CH_3)_2(CNC_6H_4CH_3)_2]$

The reactions were followed by NMR spectroscopy, measuring both the increase in intensity of the $Pt^{IV}{-}CH_3$ resonances and the decrease of the $Pt^{II}{-}CH_3$ resonances as a function of time. The kinetic data are given in Table 3 and a typical graph is illustrated in Fig. 1, showing the decrease in $Pt(CH_3)_2(CNC_6H_4CH_3)_2$ concentration as a function of time. An Arrhenius plot of the data gave activation energies of 8.6 and 8.5 kcal/mole for the additions of CH_3I and CH_3COCl to *cis*-$Pt(CH_3)_2(CNC_6H_4CH_3)_2$, respectively. It is interesting that the rate of reaction of methyl iodide with *trans*-$IrCl(CO)[P(C_6H_5)_3]_2$ [12] is about 1000 times less than with *cis*-$Pt(CH_3)_2(CNC_6H_4CH_3)_2$. Similar reactions were qualitatively investigated with *cis*-$Pt(CH_3)_2L_2$ [where $L = P(CH_3)_2(C_6H_5)$ and $As(CH_3)_3$] and the reactions were even faster than for the isocyanide compound. These low activation energies suggest that the platinum atom is very electron rich which is consistent with the stabilities of their 1/1 adducts with hexafluoro-2-butyne and tetrafluoroethylene [14]. Interestingly, if benzene is used as a solvent, there was no sign

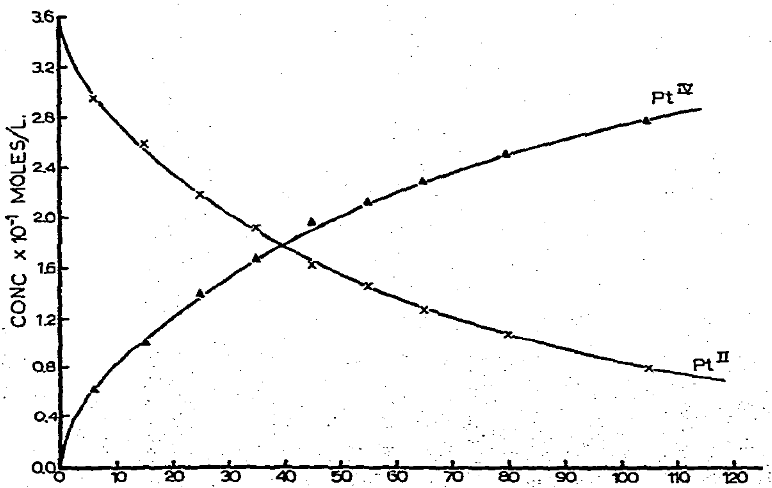


Fig. 1. A plot of the addition of CH_3I to *cis*-$Pt(CH_3)_2(CNC_6H_4CH_3)_2$ showing the increase in concentration of Pt^{IV} (▲) and decrease of Pt^{II} (X) as a function of time.

