Alkyl and Aryl Migration from Carbon Monoxide to Platinum Promoted by Silver Ion

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Abstraction of chloride with $AgPF_6$ from $Pt(PPh_3)_2Cl(RCO)$ (R = Me, Ph, p-MeC_6H_4, p-$MeOC_6H_4$, or p-$O_2NC_6H_4$) in ethanol leads to migration of R from carbon monoxide to platinum to form cationic platinum carbonyl complexes, $[Pt(PPh_3)_2(CO)R]^+$. Silver ion abstraction of chloride from $Pt(PPh_3)_2Cl(RCO)$ in acetonitrile leads to isolation of $[Pt(PPh_3)_2(RCO)(MeCN)]^+$. Migration of R was not observed for these nitrile solvated complexes, but was observed in similar acetone solvated complexes.

THE rearrangement of an acyl–metal linkage to an alkyl- or aryl-metal carbonyl linkage can be effected by thermal or photochemical methods,[1] which presumably leads to expulsion of a ligand and thus creation of a vacant co-ordination site on the metal. Recently, alkyl and aryl migration from carbon monoxide to iron has been effected with $(\pi\text{-}C_5H_5)Fe(CO)_2(RCO)$ by its reaction with $(PPh_3)_3RhCl$, which removes a CO molecule from the iron complex and thus produces a vacant co-ordination site.[2] We report another type of chemical reaction, the removal of a chloro-ligand with silver ion, to produce a vacant co-ordination site which promotes the alkyl or aryl migration from carbon monoxide to platinum.

The formation of acyl complexes $Pt(PPh_3)_2Cl(RCO)$ by the oxidative addition of acyl chlorides RCOCl to $Pt(PPh_3)_4$ has been reported for R = Me [3] and Ph.[4] Reaction of an excess of cyclopropanecarboxylic acid chloride with $Pt(PPh_3)_4$ was reported [5] to give $Pt(PPh_3)_2Cl_2$. We observed that the cyclopropyl acyl and other acyl platinum complexes could be isolated if an excess of acyl chloride was avoided in the preparation of the complexes. An excess of acyl chloride gave further reaction to $Pt(PPh_3)_2Cl_2$ and the fate of the acyl group in these reactions remains to be explored. The oxidative addition reactions of acyl chlorides with palladium(0) and nickel(0) complexes give products resulting from subsequent reactions of the acyl complexes.[6]

The acyl complexes $Pt(PPh_3)_2Cl(RCO)$ have CO stretching frequencies in the 1615—1660 cm^{-1} region, and Pt–Cl stretching frequencies in the 250—263 cm^{-1} region. These low frequencies are characteristic of chloride *trans* to a strongly *trans*-labilizing ligand and the high *trans*-labilizing effect of acyl ligands was previously reported.[7] An earlier report [4] proposes that the PhCO group has a very low *trans*-effect. The *trans*-dichloro-complex $Pt(PPh_3)_2Cl_2$ was observed to have strong absorption at 330 cm^{-1} corresponding to Pt–Cl stretching where chloride is *trans* to a weak *trans*-directing chloro-ligand.

Upon heating the acyl complexes $Pt(PPh_3)_2Cl(RCO)$ (R = Me or Ph) at 210 °C, migration of R from CO to Pt and decarbonylation were observed.[3,4] In this study the migration of R from CO to Pt was observed to proceed under mild conditions when the acyl complexes were treated with $AgPF_6$ in ethanol. The cationic carbonyl complexes $[Pt(PPh_3)_2(CO)R]^+$ have CO frequencies in the 2100—2118 cm^{-1} region similar to those reported for similar cationic *trans*-platinum carbonyl complexes.[8]

Reaction of the acyl complexes (I) with $AgPF_6$ in acetonitrile and benzonitrile gave $[Pt(PPh_3)_2(NCMe)(RCO)]^+$ and $[Pt(PPh_3)_2(NCPh)(RCO)]^+$ which had acyl CO frequencies in the 1622—1630 cm^{-1} region and CN absorptions as expected at higher frequencies than in the uncomplexed nitriles. When heated in various solvents these nitrile–acyl complexes decomposed before they could be converted to the cationic carbonyl complexes

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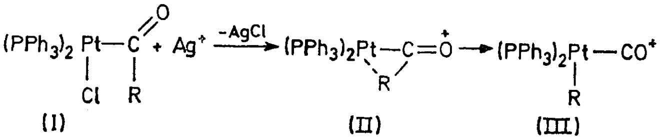
(III). The reactions of $Pt(PPh_3)_2Cl(RCO)$ with $AgPF_6$ in acetone gave mixtures of the cationic carbonyls (III) and $[Pt(PPh_3)_2(acetone)RCO]^+$. These acetone complexes have multiple bands in the 1612—1672 cm^{-1} regions which are attributed to CO stretching of the acyl and acetone bonded to platinum. By warming the acetone complexes in tetrahydrofuran, they could be readily converted to the cationic carbonyl complexes (III).

