Reactivity of Carboxylate Complexes of Platinum(II) towards Carbon Monoxide, Sulphur Dioxide, and Some Olefins and Acetylenes

By **D. M. Barlex** and **R. D. W. Kemmitt,*** Chemistry Department, The University, Leicester LE1 7RH

Reactions of the carboxylate complexes $Pt(OCOCH_3)_2(PPh_3)_2$ and $Pt(OCOCF_3)_2(PPh_3)_2$ with carbon monoxide and certain olefins and acetylenes in alcoholic media support a mechanism which involves the formation of an intermediate alkoxide complex, $Pt(OCOCY_3)(OR)(PPh_3)_2$ (Y = H or F; R = Me or Et). The alkoxide reacts with carbon monoxide to give alkoxycarbonyl complexes, $Pt(OCOCY_3)(COOR)(PPh_3)_2$ but in the presence of diphenylacetylene a hydride shift occurs to give a platinum hydride species which results in the formation of an alkenyl complex, $Pt(OCOCF_3)(PhC{=}CHPh)(PPh_3)_2$ when Y = F and $Pt(PhC{\equiv}CPh)(PPh_3)_2$ when Y = H. Reactions with hexafluorobut-2-yne, tetrafluoroethylene, tetrachloroethylene, and tetracyanoethylene are also described. Sulphur dioxide reacts with $Pt(OCOCH_3)_2(PPh_3)_2$ in methanol to give the methylsulphonate complex, $Pt(SO_2OMe)_2(PPh_3)_2$.

THE reactions of carbon monoxide and olefins with mercury(II) acetate in alcohols provide convenient syntheses of alkoxycarbonyl and substituted alkylmercury complexes, *e.g.* Hg(COOR)(OAc) and $Hg(CH_2CH_2OR)(OAc)$ respectively.[1] We now describe similar investigations with the complexes $Pt(OCOCH_3)_2(PPh_3)_2$ and $Pt(OCOCF_3)_2(PPh_3)_2$.[2]

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[2] For a preliminary account see D. M. Barlex, R. D. W. Kemmitt, and G. W. Littlecott, *Chem. Comm.*, 1969, 613.

RESULTS AND DISCUSSION

Reactions with Carbon Monoxide.—When carbon monoxide is passed through a suspension of $Pt(OCOCF_3)_2(PPh_3)_2$ in methanol an orange solution is obtained from which white crystals of trifluoroacetato(methoxycarbonyl)bis(triphenylphosphine)platinum(II), $Pt(OCOCF_3)(COOMe)(PPh_3)_2$, slowly deposit on standing. The i.r. spectrum of the complex exhibits C=O stretching frequencies which may be assigned to unidentate trifluoroacetate and methoxycarbonyl ligands, and the complex is further characterised by its reaction with lithium chloride to give $PtCl(COOMe)(PPh_3)_2$.[3] A similar ethoxycarbonyl complex is formed in ethanol as solvent; analogous products may be obtained using $Pt(OCOCH_3)_2(PPh_3)_2$.

The formation of these platinum alkoxycarbonyl products could be rationalised in terms of nucleophilic attack of the alcohol or alkoxide on a platinum carbonyl species.[3-5] Here, however, we favour the formation of an alkoxide intermediate, $Pt(carboxylate)(OR)(PPh_3)_2$, since similar intermediates are almost certainly involved in the reactions of olefins and acetylenes described later. Once formed, these alkoxide complexes can then react with carbon monoxide to give the observed products. In general platinum(II) alkoxide complexes are unstable and readily generate platinum hydride complexes [6] and it is noteworthy that in our studies the yields of the alkoxycarbonylplatinum complexes are only *ca.* 40%. Attempts to characterise other platinum complexes present have not been successful. Some stable platinum(II) alkoxide complexes are known, *e.g.* *trans*-$Pt(OEt)(GePh_3)(PEt_3)_2$ [7] but in these derivatives the high *trans*-influence of the triphenylgermyl ligand stabilises the Pt–OEt bond.[8]