TABLE 2

^{1}H AND ^{19}F NMR DATA[a] FOR NEW PLATINUM COMPLEXES

Complex	Isomer	$\delta(PtCH_3)$	$^2J(Pt{-}CH_3)$	$\delta(MCH_3)$ M = As, P	$^3J(Pt{-}M{-}CH_3)$	$\delta(CF_3)$	$^2J(Pt{-}CF_3)$	Other resonances and couplings
$PtI(CH_3)_2(CF_3)(CNC_6H_4CH_3)_2$	(III)	1.60	65.8			19.96	552	$\delta(CH_3)$ 2.46
$PtI(CH_3)_2(CF_3)(CNC_6H_4CH_3)_2$	(IV)	1.73	68.0^b			25.60	488	
		1.57	63.6^c					
$Pt(CF_3)I(CNC_6H_4CH_3)_2$						13.06	788	
$PtCl(CH_3)_2(COCH_3)A_2$	(X)	1.13	65.0	2.36	7.0			$\delta(COCH_3)$ 3.07, $^3J(Pt{-}C{-}CH_3)$ 15.5
$PtI(CF_3)(C_6H_5)_2Q_2$	(XIII)					13.39 t	236	$^3J(PF)$ 6.0
trans-$PtI(C_6H_5)Q_2$				1.66 t	32.6			$^4J + {}^2J(PH)$ 7.4
$Pt(CF_3)I_3Q_2$	(Ib)			2.75 t	18.8	5.04 t	458	$^3J(PF)$ 11.5, $^2J + {}^4J(PH)$ 7.0
$Pt(CH_3)I_3Q_2$	(Ia)	1.52	65.6	2.50 t	19.6			$^3J(P{-}Pt{-}CH_3)$ 5.2, $^4J + {}^2J(PH)$ 8.0
$PtI(CH_3)_2(CF_3)Q_2$	(IV)	c				22.6 d-d	418	$^3J(P{-}Pt{-}CF_3)$ 60 (*trans*), 12 (*cis*)
$[Pt(CH_3)_2(CF_3)Q_2(Acetone)](PF_6)$	(VI)	c				12.05 t	620	$^3J(PF)$ 11.0
	(VII)	c				32.20 d-d	400	$^3J(PF)$ 60 (*trans*), 10 (*cis*)
$PtI(CH_3)_2(CF_3)A_2$	(III)	$\approx 1.78^e$	≈65	1.79		18.73	546	
	(IV)	0.73^d	60	1.79		22.03	484	
		1.19^b	68					
$PtI(CH_3)_2(CF_3)Q_2$	(V)	0.30^b	66.4	2.33 t	19	8.34 t	280	$^3J(PF)$ 7.0, $^4J + {}^2J(PH)$ 8.0, $^3J(P{-}Pt{-}CH_3)$ 5.6
		0.30^f	44.6	2.27 t		29.45	411	$^3J(PF)$ 61.4 (*trans*), 11.4 (*cis*)
$PtCl(CH_3)_2(CF_3)Q_2$	(IV)	c						

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[a] Spectra were recorded on CH_2Cl_2 or $CHCl_3$ solutions. ^{1}H chemical shifts are given in ppm downfield of TMS and ^{19}F chemical shifts are given in ppm upfield from $CFCl_3$. Coupling constants are given in Hz. d-d = doublet of doublets, t = triplet, c = complex. A = $As(CH_3)_3$, R = $P(CH_3)_2C_6H_5$. [b] *trans* to I^-. [c] *trans* to $CNC_6H_4CH_3$. [d] *trans* to $As(CH_3)_3$. [e] Obscured by $As(CH_3)_3$ resonance. [f] *trans* to (CF_3).

TABLE 3

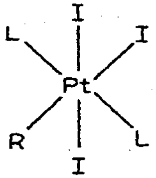
TYPICAL KINETIC DATA FOR THE REACTIONS
$XY + (CH_3)_2Pt(CNC_6H_4CH_3)_2 \rightarrow PtXY(CH_3)_2(CNC_6H_4CH_3)_2$

X—Y	Temp. (°C)	XY concn. (*M*)	Pt^{II} complex concn. (*M*)	k_1 ($M^{-1} \cdot sec^{-1}$)	E_{act} (kcal/mole)
CH_3I	31	0.477	0.358	2.9	8.6
		1.07	0.358	3.1	
	0	0.637	0.358	0.61	
	15	0.575	0.358	1.42	
CH_3COCl	31	0.570	0.358	3.7	8.5
	15	0.778	0.358	3.0	
	0	0.558	0.358	0.93	

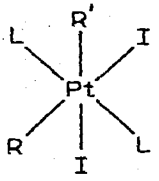
of oxidative addition, after several hours, under identical conditions, suggesting that a polar transition state may be involved.