Although mechanistic studies were not undertaken it is likely that the rearrangement of the acyl complexes (I) to the cationic carbonyl complexes (III) proceeds through an intermediate (II) in which the alkyl or aryl group interacts with the metal atom through one of its co-ordination sites. From the observed rearrangements in ethanol and acetone, the lack of rearrangement in nitriles, and the isolation of four-co-ordinated solvated cationic complexes, it is very likely that the site is a vacant fourth co-ordinate site rather than a vacant fifth co-ordination site of intermediate (II) which is involved. When the reaction occurs in acetonitrile, the solvent binds the platinum atom thus blocking the fourth vacant site and alkyl(aryl)-metal interaction. Acetone can also block the fourth vacant site, but the acetone solvated intermediate can be readily converted to the carbonyl (III) by displacement of the acetone and interaction through the vacant site as in (II). Kinetic evidence for a three-co-ordinated acyl platinum(II) intermediate analogous to (II) has been previously reported.[9] Evidence for the intermediacy of a three-co-ordinated platinum(II) complex in the thermal decomposition of $Pt(PPh_3)_2(Bu^n)_2$ has also been presented.[10] Interaction of the alkyl or aryl group with the unsolvated metal atom such as in (II) has also been proposed for acyl-alkyl(aryl)carbonyl rearrangements at iron.[11] The type of intramolecular rearrangement described in this report may be operative in the recently reported 'three-fragment oxidative addition' processes.[12]



Compound	Colour	M.p.[a]	Analytical data[b] C	H	Other	Infrared spectral data/cm^{-1} ν_{acyl}	Other bands			
$Pt(PPh_3)_2Cl(MeCO)$	White	160	57·4 (57·2)	3·95 (4·15)	Cl, 5·0 (4·44)	1650	257	ν(Pt–Cl)		
$Pt(PPh_3)_2Cl(PhCO)$	White	294	60·0 (60·0)	4·15 (4·1)	Cl, 4·3 (4·12)	1616	260			
$Pt(PPh_3)_2Cl(EtCO)$	White	150	58·0 (57·7)	4·3 (4·35)	Cl, 4·85 (4·36)	1661	254			
$Pt(PPh_3)_2Cl(Me_2CHCO)$	Pale yellow	160	58·8 (58·1)	4·15 (4·55)	Cl, 5·8 (4·29)	1641	250			
$Pt(PPh_3)_2Cl(p\text{-}MeOC_6H_4CO)$	White	205	60·1 (59·4)	4·3 (4·2)		1613	260			
$Pt(PPh_3)_2Cl(p\text{-}MeC_6H_4CO)$ [c]	Pale yellow	135	57·0 (56·4)	4·05 (4·1)	Cl, 10·6 (11·1)	1632	263			
$Pt(PPh_3)_2Cl(p\text{-}O_2NC_6H_4CO)$ [c]	Yellow	204	53·3 (53·3)	3·7 (3·55)	Cl, 11·4 (10·7)	1630	270			
$Pt(PPh_3)_2Cl(C_3H_5CO)$ [d]	White	160	58·0 (58·3)	4·15 (4·3)		1628, 1641	260			
$[Pt(PPh_3)_2(CO)(Me)]PF_6$	Cream	148	49·6 (50·3)	3·35 (3·65)	P, 9·65 (10·2)		2118	ν(CO)	840	ν(PF_6
$[Pt(PPh_3)_2(CO)(Et)]PF_6$	Brown	154	50·6 (50·8)	3·7 (3·85)	P, 8·85 (10·0)		2080		838	
$[Pt(PPh_3)_2(CO)(Ph)]PF_6$	Cream	148	52·5 (53·3)	3·65 (3·65)	P, 8·9 (9·6)		2118		835	
$[Pt(PPh_3)_2(CO)(p\text{-}MeOC_6H_4)]PF_6$	Tan	185	52·7 (52·9)	3·75 (3·75)	P, 9·4 (9·3)		2100		827	
$[Pt(PPh_3)_2(CO)(p\text{-}MeC_6H_4)]PF_6$	Tan	189	52·4 (53·7)	3·65 (3·8)	P. 9·05 (9·45)		2105		846	
$[Pt(PPh_3)_2(CO)(p\text{-}O_2NC_6H_4)]PF_6$ [e]	Pale	180	50·2 (49·2)	3·35 (3·25)	P, 8·45 (8·85)		2110		838	
$[Pt(PPh_3)_2(MeCN)(PhCO)]PF_6$	Cream	121	51·6 (53·4)	3·65 (3·8)	N, 1·1 (1·4)	1630	2300,[f] 2322[f]		843	
$[Pt(PPh_3)_2(MeCN)\text{-}(p\text{-}O_2NC_6H_4CO)]PF_6$	Pale yellow	223	50·9 (51·2)	3·65 (3·55)	N, 2·4 (2·65)	1638	2295,[f]		842	
$[Pt(PPh_3)_2(PhCN)(PhCO)]PF_6$	White	180—182	55·8 (56·0)	3·95 (3·75)	N, 1·2 (1·3)	1622	2275[f]		827	
$Pt(PPh_3)_2(Me_2CO)\text{-}(p\text{-}O_2NC_6H_4CO)PF_6$	Yellow	202	51·3 (49·9)	3·65 (3·65)	N, 1·55 (1·25)	1632			837	
$Pt(PPh_3)_2(Me_2CO)(EtCO)PF_6$	Gray	116	52·3 (51·5)	4·3 (4·3)		1650, 1630sh			840	
$Pt(PPh_3)_2(Me_2CO)(PhCO)PF_6$	White	188	53·6 (53·8)	3·85 (4·0)		1612, 1625			840	

