Cleavage of α-Nitroketones by Platinum(II) and Platinum(0) and Formation of Platinum(II) Complexes Containing Fulminato- and Carboxylato-groups[1]

By **Saverio Alessandrini**, **Ines Collamati**, and **Claudio Ercolani**,* C.N.R. Laboratory, Istituto di Chimica Generale ed Inorganica, Università di Roma, Roma, Italy

Reaction of the complex $[(PPh_3)_2PtCl_2]$ with Tl^I salts of 2-nitroacetophenone ($PhCOCH_2NO_2$), nitroacetone ($MeCOCH_2NO_2$), and 1-nitrobutan-2-one ($MeCH_2COCH_2NO_2$) (molar ratio 1:1 to 1:2) in benzene occurs with breaking of the carbon–carbon bond internal to the α-nitroketonic group, the fragments produced then co-ordinating to Pt^{II} as fulminato- and carboxylato-groups. The complexes isolated have formulae $[(PPh_3)_2PtCl(CNO)]$, $[(PPh_3)_2Pt(OCOR)(CNO)]$, and $[(PPh_3)_2PtCl(OCOR)]$ (R = Me, Et, or Ph). Reaction of the complex $[Pt(PPh_3)_4]$ and 2-nitroacetophenone in benzene–ethanol–water (4:1:1) has also been studied and the complexes $[(PPh_3)_2Pt(OCOPh)(CNO)]$ and $[(PPh_3)_2Pt(CNO)_2]$ isolated. I.r. spectra indicate that isomerization of the fulminato-groups to isocyanato-groups occurs.

IT has been shown that 2-nitroacetophenone and other α-nitroketones usually behave as bidentate *O*-donors with bivalent[2] and trivalent[3] transition- and non-transition-metal ions, and the similarity of the chelating moiety in α-nitroketonates (Ia) to that in β-diketonates (Ib) discussed. It is also known that, mainly with Pt^{II}, β-diketones provide clear evidence of their versatility as ligands and show a tendency to bind to this metal ion in several, distinguishable, ways.[4] As a continuation of our investigation on the complexing properties of α-nitroketones we have examined the formation of Pt^{II} complexes by the reaction of dichlorobis(triphenylphosphine)platinum(II) with Tl^I salts of 2-nitroacetophenone, [Tl(nap)], nitroacetone, [Tl(na)], and 1-nitrobutan-2-one, [Tl(nbo)], and of tetrakis(triphenylphosphine)platinum(0) with 2-nitroacetophenone. Although these reactions did not lead to platinum(II) α-nitroketonato-complexes, they nevertheless showed unusual paths and final products, the most important features of which are given and discussed here. Unsuccessful attempts were made to obtain Pt^{II} complexes by the reaction of 2-nitroacetophenone with $K_2[PtCl_4]$,

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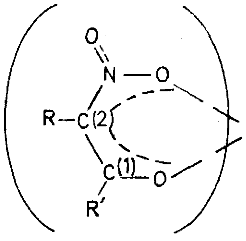
[1] Presented in part at the 'Quinto Convegno Nazionale di Chimica Inorganica,' Taormina, Italy, 25—29th September, 1972.

[2] D. Attanasio, I. Collamati, and C. Ercolani, *J.C.S. Dalton*, 1972, 772 and references therein.

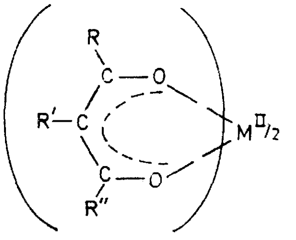
[3] R. Astolfi, I. Collamati, and C. Ercolani, *J.C.S. Dalton*, 1973, 2238.

[4] G. Hulley, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc.* (*A*), 1970, 1732 and references therein.

under experimental conditions ordinarily leading to formation of β-diketonates containing either oxygen- or carbon-bonded β-diketonato-groups.



(Ia)



(Ib)

RESULTS AND DISCUSSION

Reaction of $[(PPh_3)_2PtCl_2]$ *with* Tl *α-Nitroketonates.*—The reaction of $[(PPh_3)_2PtCl_2]$ with [Tl(nap)] has been studied in benzene using molar ratios of reactants (in the order given) varying from 1 : 1 to 1 : 2 and leads to formation of the complexes $[(PPh_3)_2PtCl(CNO)]$, $[(PPh_3)_2Pt(OCOPh)(CNO)]$, and $[(PPh_3)_2PtCl(OCOPh)]$. The complex $[(PPh_3)_2PtCl(CNO)]$ is also formed in the reaction between $[(PPh_3)_2PtCl_2]$ and [Tl(na)] (molar ratio 1 : 1 to 1 : 2) together with $[(PPh_3)_2Pt(OCOMe)(CNO)]$ and $[(PPh_3)_2PtCl(OCOMe)]$. Similarly, the reaction between $[(PPh_3)_2PtCl_2]$ and [Tl(nbo)] (molar ratio 1 : 1 to 1 : 2) yields $[(PPh_3)_2PtCl(CNO)]$, $[(PPh_3)_2Pt(OCOCH_2Me)(CNO)]$, and $[(PPh_3)_2PtCl(OCOCH_2Me)]$ (Table).

