Preparation and Reactions of Alkyl Carbonyl Complexes of Platinum(II)

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One-step reduction of $PtCl_2$ to platinum(0) cluster complexes $[Pt_4(CO)_5L_4]$, followed by oxidative addition with MeI, provides a route to new platinum(II) complexes [Pt(CO)L(I)Me] (where L is a phosphorus ligand). These react with uncharged ligands L′ to give carbonyl substitution or insertion products or a mixture of both. Both electronic and steric effects help to determine the type of product obtained and, in the case of the insertion reactions, the position of equilibrium between the complexes [Pt(CO)L(I)Me] and [PtLL′I(COMe)].

RECENTLY we reported kinetic data for reaction (1) ($L = L' = AsPh_3$; X = Cl; and R = Et).[1] These data

$$[\mathrm{Pt(CO)L(X)R}] + \mathrm{L}' \longrightarrow [\mathrm{PtLL'X(COR)}] \qquad (1)$$

suggested a two-step mechanism for the reaction. The accepted mechanism for *substitution* reactions of square-planar complexes is an associative one involving a five-co-ordinate transition state or intermediate. It was

$$[\mathrm{Pt(CO)L(X)R}] \overset{k_1}{\underset{k_{-1}}{\rightleftharpoons}} [\mathrm{PtLX(COR)}] \qquad (2)$$

$$[\mathrm{PtLX(COR)}] + \mathrm{L}' \xrightarrow{k_2} [\mathrm{PtLL'X(COR)}] \qquad (3)$$

therefore surprising to find that neither the incoming nucleophile nor the solvent was involved in the step [equation (2)] which was essentially rate determining in reaction (1). The complex used as a starting material for the kinetic study was $[Pt(CO)ClEt]_2$, converted to the desired $[Pt(CO)(AsPh_3)(Cl)Et]$ by reaction with triphenylarsine. This system is an unsatisfactory one since the yields obtained in the preparation [2] of the complex $[Pt(CO)ClEt]_2$ are very variable, and the only combination of ligands L and L′ which can be used without complications from side reactions is $L = L' = AsPh_3$.[1] This meant that the independence of the crucial rate constant k_1 of the nature of L′ could not be demonstrated, nor could one study the dependence of k_1 on the nature of the ligand L. This paper describes an alternative route to complexes [Pt(CO)L(X)R], and some of the reactions which these complexes undergo.

RESULTS

[Pt(CO)L(X)R] *Complexes.—Preparation.* The reaction of carbon monoxide with $Li_2[PtCl_4]$ in dimethylformamide–ethanol solution gave a dark green solution. Addition of PPh_3 followed by hydrazine hydrate and potassium hydroxide produced a dark red solution from which a purple solid was rapidly precipitated. The i.r. spectrum of this crude product is similar to that reported for $[Pt_4(CO)_5(PPh_3)_4]$, as obtained by a two-step route.[3] Recrystallization from benzene gave the solvate $[Pt_4(CO)_5(PPh_3)_4],C_6H_6$, (Ia): the benzene is not lost *in vacuo* at 333 K but appears to be released slowly above 377 K. Similar reaction sequences yielded the related complexes $[Pt_4(CO)_5L_4],C_6H_6$ [$L = PPh_2(o\text{-}MeC_6H_4)$, (Ib), and $PPh(o\text{-}MeC_6H_4)_2$, (Ic)]. I.r. spectra of complexes (Ia)—(Ic) are given in Table 1.

All three complexes underwent reaction with iodomethane to form platinum(II) products of the desired type, [Pt(CO)L(I)Me] [$L = PPh_3$, (IIa), $PPh_2(o\text{-}MeC_6H_4)$, (IIb), and $PPh(o\text{-}MeC_6H_4)_2$, (IIc)]. I.r. and n.m.r. spectra of these complexes are given in Tables 1 and 2 respectively. Other species, not fully characterized, were obtained as by-products: one, which was formed in all three cases, possessed characteristic i.r. bands at 2 043 and 2 046 cm^{-1}, and is probably the dicarbonyl species $[Pt(CO)_2(I)Me]$. Each reaction mixture also contained a species which gave rise to a band in the acyl C–O stretching region [1 638 cm^{-1} for the reaction of complex (Ia)]: this may well be $[PtL_2I(COMe)]$.