[a] Decomposition starts at the temperature indicated. [b] Calculated value in parentheses. [c] Dichloromethane adduct. [d] Cyclopropyl derivative. [e] Calc. for N: 1·33, Found: 1·05%. [f] ν(CN).

EXPERIMENTAL

Acyl chlorides were reagent grade samples which were distilled before use or prepared by reaction of thionyl chloride and the carboxylic acid. $Pt(PPh_3)_4$ was prepared by the method of Malatesta and Cariello.[13] All other chemicals were reagent grade materials used without further treatment. Platinum(0) complexes were manipulated under a nitrogen atmosphere. Microanalyses were performed by Chemalytics, Inc., Tempe, Arizona. I.r. spectra were recorded in Nujol mulls on a Perkin-Elmer 621 Spectrophotometer. M.p.s were measured on a Mel-Temp apparatus and are uncorrected.

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Acetyl chloride (0·05 ml, 4 mmol) was added to a refluxing solution of $Pt(PPh_3)_4$ (0·5 g, 4 mmol) in benzene (5 ml). The solution was stirred for 5—30 min until the yellow colour of $Pt(PPh_3)_4$ had faded. Hexane was added to precipitate the white product which was recrystallized from benzene–hexane, or dichloromethane–ether. The yield was 286 mg (89%). Similar procedures were used to prepare the other acyl complexes $Pt(PPh_3)_2Cl(RCO)$.

$Pt(PPh_3)_2Cl(PhCO)$ (120 mg) and $AgPF_6$ (35 mg) in ethanol (5 ml) were refluxed for 20 min. Ethanol was stripped under reduced pressure. Dichloromethane (5 ml) was added and the mixture centrifuged to remove the solution from the precipitated silver chloride. A 1 : 1 mixture of hexane–ether was added to precipitate the product. Recrystallization was from dichloromethane–hexane–ether. The other cationic carbonyl complexes were prepared in a similar fashion except that chloride removal could be effected by stirring the complexes for 10 min with $AgPF_6$ at room temperature.

$Pt(PPh_3)_2Cl(PhCO)$ (120 mg) and $AgPF_6$ (35 mg) in acetonitrile, benzonitrile, or acetone (5 ml) were refluxed for 5 min. The reaction mixture was centrifuged and the solution separated from the silver chloride. Diethyl ether–hexane (1 : 1, 20 ml) was added to precipitate the solvated complexes $[Pt(PPh_3)_2(solvent)PhCO]^+PF_6^-$. The acetone complexes could not be recrystallized. When the acetone complexes were stirred in dichloromethane, rapid conversion of the benzoyl to phenyl(carbonyl) was observed.

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