Replacement of triphenylphosphine in the complex, $Pt(OCOCF_3)_2(PPh_3)_2$ by the more basic phosphine, PMe_2Ph, greatly reduces the reactivity of the system towards carbon monoxide. Thus $Pt(OCOCF_3)_2(PMe_2Ph)_2$ in alcoholic media gave no alkoxylcarbonyl complexes with carbon monoxide even under 100 atm. pressure. From the resulting brown solutions only starting material could be obtained. In this context it is noteworthy that *trans*-$[PtCl(CO)(PEt_3)_2][BF_4]$ gives an unstable methoxycarbonyl complex on treatment with methanol whereas the triphenylphosphine complex readily forms $PtCl(COOMe)(PPh_3)_2$.[3]

Alkoxycarbonyl complexes are probably involved in certain palladium(II) catalysed carbonylation reactions of olefins in the presence of alcohols [9] and also in the carbonylation of piperidine in the presence of methanolic copper(II) acetate.[10]

Reactions with Sulphur Dioxide.—Passage of sulphur dioxide through a methanolic solution of $Pt(OCOCH_3)_2(PPh_3)_2$ at room temperature produces pale pink crystals of the complex, $Pt(SO_3CH_3)_2(PPh_3)_2$. The i.r. spectrum of the complex contains no bands characteristic of an acetate group in contrast to the products formed with carbon monoxide. However, there are two bands at 1270 and 1100 cm^{-1} which may be assigned to $\nu_{asym}(SO_2)$ and $\nu_{sym}(SO_2)$ respectively which are some 100 cm^{-1} lower than those quoted for covalent sulphonates.[11] In addition to these two bands there is a third absorption at 990 cm^{-1} which may be assigned to ν(S–O) and we therefore formulate the complex as bis(methylsulphonato)bis(triphenylphosphine)platinum(II), $Pt(SO_2OMe)_2(PPh_3)_2$ with two Pt–S bands. A band at 306 cm^{-1} may tentatively be assigned to ν(Pt–S). A similar insertion of sulphur dioxide into a metal–oxygen bond has recently been reported for palladium(II).[12] Treatment of $Pt(OCOCF_3)_2(PPh_3)_2$ with sulphur dioxide in methanol gives only unchanged starting material.

Reactions with Acetylenes.—When diphenylacetylene and $Pt(OCOCF_3)_2(PPh_3)_2$ are refluxed together in methanol an almost quantitative yield of the alkenyl complex, $Pt(OCOCF_3)(CPh{=}CHPh)(PPh_3)_2$, (I) may be isolated. There is no evidence for the formation of a product containing the group, Pt–CPh=C(OMe)Ph, as might have been expected on the basis of the reactions described with carbon monoxide. The i.r. spectrum of (I) exhibits bands typical of a unidentate trifluoroacetate ligand and a weak band at 1574 cm^{-1} may be assigned to a C=C stretching frequency. Further confirmation for the presence of the alkenyl ligand, –CPh=CHPh, is provided by the reaction of the complex with trifluoroacetic acid which gives *trans*-stilbene and $Pt(OCOCF_3)_2(PPh_3)_2$. The i.r. spectrum and melting point of the alkenyl complex, (I), are slightly different to that obtained from $Pt(PhC{\equiv}CPh)(PPh_3)_2$ and trifluoroacetic acid [1,13] which has been shown to have the structure *trans*-$Pt(OCOCF_3)$(*cis*-CPh=CHPh)$(PPh_3)_2$, (II).[13] It therefore seems possible that in complex (I) there may be a different geometry either about the platinum or double bond or both. The observation that trifluoroacetic acid and (I) give *trans*-stilbene gives no information concerning the geometry of the alkenyl ligand since (II) similarly gives *trans*-stilbene.[13]

Analysis of the gaseous products formed in the preparation of (I) from $Pt(OCOCH_3)_2(PPh_3)_2$ reveals that there is some oxidation of the solvent methanol to formaldehyde. It therefore appears that in this instance the complex $Pt(OCOCF_3)(OMe)(PPh_3)_2$ generates a platinum hydride species, possibly $Pt(OCOCF_3)(H)(PPh_3)_2$, *via* a

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hydride shift mechanism[6] which subsequently reacts with diphenylacetylene to give (I). Further evidence for the hydride shift mechanism is provided by the observation that in CD_3OD as solvent, the deuterium substituted derivative, $Pt(OCOCF_3)(CPh{=}CDPh)(PPh_3)_2$, can be isolated. In CH_3OD only (I) is obtained.