TABLE 1

I.r. spectra in the C–O stretching region [a]

Complex	ν_{C-O}/cm^{-1}
(Ia) [b]	1 789, 1 822, 1 850
(Ib) [b]	1 785, 1 811, 1 855
(Ic) [b]	1 788, 1 810, 1 853
(IIa)	2 080
(IIb)	2 078
(IIc)	2 078
$[Pt(PPh_3)(py)I(COMe)]$	1 636
$[Pt(PPh_3)(2\text{-}Mepy)I(COMe)]$	1 636
$[Pt(PPh_3)(3\text{-}Mepy)I(COMe)]$	1 635
$[Pt(PPh_3)(4\text{-}Mepy)I(COMe)]$	1 640
$[Pt(PPh_3)(4\text{-}NCpy)I(COMe)]$	1 648
$[Pt(PPh_3)_2I(COMe)]$	1 638
$[Pt(PPh_3)(AsPh_3)I(COMe)]$	1 642
$[Pt(PPh_3)\{As(p\text{-}MeC_6H_4)_3\}I(COMe)]$	1 640
$[Pt(PPh_3)\{AsMe(o\text{-}MeC_6H_4)_2\}I(COMe)]$	1 638
$[Pt(PPh_3)\{As(o\text{-}MeC_6H_4)_3\}I(COMe)]$	1 636
$[Pt(PPh_3)(AsMePh_2)I(COMe)]$	1 640
$[Pt(PPh_3)(SbPh_3)I(COMe)]$	1 640
$[Pt(PPh_3)(SMe_2)I(COMe)]$	1 648
$[Pt\{PPh_2(o\text{-}MeC_6H_4)\}(AsPh_3)I(COMe)]$	1 635
$[Pt\{PPh(o\text{-}MeC_6H_4)_2\}(AsPh_3)I(COMe)]$	1 636

[a] Recorded on solutions in CH_2Cl_2, except where otherwise stated. [b] Benzene solution.

Reactions. Addition of pyridine (py) to a solution of complex (IIa) in dichloromethane caused the disappearance of the C–O stretching band at 2 080 cm^{-1} in the i.r. spectrum of (IIa), while a new band appeared in the acyl C–O stretching region at 1 636 cm^{-1}. Analytical data for the isolated product showed it to be $[Pt(PPh_3)(py)I(COMe)]$. Small-scale reactions of complex (IIa) with some substituted pyridines (L′) in the same solvent resulted in almost identical changes in i.r. spectrum, indicating formation of similar 'carbonyl-insertion' products $[Pt(PPh_3)L'I(COMe)]$. It was not considered necessary to repeat the reactions on a preparative scale, but the position of the acyl C–O stretching band in the spectrum of each product is given in Table 1. In the case of 4-cyanopyridine the reaction does not go to completion: equilibrium (4) ($L = PPh_3$ and L′ = 4-cyanopyridine) is shifted to the right by lowering the temperature

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[1] R. W. Glyde and R. J. Mawby, *Inorg. Chem.*, 1971, **10**, 854.

[2] E. Lodewijk and D. Wright, *J. Chem. Soc.* (*A*), 1968, 119.

[3] J. Chatt and P. Chini, *J. Chem. Soc.* (*A*), 1970, 1538.

or adding excess of amine. In contrast to the pyridine ligands, aniline failed to react with complex (IIa).

$$[\mathrm{Pt(CO)L(I)Me}] + \mathrm{L'} \rightleftharpoons [\mathrm{PtLL'I(COMe)}] \qquad (4)$$

When solutions of complex (IIa) and any of the phosphorus ligands PPh_3, $P(p\text{-}MeC_6H_4)_3$, and $P(OMe)_3$ were mixed, CO was evolved. I.r. spectra of the reaction mixtures contained no bands in the terminal or acyl C–O stretching regions. No attempt was made to isolate the products, which clearly result from carbonyl-substitution rather than insertion reactions. When, on the other hand, a very dilute solution of PPh_3 was added dropwise to a solution of complex (IIa), a new i.r. band grew at 1 638 cm^{-1} as the band at 2 080 cm^{-1} in the spectrum of (IIa) diminished, suggesting that some of the insertion product $[Pt(PPh_3)_2I(COMe)]$ can be formed under these conditions.