(ii). Oxidative addition reactions of trans-PtRI$\{P(CH_3)_2(C_6H_5)\}_2$

trans-$PtI(CH_3)L_3$ [$L = P(CH_3)_2(C_6H_5)$] is instantaneously oxidized by one mole of iodine to the complex (Ia)



(Ia) R = CH_3
(Ib) R = CF_3



(IIa) R = R′ = CH_3
(IIb) R = CH_3, R′ = CF_3

Ruddick and Shaw did not examine this reaction but obtained analogous results [4] for oxidation of *trans*-$Pt(CH_3)XL_2$ (X = Cl, Br) by X_2. The Pt—CH_3 coupling constant (65.5 Hz) and Pt—P—CH_3 coupling constant (19.6 Hz) are typical of a methyl group *trans* to a halide and a phosphine *trans* to another phosphine in Pt^{IV} complexes [4,6,10]. Furthermore, the appearance of the phosphine methyl resonance as a triplet indicates the presence of mutually *trans* phosphines [11]. *trans*-$Pt(CF_3)IL_2$ also undergoes rapid oxidative addition by iodine in chloroform to give the complex (Ib) whose structure is substantiated by comparison of NMR coupling constants with those obtained for other (trifluoromethyl)platinum(IV) compounds.

These results contrast with those of Kistner et al. [14] for the reaction of *trans*-$Pt(CH_3)I[P(C_6H_5)_3]_2$ with iodine. Although Chatt and Shaw [15] had originally described the product as a platinum(IV) complex analogous to (Ia), Kistner considered the complex to be the platinum(II) compound *trans*-Pt-$(CH_3)(I_3)[P(C_6H_5)_3]_2$ on the basis of absorption bands, in the ultraviolet spectrum of the complex, at 295 and 365 nm, characteristic of the I_3^- ion [16]. We have recorded the UV spectra of complexes (Ia) and (Ib), under the same conditions as Kistner, and found absorptions near 290 and 360 nm. When an extra mole of iodine was added to solutions of $PtRL_2I_3$, no band characteristic of free I_2 was observed in the UV spectra, presumably indicating the formation of $Pt^{IV}I_3$ groups, but there was little change in the UV spectra of the complexes. Since the NMR coupling constants clearly indicate the presence of Pt^{IV}, we suggest that UV spectra do not provide a reliable means of distinguishing between $Pt^{II}R(I_3)L_2$ and $Pt^{IV}RI_3L_2$. Evaporation of a solution of $PtRI_3L_2$ containing a further mole of iodine, presumably containing the species $PtR(I_3)I_2L_2$, gave black solids from which iodine could be slowly washed with hexane.

$Pt(CH_3)IL_2$ reacts readily with CH_3I [4,10] to give (IIa) and with CF_3I [8] to give (IIb). *trans*-$PtRIL_2$ [$L = P(CH_3)_2(C_6H_5)$; $R = C_6H_5, CF_3$] did not react with an excess of CH_3I or CF_3I, even when heated. The fact that the reaction of *trans*-$Pt(CF_3)IL_2$ with CH_3I did not occur, even though the expected product, (IIb), is a stable complex [8], clearly illustrates the lesser tendency of Pt—CF_3 complexes to undergo oxidative addition reactions compared with their Pt—CH_3 analogues. Iodine, which is a good oxidizing reagent is capable of oxidizing *trans*-$Pt(CF_3)IL_2$, whereas the less powerful oxidants such as CH_3I and CF_3I, are not. The ease of oxidation decreases in the order $CH_3^- > C_6H_5^- > CF_3^-$, which is the reverse order for the electronegativities of the R groups [9,17]. These results provide another example of an electron-rich metal atom favoring oxidative addition reactions.

(iii). Oxidative addition reactions of complexes cis-PtR_2L_2, and isomerization and reductive elimination reactions of the products

For a vast majority of oxidative addition reactions of X—Y to a square planar platinum(II) complex, the initial addition of XY has been shown to be *trans* [4,8]. This stereochemistry is often not the most stable, thermodynamically, so that there is a tendency for the initial product to isomerize to the most stable isomer. The ease with which this isomerization occurs depends on the activation energy for the isomerization reaction; if the activation energy is low the initial isomer with *trans*-X—Y groups may not be detected. We have found that the isomerization activation energy is lowered by the formation of cationic compounds. Another possible reaction of the complexes $PtIR_2R'L_2$ is reductive elimination of one of the possible pairs R—R, R′—R, R—I and R′—I to give platinum(II) complexes. We have also found that these reactions are enhanced by the formation of cationic species [10].