The reaction between hexafluorobut-2-yne and $Pt(OCOCF_3)_2(PPh_3)_2$ in methanol at 70° is slightly different since in addition to the alkenyl complex, $Pt(OCOCF_3)(C{\cdot}CF_3{=}CHCF_3)(PPh_3)_2$, (III), some of the zerovalent complex, $Pt(CF_3C{\equiv}CCF_3)(PPh_3)_2$, is also formed. This reaction can again be rationalised in terms of an intermediate $Pt(OCOCF_3)(H)(CF_3C{\equiv}CCF_3)(PPh_3)_2$ which can either give the alkenyl complex (III) or lose trifluoroacetic acid under the reaction conditions to give $Pt(CF_3C{\equiv}CCF_3)(PPh_3)_2$. The product (III) is identical to the complex obtained from trifluoroacetic acid and $Pt(CF_3C{\equiv}CCF_3)(PPh_3)_2$.[14]

In contrast to the reaction of diphenylacetylene with $Pt(OCOCF_3)_2(PPh_3)_2$ in methanol, diphenylacetylene reacts with $Pt(OCOCH_3)_2(PPh_3)_2$ to give a 50% yield of $Pt(PhC{\equiv}CPh)(PPh_3)_2$. The zerovalent complex is also isolated in ethanol and propanol as solvents and again some oxidation of the solvent to an aldehyde takes place. No alkenyl complexes can be isolated from these reactions and here the elimination of acetic acid from the postulated intermediate, $Pt(OCOCH_3)(H)(PhC{\equiv}CPh)(PPh_3)_2$, appears to be the preferred step. In this context it is also noteworthy that acetic acid does not react with $Pt(PhC{\equiv}CPh)(PPh_3)_2$ to give an alkenyl complex. Hydride intermediates are also involved in the formation of $Pt[C_2(CN)_4](PEt_3)_2$ from tetracyanoethylene and $PtClH(PEt_3)_2$,[15] however, the reactions of tetracyanoethylene with methanolic solutions of $Pt(OCOCH_3)_2(PPh_3)_2$ and $Pt(OCOCF_3)_2(PPh_3)_2$ give only $Pt(CN)_2(PPh_3)_2$.

Melting points, microanalytical and molecular weight data

Compound	Colour	M.p. [a]	Found C	Found H	Found F	Found M [b]	Required C	Required H	Required F	Required M
$Pt(OCOCF_3)_2(PMe_2Ph)_2$	White	120—122	34·4	3·15	16·3	690	34·4	3·1	16·4	697
$Pt(OCOCF_3)(COOCH_3)(PPh_3)_2$	White	188—195	54·0	3·85	6·5	986	53·9	3·7	6·4	892
$Pt(OCOCF_3)(COOC_2H_5)(PPh_3)_2$	White	185—187	54·5	3·85	8·1	925	54·4	3·9	7·3	906
$Pt(OCOCH_3)(COOCH_3)(PPh_3)_2$	White	224—227	56·4	4·15		830	57·4	4·3		838
$Pt(OCOCF_3)(CPh{=}CHPh)(PPh_3)_2$	White	218—221	61·8	4·0	5·7	1011	61·7	4·1	5·6	1012
$Pt(SO_2OMe)_2(PPh_3)_2$ [c]	Pale pink	183—185	49·9	4·0		*d*	49·1	3·9		

[a] With decomposition. [b] Determined osmometrically in $CHCl_3$. [c] S = 7·0%, calc. 6·9%. [d] Too insoluble to be determined.