TABLE 2

N.m.r. spectra of selected complexes [a]

Complex	Chemical shift	Coupling constants/Hz	Assignment
$[Pt(CO)(PPh_3)(I)Me]$	1·05(d) [b]	^3J(PPtCH) 6·0 ^2J(PtCH) 60	PtCH_3
$[Pt(CO)\{PPh_2(o\text{-}MeC_6H_4)\}(I)Me]$	2·41(s)		$o\text{-}CH_3C_6H_4$
	0·93(d) [b]	^3J(PPtCH) 6·0 ^2J(PtCH) 60	PtCH_3
$[Pt(CO)\{PPh(o\text{-}MeC_6H_4)_2\}(I)Me]$	2·37(s)		$o\text{-}CH_3C_6H_4$
	0·85(d) [b]	^3J(PPtCH) 6·0 ^2J(PtCH) 60	PtCH_3
$[Pt(PPh_3)(AsPh_3)I(COMe)]$	1·33(s) [b]	^3J(PtCCH) 6·5	PtCOCH_3
$[Pt\{PPh_2(o\text{-}MeC_6H_4)\}(AsPh_3)I(COMe)]$	2·43(s)		$o\text{-}CH_3C_6H_4$
	1·31(s) [b]	^3J(PtCCH) 6·6	PtCOCH_3
$[Pt\{PPh(o\text{-}MeC_6H_4)_2\}(AsPh_3)I(COMe)]$	2·42(s)		$o\text{-}CH_3C_6H_4$
	1·22(s) [b]	^3J(PtCCH) 7·1	PtCOCH_3

[a] In $CDCl_3$ solution at 306·5 K, using Me_4Si as internal standard. Values for chemical shifts are on the δ scale. Aromatic ring protons excluded. s = Singlet, c = complex, d = doublet. [b] Sidebands also observed due to coupling to ^{195}Pt.

The arsenic and antimony ligands L′ = $AsPh_3$, $As(p\text{-}MeC_6H_4)_3$, $AsMe(o\text{-}MeC_6H_4)_2$, and $SbPh_3$ all underwent reaction with complex (IIa) to form insertion products $[Pt(PPh_3)L'I(COMe)]$, which have been isolated and characterized. In contrast, $AsMe_2Ph$ gave only carbonyl-substitution products, while $AsMePh_2$ gave a mixture of insertion and substitution products. The very bulky ligand $As(o\text{-}MeC_6H_4)_3$ behaved like 4-cyanopyridine [see equation (4) above].

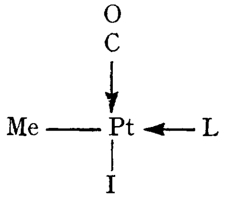
When dimethyl sulphide was added to a solution of complex (IIa), an i.r. band appeared at 1 648 cm^{-1} as that at 2 080 cm^{-1} disappeared, indicating that the complex $[Pt(PPh_3)(SMe_2)I(COMe)]$ is formed in solution. The volatility of dimethyl sulphide can be used to demonstrate the reversibility of the insertion reaction: when the solution was purged with nitrogen the 1 648 cm^{-1} band was replaced by the 2 080 cm^{-1} band characteristic of complex (IIa). Because of this facile reconversion to (IIa), the product cannot be obtained pure in the solid state, even from solutions containing excess of dimethyl sulphide.

Unlike (IIa), complexes (IIb) and (IIc) were not completely converted to acetyl complexes by treatment with $AsPh_3$, although the products could be isolated by low-temperature crystallization. Under a given set of conditions, the equilibrium [equation (4), L′ = $AsPh_3$] moves to the left as L is changed from PPh_3 to $PPh_2(o\text{-}MeC_6H_4)$ to $PPh(o\text{-}MeC_6H_4)_2$.

I.r. and n.m.r. spectra of complexes [PtLL′I(COMe)] are listed in Tables 1 and 2 respectively.