(a). Products from cis-$Pt(CH_3)_2L_2$. *cis*-$Pt(CH_3)_2L_2$ [$L = P(CH_3)_2(C_6H_5)$ or $As(CH_3)_3$] reacts very readily with methyl iodide to give the platinum(IV) compounds *fac*-$Pt(CH_3)_3L_2I$ [4,10]. We have previously examined a number of reductive elimination reactions of these platinum(IV) compounds [10] (scheme 1).

Two reaction pathways are possible, depending on the nature of L and L′. Two conditions were established [10] that had to be met, simultaneously, for reductive elimination, via loss of ethane, to occur from the trimethylplatinum(IV) cations:

(1). Two of the three methyl groups must be *trans* to ligands of high NMR-*trans*-influence*. For example, *fac*-$\{Pt(CH_3)_3(NC_5H_5)_2\text{-}[P(CH_3)_2(C_6H_5)]\}^+$

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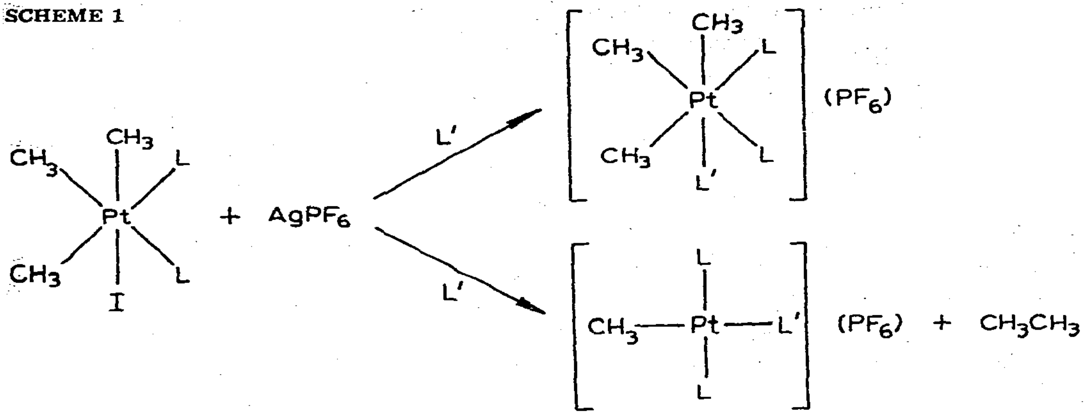
* For a review of the *trans*-influence see ref. 18. For a classification of neutral ligands according to their NMR-*trans*-influence see ref. 6.

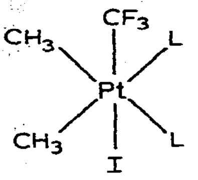
SCHEME 1



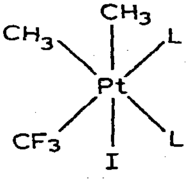
is quite stable whereas *fac*-$\{Pt(CH_3)_3(NC_5H_5)[P(CH_3)_2(C_6H_5)]_2\}^+$ reduces to *trans*$\{Pt(CH_3)(NC_5H_5)[P(CH_3)_2(C_6H_5)]_2\}^+$ and;

(2). The three methyl groups must not be chemically equivalent, e.g. *fac*-$\{Pt(CH_3)_3[P(CH_3)_2(C_6H_5)]_3\}^+$ and *fac*-$[Pt(CH_3)_3(CH_3OH)_3]^+$ are quite stable with respect to reductive elimination while *fac*-$\{Pt(CH_3)_3$-$[P(CH_3)_2(C_6H_5)]_2$-$(CH_3OH)\}^+$ reduces rapidly to platinum(II). It should be emphasized that these reductive elimination reactions apply only to trimethylplatinum(IV) *cations*.