Reactions with Olefins.—Treatment of methanolic solutions of both $Pt(OCOCH_3)_2(PPh_3)_2$ and $Pt(OCOCF_3)_2(PPh_3)_2$ with ethylene at 70° in a sealed tube give dark red solutions, but as yet no pure complexes have been isolated. However, tetrachloroethylene and $Pt(OCOCF_3)_2(PPh_3)_2$ react in methanol as solvent at 80° to give a small amount of the vinyl, *trans*-$PtCl(CCl{=}CCl_2)(PPh_3)_2$ together with another platinum complex which we have not been able to completely identify and which is under further investigation.

Treatment of $Pt(OCOCH_3)_2(PPh_3)_2$ with tetrachloroethylene in refluxing methanol or ethanol gives a mixture of *trans*-$PtCl(CCl{=}CCl_2)(PPh_3)_2$ and *cis*-$PtCl_2(PPh_3)_2$.

The chloro-vinyl complexes isolated from the above reactions are probably formed *via* the zerovalent complex, $Pt(C_2Cl_4)(PPh_3)_2$, which is known to give a vinyl in hydroxylic solvents.[16] Some evidence for the formation of an olefin complex is provided by the isolation of $Pt(C_2F_4)(PPh_3)_2$ from the reactions of tetrafluoroethylene with $Pt(OCOCH_3)_2(PPh_3)_2$ and $Pt(OCOCF_3)_2(PPh_3)_2$ in methanol. However, in addition to $Pt(C_2F_4)(PPh_3)_2$ both reactions lead to an unidentified platinum complex which did not give consistent analytical results. These zerovalent olefin complexes are presumably formed *via* an analogous mechanism to that suggested for the corresponding acetylene complexes.

EXPERIMENTAL

I.r. spectra of Nujol mulls were recorded on a Perkin-Elmer 225 spectrophotometer. ^1H N.m.r. were measured at 60 MHz on a Varian T60 spectrometer and ^{19}F n.m.r. were measured at 56·4 MHz on a Varian DA60 spectrometer. M.p.s were recorded on a Reichart hot stage apparatus and are uncorrected. Analytical data are given in the Table. Benzene and ether were dried over sodium before use. AnalaR methanol and absolute ethanol were always used. The complexes $Pt(OCOCH_3)_2(PPh_3)_2$,[17] $Pt(OCOCF_3)_2(PPh_3)_2$,[17] and $Pt(OCOCF_3)_2(PMe_2Ph)_2$ were prepared by refluxing the appropriate dichlorobis(phosphine)-platinum(II) compound with the appropriate silver carboxylate in methylene chloride for 8 h. The ^1H n.m.r. spectrum of $Pt(OCOCF_3)_2(PMe_2Ph)_2$ consisted of an apparent triplet, $J(P-H) = 12$ Hz, centred at τ 8·43 with ^{195}Pt satellites, $J(Pt-H) = 36$ Hz. This spectrum is consistent with a *trans*-configuration.[18]

Preparation of $Pt(OCOCF_3)(COOCH_3)(PPh_3)_2$.—Carbon monoxide was passed through a stirred suspension of $Pt(OCOCF_3)_2(PPh_3)_2$ (0·5 g) in methanol (25 ml) for 30 min at room temperature. The resultant orange solution was filtered and the filtrate was allowed to stand overnight. The crystalline product which formed was filtered, washed with cold methanol, and dried *in vacuo* (yield 0·2 g, 47%), $\nu(CO_2)$ 1710s, 1692s, and 1408 cm^{-1}, $\nu(CO)$, 1652 cm^{-1}.

The complexes $Pt(OCOCF_3)(COOC_2H_5)(PPh_3)_2$ and Pt-

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$(OCOCH_3)(COOCH_3)(PPh_3)_2$ were similarly prepared. $Pt(OCOCF_3)(COOC_2H_5)(PPh_3)_2$ (yield 31%) $\nu(CO_2)$, 1708m, 1695s, and 1406m cm^{-1}; ν(CO), 1645s cm^{-1}. $Pt(OCOCH_3)(COOCH_3)(PPh_3)_2$ (yield 40%) $\nu(CO_2)$, 1620s and 1312m cm^{-1}; ν(CO), 1645s cm^{-1}.