DISCUSSION

Stereochemistry.—The magnitude of $|^3J(\mathrm{PPtCH})|$ cannot be used as a guide to the relative orientation of the methyl and phosphorus ligands in complexes (IIa)—(IIc), since it is reported to be much the same for both *cis*- and *trans*-arrangements, but the values for $|^2J(\mathrm{PtCH})|$ are in the range characteristic of a methyl group *trans* to phosphorus and *cis* to halogen (50—60 Hz) rather than the reverse (*ca.* 80 Hz).[4] If it is assumed that the ability of the complexes to undergo carbonyl-insertion reactions indicates that the methyl and carbonyl ligands are *cis* to one another, complexes (IIa)—(IIc) can be assigned the stereochemistry (A) which implies *cis*-addition [5] of iodomethane to the platinum(0) complexes (Ia)—(Ic) (although it is possible that *trans*-addition is followed by isomerization). N.m.r. data for the insertion products [PtLL′I(COMe)] do not provide enough information to allow their stereochemistry to be determined.



(A)

Reaction Path.—It is clear from the reactions of complex (IIa) that the balance between carbonyl substitution and insertion is a delicate one. The choice of donor atom in the incoming ligand is obviously important: since phosphorus ligands are more prone to give rise to substitution, as opposed to insertion, than either nitrogen or arsenic ligands the effect is presumably mainly electronic rather than steric in origin. The results with the arsenic ligands, however, imply that insertion is favoured over substitution by increasing the bulkiness of the incoming ligand: this agrees with the scheme shown for the insertion reaction in equations (2) and (3), in which the ligand attacks the less crowded three-co-ordinate intermediate, whereas the normal S_N2 substitution mechanism requires attack on the four-co-ordinate alkyl complex. The results with PPh_3 as the attacking ligand also fit the scheme: the rate of S_N2 substitution will be

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[4] F. H. Allen and A. Pidcock, *J. Chem. Soc.* (*A*), 1968, 2700.

[5] R. Ugo, *Co-ordination Chem. Rev.*, 1968, **3**, 319.

directly proportional to PPh_3 concentration, whereas the first step in the insertion process [equation (2)] is ligand-independent; hence it is not surprising that dropwise addition of a dilute solution of PPh_3 favours the insertion process.

Unlike the substitution reaction, where CO is lost from the solution, the insertion reaction is in some cases reversible [equation (4)] (in these instances there is clearly no competition from a substitution process, since this, by virtue of its irreversible nature, would ultimately lead to complete conversion to a substitution product). The results from the ligands containing *o*-tolyl groups show that the equilibrium can be displaced towards the less-crowded starting material by increasing the bulk of either the ligand L in the starting material or the incoming ligand L′. Electronic effects must also be of some importance, since complex (IIa) is completely converted to an acetyl product by pyridine but only partially by the less basic 4-cyanopyridine. The effect of temperature on the equilibrium reflects the expected decrease in entropy in going from left to right.

EXPERIMENTAL

Except where otherwise stated, experiments were carried out under a nitrogen atmosphere.

Platinum(0) *Complexes*.—(I*a*). A solution of platinum(II) chloride (5·33 g) and lithium chloride (1·8 g) in dimethylformamide (50 cm^3) and ethanol (100 cm^3) was stirred under carbon monoxide for 6 h. Triphenylphosphine (5·25 g) in ethanol (50 cm^3) was added dropwise over 1 h, the solution was warmed to 333 K and hydrazine hydrate (2 cm^3) in ethanol (20 cm^3) was added dropwise. After heating under reflux for 0·5 h, potassium hydroxide (2 g) in ethanol (10 cm^3) and water (10 cm^3) was added, and heating was continued for a further 0·5 h. The crude purple product was filtered off from the hot solution, impurities were removed by Soxhlet extraction with methanol for 3 h, and the residue was recrystallized from benzene and dried *in vacuo*.

Complexes (Ib) and (Ic) were similarly prepared.

Oxidative-addition Reactions.—*Complex* (II*a*). Complex (Ia) (2·0 g) was dissolved in iodomethane (10 cm^3). After 12 h the solution was poured into light petroleum (b.p. 313—333 K). The immediate dark precipitate was filtered off and the filtrate concentrated under reduced pressure. The yellow product obtained was purified by silica-gel column chromatography using dioxan–light petroleum (b.p. 333—353 K) mixtures as eluant.