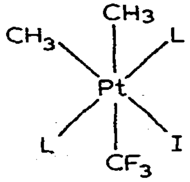
Therefore, it was of interest to prepare other triorganoplatinum(IV) compounds and to investigate their stability with respect to reductive elimination. *cis*-$Pt(CH_3)_2L_2$ $[L = P(CH_3)_2(C_6H_5)]$ reacts readily with CF_3I to give (III), which can be refluxed in methanol without change, although pyrolysis at 165° yields *trans*-$Pt(CF_3)L_2I$ and CH_3—CH_3 [8].



(III)

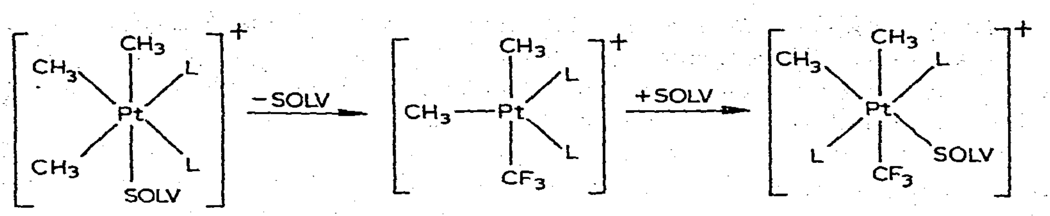


(IV)



(V)

The addition of a silver salt of a non-coordinating anion such as $AgClO_4$ to an acetone or methanol solution of (III), readily precipitated AgI. The silver iodide was filtered off and an acetone, or methanol, solution of NaI was added to the filtrate. The NMR spectrum of the resultant products was shown to consist mainly of isomer IV, $[L = P(CH_3)_2(C_6H_5)]$ with small amounts of (III) and the platinum(II) compound *trans*-$Pt(CF_3)L_2I$. The various species are readily identified by their characteristic ^{19}F NMR spectra (Table 2). When the reaction is carried out in acetone and the filtrate, after removal of AgI, is refluxed for one hour, or allowed to stand 3 days at room temperature before the addition of sodium iodide, the product is entirely $Pt(CF_3)IL_2$. In methanol, refluxing for one hour has the same result, but refluxing for 15 minutes or standing at room temperature for three days gives rise, predominantly to the



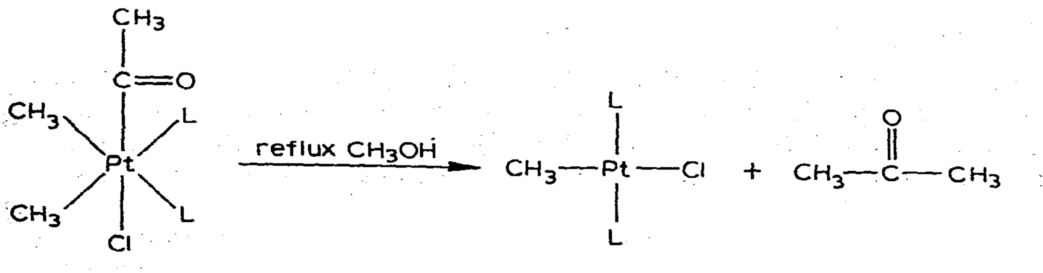
(2)

It is interesting to note that Puddephatt et al. [19] have suggested scrambling of methyl and methyl-d_3 groups in *fac*-Pt$(CH_3)_2(CD_3)[P(CH_3)_2(C_6H_5)]_2I$ does *not* occur prior to reductive elimination whereas for the analogous trimethylplatinum(IV) cations we have suggested [10] that isotopic scrambling occurs much more quickly than the rate of reductive elimination.

The oxidative addition of CF_3I to *cis*-Pt$(CH_3)_2L_2$ [where L = As$(CH_3)_3$] occurs very rapidly to give isomer (III). When the iodide ion was abstracted with $AgPF_6$ and then replaced, regardless of whether the intermediate solution (i.e. the filtrate from AgI removal) was treated immediately with NaI, refluxed, or allowed to stand for several days, a mixture of isomers (III) and (IV) was obtained in approximately equal quantities. No reductive elimination products or isomer (V) were detected. Our previous study on the stabilities of trimethylplatinum(IV) cations would predict that the trimethylarsine cations should show no tendency towards reductive elimination, as observed.