Preparation of the Complexes $PtCl(COOR)(PPh_3)_2$.—A solution of the complex, $Pt(OCOR^1)(COOR)(PPh_3)_2$, ($R^1 = CF_3$, $R = CH_3$ or C_2H_5; $R^1 = CH_3$, $R = CH_3$), (0·5 g) and excess lithium chloride was refluxed in a 1 : 1 mixture of methylene chloride–methanol (40 ml) for 2 h. The solution was then evaporated to dryness. The residue was extracted with water and then recrystallised from methylene chloride–methanol. The products $PtCl(COOR)(PPh_3)_2$ (yield 100%) were identified by their m.p.s and i.r. spectra.[3]

Reactions of $Pt(OCOCF_3)_2(PPh_3)_2$.—(*a*) *With diphenylacetylene.* Diphenylacetylene (0·1 g) and $Pt(OCOCF_3)_2(PPh_3)_2$ (0·5 g) were refluxed in methanol (25 ml) for 8 h. The pale orange crystals which formed were washed with cold methanol and recrystallised from methanol–methylene chloride to give $Pt(OCOCF_3)(PhC{=}CHPh)(PPh_3)_2$ (0·5 g, 92%). The same complex was formed in ethanol (yield 77%) and in n-propanol (yield 56%). Passage of a stream of nitrogen through the reaction mixture and then through methanolic 2,4-dinitrophenylhydrazine sulphate (2,4-dinitrophenylhydrazine 0·45 g, sulphuric acid 0·5 g, methanol 30 ml, and water 3 ml) gave formaldehyde 2,4-dinitrophenylhydrazone. The product was isolated and recrystallised from ethanol, m.p. 166°. Similarly when ethanol and n-propanol were used as solvents, acetaldehyde 2,4-dinitrophenylhydrazone, m.p. 168°, and propionaldehyde 2,4-dinitrophenylhydrazone, m.p. 154°, were isolated respectively. In CD_3OD as solvent, the deuterium complex, $Pt(OCOCF_3)(PhC{=}CDPh)(PPh_3)_2$ was formed, ν(C–D), 2240 cm^{-1}. I.r. data for $Pt(OCOCF_3)(CPh{=}CHPh)(PPh_3)_2$ ν(OCO), 1695s and 1415m cm^{-1}; ν(C=C), 1574w cm^{-1}.

(*b*) *With hexafluorobut-2-yne.* $Pt(OCOCF_3)_2(PPh_3)_2$ (0·5 g) and excess of hexafluorobut-2-yne were heated in a sealed tube at 70° for 2 h. The tube was then cooled in liquid nitrogen, opened, and warmed to room temperature. The solution was filtered and evaporated to dryness to give an oil. The oil was dissolved in a minimum of methylene chloride and the solution was chromatographed on an alumina–hexane column to give $Pt(CF_3C{\equiv}CCF_3)(PPh_3)_2$ [19] (0·14 g, 30%) and *trans*-$Pt(OCOCF_3)(CF_3C{=}CHCF_3)(PPh_3)_2$ [14] (0·15 g, 30%). Both complexes were identified by their m.p.s, n.m.r. and i.r. spectra.

(*c*) *With tetrachloroethylene.* Redistilled tetrachloroethylene (1 ml) and $Pt(OCOCF_3)_2(PPh_3)_2$ (0·5 g) in methanol (20 ml) were heated in a sealed glass tube at 80° for 8 h. The resulting yellow solution when cooled to room temperature deposited white crystals, which were filtered off, washed with methanol, and dried *in vacuo* to give *trans*-$PtCl(CCl{=}CCl_2)(PPh_3)_2$ (0·15 g, 32%) identified by its m.p. and i.r. spectrum.[16] The yellow filtrate was evaporated to dryness and the residue was recrystallised from methylene chloride–diethyl ether to give yellow crystals of an unidentified platinum complex, m.p. 163—164° decomp. (0·13 g, 30%). Found: C, 56·4; H, 4·0; F, 4·2; P, 7·55, *M* ($CHCl_3$), 1640 ν_{asym} (CO_2) 1690 cm^{-1}.