Complex (II*b*). Complex (Ib) was treated in the same way as (Ia). In this case, however, the first solid obtained on concentration of the filtrate was not a carbonyl complex and was discarded. The mother liquor, which contained (IIb) and a second species {probably $[Pt(CO)_2(I)Me]$, see text}, was treated with diphenyl(*o*-tolyl)phosphine (0·02 g) in light petroleum (b.p. 333—353 K, 20 cm^3) and a little activated charcoal. The mixture was shaken for 0·2 h at 308 K and then filtered. Reduction of the volume of the filtrate yielded the yellow crystalline product, which was filtered off, washed with light petroleum (b.p. 313—333 K), and dried *in vacuo*.

Complex (IIc) was prepared in the same way as (IIb).

Carbonyl-insertion Reactions.—*Reaction of complex* (IIa) *with triphenylarsine*. A solution of complex (IIa) (0·2 g) and triphenylarsine (1·0 g) in dichloromethane (15 cm^3) was kept at room temperature until the i.r. spectrum of the solution indicated that the reaction was complete. Light petroleum (b.p. 353—373 K, 20 cm^3) was then added: slow evaporation under reduced pressure gave pale yellow crystals of the product $[Pt(PPh_3)(AsPh_3)I(COMe)]$. These were washed with light petroleum (b.p. 313—333 K) and recrystallized from an 0·1M-solution of triphenylarsine in mixed dichloromethane and light petroleum (b.p. 353—373 K). Other reactions of complex (IIa) were carried out in the same way.

Reaction of complex (IIb) *with triphenylarsine*. A solution of (IIb) (0·2 g) and triphenylarsine (1·0 g) in the minimum volume of 1 : 4 dichloromethane–light petroleum (b.p. 333—353 K) was allowed to stand for 4 days at room temperature and then for 3 days at 273 K. Pale yellow crystals of $[Pt\{PPh_2(o\text{-}MeC_6H_4)\}(AsPh_3)I(COMe)]$ were obtained. These were washed with light petroleum (b.p. 313—333 K) and dried *in vacuo*.

The reaction between complex (IIc) and triphenylarsine was carried out in the same way.

TABLE 3

Analytical data (%)

Complex	Found C	Found H	Found I	Calc. C	Calc. H	Calc. I
(Ia)	48·6	3·4		48·7	3·3	
(Ib)	50·1	3·5		49·7	3·6	
(Ic)	50·5	4·0		50·6	3·8	
(IIa)	38·3	2·9	20·5	38·3	2·9	20·2
(IIb)	39·2	3·1	19·6	39·3	3·1	19·8
(IIc)	40·0	3·4	19·0	40·3	3·4	19·4
$[Pt(PPh_3)(py)I(COMe)]$ [a]	42·5	3·3	18·2	42·5	3·3	18·0
$[Pt(PPh_3)(AsPh_3)I(COMe)]$	48·5	3·6	13·5	48·9	3·6	13·6
$[Pt(PPh_3)\{As(p\text{-}MeC_6H_4)_3\}I(COMe)]$	50·2	4·2	13·2	50·5	4·0	13·0
$[Pt(PPh_3)\{AsMe(o\text{-}MeC_6H_4)_2\}I(COMe)]$	46·9	3·6	14·4	46·7	3·9	14·1
$[Pt(PPh_3)(SbPh_3)I(COMe)]$	46·5	3·5	12·9	46·6	3·4	12·9
$[Pt\{PPh_2(o\text{-}MeC_6H_4)\}(AsPh_3)I(COMe)]$	49·5	3·7	13·1	49·4	3·7	13·4
$[Pt\{PPh(o\text{-}MeC_6H_4)_2\}(AsPh_3)I(COMe)]$	50·0	4·0	13·3	50·0	3·9	13·2

[a] N: found 2·2, calc. 2·0%.

Analytical data are given in Table 3. I.r. spectra were recorded on a Perkin-Elmer 257 grating spectrophotometer and n.m.r. spectra on a Perkin-Elmer R10 60 MHz spectrometer.

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