The oxidative addition reaction of CF_3I with *cis*-Pt$(CH_3)_2$(*p*-$CNC_6H_4CH_3)_2$ gave a mixture of two isomers (III), (IV) in the approximate ratio of 2/1. The activation energy for the isomerization of isomer (III) to (IV) must be lower for this complex than for the phosphine and arsine complexes [L = P$(CH_3)_2(C_6H_5)$ and As$(CH_3)_3$] for which isomerization occurred only after complete removal of the iodide ion as AgI and formation of cationic species. When $AgPF_6$ was added to a solution of the two isomers and then iodide replaced, the predominant species was (IV), especially if the solutions were refluxed. As predicted a small amount of reductive elimination occurred to give Pt(CF_3)I$(CNC_6H_4CH_3)_2$. Several other minor resonances were present in the ^{19}F NMR spectrum of the reaction mixture, with values of ^2J(Pt—F) ca. 480 Hz, however we have been unable to isolate and identify these products.

Acetyl chloride reacts readily with *cis*-Pt$(CH_3)_2L_2$ (L = P$(CH_3)_2(C_6H_5)$) [4] to give, exclusively, (X) (eqn. 3), which in refluxing methanol eliminates acetone to give *trans*-Pt(CH_3)ClL$_2$. When the chloride in X is removed by $AgPF_6$, reductive elimination occurs readily at room temperature.



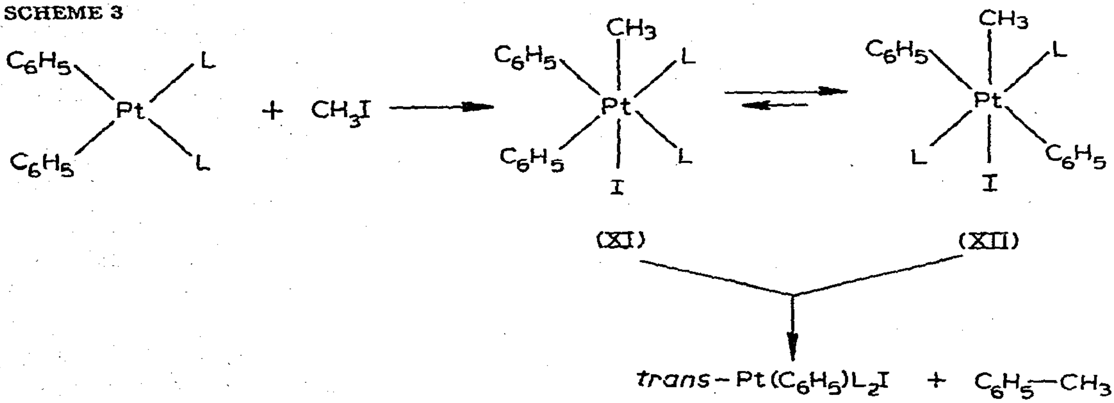
(X)

(3)

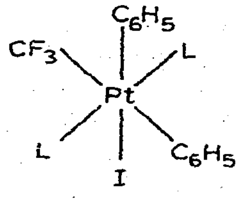
Acetyl chloride also reacts very rapidly with *cis*-$Pt(CH_3)_2L_2$ [L = $As(CH_3)_3$] to give (X). Refluxing in methanol for one hour yields *trans*-$Pt(CH_3)L_2Cl$ in quantitative yields and thus provides a much improved synthetic route to this compound, over the reaction of HCl with the dimethyl compound.

(b). Products from cis-$Pt(C_6H_5)_2L_2$. *cis*-$Pt(C_6H_5)_2[P(CH_3)_2(C_6H_5)]_2$ reacted slowly (over 24 hours) with excess methyl iodide at room temperature to give a mixture of products. The platinum(IV) products, although detected by NMR in solution, were unstable and attempts to isolate them were unsuccessful; only the decomposition products (Pt^{II}) could be isolated. From the NMR spectrum, it appears likely that isomer (XI) is initially formed but rearranges in chloroform solution to (XII) [Scheme 3, L = $P(CH_3)_2(C_6H_5)$]. If the reaction mixture is heated, *trans*-$Pt(C_6H_5)IL_2$ is obtained with the formation of toluene, $C_6H_5—CH_3$.