(*d*) *With trichloroethylene.* As in (*c*) but with trichloroethylene gave *cis*-$PtCl_2(PPh_3)_2$ (100%) identified by its m.p. (285° decomp.) and i.r. spectrum.[16]

(*e*) *With tetrafluoroethylene.* Excess of tetrafluoroethylene and $Pt(OCOCF_3)_2(PPh_3)_2$ (0·5 g) were heated at 100° in a sealed glass tube for 8 h. The tube was cooled and opened and the colourless crystals deposited in the orange solution were filtered, washed with methanol, and dried. The product was identified by its m.p. and i.r. spectrum as $Pt(C_2F_4)(PPh_3)_2$ (0·2 g, 42%).[20] The orange filtrate on addition of diethyl ether gave an orange solid (0·3 g) but no consistent analytical results could be obtained.

Reactions of $Pt(OCOCH_3)_2(PPh_3)_2$.—(*a*) *With diphenylacetylene.* Diphenylacetylene (0·1 g) and $Pt(OCOCH_3)_2(PPh_3)_2$ (0·5 g) were refluxed in methanol (25 ml) for 8 h. The yellow crystals which formed were washed with cold methanol, dried *in vacuo*, and identified as $Pt(PhC{\equiv}CPh)(PPh_3)_2$ (0·25 g, 51%) by the m.p. and i.r. spectrum.[21] Identical yields were obtained in ethanol and n-propanol.

(*b*) *With hexafluorobut-2-yne.* The reaction was carried out as described in (*b*) above but no pure products could be isolated.

(*c*) *With tetrachloroethylene.* As in (*c*) above but using $Pt(OCOCH_3)_2(PPh_3)_2$ gave a mixture of *cis*-$PtCl_2(PPh_3)_2$ and *trans*-$PtCl(CCl{=}CCl_2)(PPh_3)_2$ identified by their m.p.s and i.r. spectra.[16]

(*d*) *With trichloroethylene.* As in (*d*) above to give *cis*-$PtCl_2(PPh_3)_2$ (100%).

(*e*) *With tetrafluoroethylene.* As in (*e*) above to give $Pt(C_2F_4)(PPh_3)_2$ (8%) and an unidentified orange solid.

Reactions of $Pt(OCOCF_3)_2(PPh_3)_2$ *and* $Pt(OCOCH_3)_2(PPh_3)_2$ *with Tetracyanoethylene.*—The complexes (0·3 g) and tetracyanoethylene in methanol (30 ml) were refluxed for 8 h. The white crystalline product was isolated, washed with methanol, and dried *in vacuo*. In both cases this was identified as $Pt(CN)_2(PPh_3)_2$ (100% yield) by its m.p. and i.r. spectrum.[22]

Reaction of $Pt(OCOCH_3)_2(PPh_3)_2$ *with Sulphur Dioxide.*—Dry sulphur dioxide was passed through a stirred suspension of the complex (0·3 g) in methanol (30 ml) for 20 min. The solution was filtered and on standing for 1 h the pale pink crystals of $Pt(SO_2OMe)_2(PPh_3)_2$ were deposited. The product was filtered off, washed with methanol and dried *in vacuo* (Yield, 80%).

Reaction of $Pt(OCOCF_3)(CPh{=}CHPh)(PPh_3)_2$ *with Trifluoroacetic Acid.*—Trifluoroacetic acid (1 g) was added to a solution of $Pt(OCOCF_3)(CPh{=}CHPh)(PPh_3)_2$ in benzene (30 ml). The solution was warmed for 1 min and then evaporated to dryness. Recrystallisation of the residue from methylene chloride–ethanol gave white crystals of $Pt(OCOCF_3)_2(PPh_3)_2$ (Yield 80%).

Evaporation of the remaining solution to dryness and recrystallisation of the residue from aqueous ethanol afforded *trans*-stilbene (0·05 g). M.p. 120—122°, lit. 124°.

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