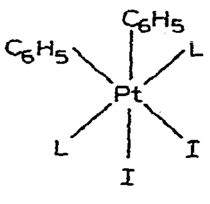
SCHEME 3



When *cis*-$Pt(C_6H_5)_2[P(CH_3)_2(C_6H_5)]_2$ was allowed to react with CF_3I in dichloromethane, complex (XIII) was obtained, probably through isomerization of the initially formed *trans*-addition product. When (XIII) is refluxed in methanol *trans*-$Pt(CF_3)IL_2$ [L = $P(CH_3)_2(C_6H_5)$] is formed, presumably with loss of biphenyl.



(XIII)



(XIV)

Similarly, the addition of CF_3I to *cis*-$Pt(C_6H_5)_2(CNC_6H_4CH_3)_2$ gave a good yield of $Pt(CF_3)I(CNC_6H_4CH_3)_2$. The reaction gave initially the platinum(IV) product of *trans*-addition, followed by reductive elimination which occurred smoothly at room temperature over several days, or more quickly on refluxing in acetone.

cis-$Pt(C_6H_5)_2[P(CH_3)_2(C_6H_5)]_2$ was readily oxidized by iodine to give complex (XIV), analogous to the reactions reported using triethylphosphine. Ettore [20] suggested that reductive elimination of $C_6H_5—I$ from (XIV) proceeded via the cationic species $\{PtI(C_6H_5)_2[P(CH_3)_2(C_6H_5)]_2\}^+I^-$. However, we have found that a simple reductive elimination reaction was not induced by the removal of one iodide with silver hexafluorophosphate.

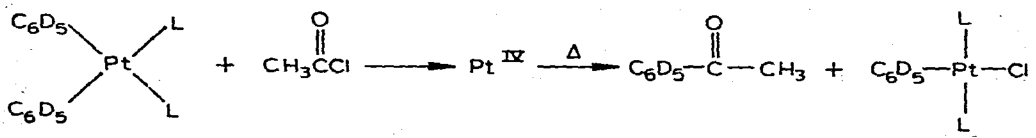
Conclusions

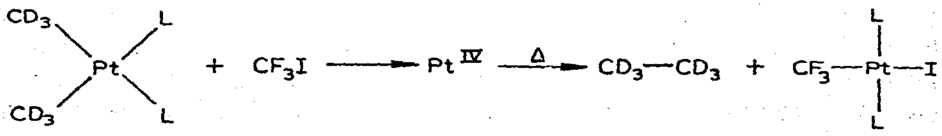
Although only a limited number of reactions have been examined we believe several conclusions may be drawn regarding isomerization and reductive elimination reactions of organoplatinum compounds.

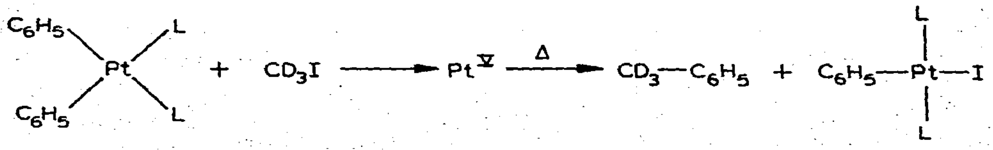
(1). Oxidative addition reactions to square planar platinum(II) complexes proceed, initially, to give the *trans*-adduct which is not necessarily the most thermodynamically stable isomer. The isomerization activation energy may be lowered by the formation of cationic species.

(2). The stereochemistry of the isomerization products is difficult to predict; however we propose the following ordering of ligands: $CH_3^- > C_6H_5^- > CF_3^- > PR_3 > AsR_3 \gg I^- > CH_3C(O)CH_3, CH_3OH$. Generally, the most favourable isomer is the one in which the ligands at the top of the series are *trans* to ligands at the low end of the series. For example, CF_3I adds to *cis*-$Pt(CH_3)_2[As(CH_3)_3]_2$ to give isomer (III). Removal of the iodide in acetone with $AgPF_6$ places a CF_3^- group *trans* to acetone, so this isomer rearranges, placing a CH_3^- group *trans* to the acetone, and both CH_3^- and CF_3^- *trans* to $As(CH_3)_3$, (IV). Unfortunately, for the phosphine complexes a further complication arises. The most favourable isomer appears to be the one with mutually *trans*-phosphines [cf. $PtX_2(PR_3)_2$ [21]] for which enthalpy favours *cis*-isomers, while entropy, which is solvent dependent, favours *trans*-isomers].

(3). The reductive elimination reaction products may be predicted from the following "leaving group order" $CH_3{-}C(O){-} > CH_3 > C_6H_5 \gg CF_3$. The reductive elimination reactions discussed in this paper present a possible synthetic route to a variety of organic molecules, especially partially deuterated molecules. Several hypothetical examples are illustrated below.







Experimental

For the preparations described below $Q = P(CH_3)_2C_6H_5$, $A = As(CH_3)_3$.

^1H NMR spectra were recorded on a Varian HA-100 spectrometer at 100 MHz using chloroform or dichloromethane as solvent and ^{19}F spectra were recorded at 94.1 MHz. Microanalyses were performed by Chemalytics Inc., Tempe, Arizona and Schwarzkopf Laboratory Inc., Woodside, N.Y.

Only representative examples of the oxidative addition, isomerization and reductive elimination reactions will be described in detail.

(a). Preparation of trans-$Pt(C_6H_5)IQ_2$

To a solution of *cis*-$Pt(C_6H_5)_2Q_2$ [17] (0.903 g) in a 1/1 methanol/chloroform mixture (30 ml) was added 5 ml of methyl iodide. The solution was refluxed for 5 h, then evaporated to dryness. The solid was recrystallized from ether/pentane. Yield 0.50 g.

(b). Preparation of $Pt(CF_3)(C_6H_5)_2IQ_2$

0.32 g of *cis*-$Pt(C_6H_5)_2Q_2$ was dissolved in the minimum volume of dichloromethane in a Carius tube. Excess CF_3I was condensed in, the tube was sealed and shaken for six days. The tube was then opened and the solution evaporated to dryness to give a yellow solid which was recrystallized from dichloromethane/hexane. Yield was 74%.

(c). Reaction of cis-$Pt(C_6H_5)_2Q_2$ with iodine

To 0.297 g of cis-$Pt(C_6H_5)_2Q_2$ in dichloromethane was added 0.122 g of iodine in CH_2Cl_2. The solution immediately turned red. Evaporation of the solution gave an orange-red solid which was recrystallized from CH_2Cl_2/hexane. Yield was 95%.

(d). Reaction of $PtCl(CH_3)_2(COCH_3)Q_2$ with $AgClO_4$

0.112 g of $PtCl(CH_3)_2(COCH_3)Q_2$ was dissolved in acetone and 0.060 g of $AgClO_4$ in acetone was added. The silver chloride was filtered and an excess of lithium chloride was added. The solution was evaporated to dryness. Dichloromethane was added, the solution filtered and evaporated to dryness to give a white solid which was identified as *trans*-$Pt(CH_3)ClQ_2$ [4]. Yield was 90%.

(e). Preparation of trans-$Pt(CH_3)ClA_2$ from cis-$Pt(CH_3)_2A_2$

To a solution of $Pt(CH_3)_2A_2$ (5.44 g) in 100 ml of diethyl ether was added CH_3COCl (0.77 ml). The solution was allowed to stand for 15 min and white crystals of $Pt(CH_3)_2(COCH_3)ClA_2$ deposited. The solution was cooled for several hours at 0° and the ether decanted. The yield of the Pt^{IV} complex was 6.35 g. The Pt^{IV} complex was suspended in $\approx$ 50 ml of methanol, refluxed for 1 h, and the solvent was removed by rotary evaporation to give white crystals which were filtered and washed with ether. Yield 5.27 g [94% based on $Pt(CH_3)_2A_2$].

Acknowledgements

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