Elemental analyses (%) and some properties of the Pt^{II} complexes

Complex	M.p.	Analyses										I.r. spectra/cm^{-1}		
		Calc.					Found							
	t/(°C)	C	H	N	P	Cl	C	H	N	P	Cl	$\nu_{asym}(CO_2)$	$\nu_{sym}(CO_2)$	Δ/ cm^{-1}
$[(PPh_3)_2PtCl(CNO)]$	245	55·75	3·75	1·75	7·8	4·45	55·65	3·9	1·9	7·7	3·8			
$[(PPh_3)_2Pt(OCOPh)(CNO)]$	205	59·85	3·95	1·6	7·05		59·9	4·1	1·9	7·5		1 640, 1 620, 1 575	1 335	285
$[(PPh_3)_2Pt(OCOMe)(CNO)]$	225	57·05	4·0	1·7			56·9	4·1	1·65			1 650, 1 625	1 365, 1 315	285
$[(PPh_3)_2Pt(OCOCH_2Me)(CNO)]$	210	57·55	4·2	1·7			57·4	4·15	1·75			1 630	1 345, 1 320	285
$[(PPh_3)_2Pt(OCOCH_2Me)(CNO)]$,-$CHCl_3$	210	51·6	3·75	1·45		11·15	51·5	3·85	1·5		10·8	1 625	1 365, 1 260	260
$[(PPh_3)_2PtCl(OCOPh)]$	212	58·95	4·05			4·1	58·9	4·3			4·8	1 635, 1 620, 1 575	1 345	290
$[(PPh_3)_2PtCl(OCOMe)]$	204	56·05	4·05			4·35	56·1	4·15			4·7	1 635, 1 610	1 365, 1 315	270
$[(PPh_3)_2PtCl(OCOCH_2Me)]$	202	56·55	4·25			4·3	56·7	4·3			4·9	1 640	1 375, 1 275	265
$[(PPh_3)_2Pt(CNO)_2]$		56·8	3·75	3·5			56·35	3·9	3·7					

The complex $[(PPh_3)_2PtCl(CNO)]$, formed in all the above reactions, easily retains solvent molecules upon crystallization, forming 1 : 1 adducts with chloroform, and probably also with dichloromethane, benzene, and acetone. Because of the presence of the triphenylphosphine groups, the i.r. spectrum of $[(PPh_3)_2PtCl(CNO)]$ closely resembles that of the complex $[(PPh_3)_2PtCl_2]$ in the region 4 000—250 cm^{-1}, apart from an intense absorption at 2 200 cm^{-1}, accompanied by two very weak absorptions at *ca.* 2 300 and 2 250 cm^{-1}, and another intense absorption, centred at 1 180 cm^{-1}, close to partially overlapping absorptions of weak-to-medium intensity due to the triphenylphosphine groups [Figure, spectrum (*a*)]. In Figure (*b*) the i.r. spectrum of $[(PPh_3)_2PtCl(CNO)]$ treated in different ways during purification and then separated as the chloroform adduct is given. The latter complex was desolvated by heating *in vacuo* at 100 °C for 1 h and the i.r. spectrum of the unsolvated form so obtained [having the same analysis as, and isomorphous with, the form in Figure (*a*)] recorded [(*c*)]. I.r. spectral variations on going from the form (*a*) of $[(PPh_3)_2PtCl(CNO)]$ to its adduct (*b*) mainly consist of an increase in intensity of the absorption band at *ca.* 2 250 cm^{-1}. In the i.r. spectrum of the unsolvated material (*c*) the 2 250 cm^{-1} band is also present. Furthermore, it was observed that, for an assumed constant intensity of all the other absorptions in the i.r. spectra of (*b*) and (*c*), the greater intensity of the 2 250 cm^{-1} band corresponds to weaker relative intensity of the bands at 2 200 and 1 180 cm^{-1}.

It seems reasonable to associate the 2 300, 2 200, and 1 180 cm^{-1} bands with the presence in $[(PPh_3)_2PtCl(CNO)]$ of a CNO group *C*-bonded to Pt^{II}, *i.e.* as a fulminato-group (Pt–C–N–O). It has been established[5] that in the i.r. spectra of a series of M^{II} (including Pt^{II}) and M^{IV} fulminato-complexes, 2ν(N–O) and ν(C–N) are found in the range 2 300—2 150 cm^{-1}, whereas ν(N–O) always falls in the region 1 200—1 150 cm^{-1}. In the light of this, the intense 2 200 and 1 180 cm^{-1} bands are assigned as ν(C–N) and ν(N–O) respectively, and the weak band at 2 300 cm^{-1} as 2ν(N–O).

In order to explain the presence of the 2 250 cm^{-1} band account must be taken of the fact that a cyanate group, instead of a fulminato-group, would also, of course, be in keeping with the empirical formula of $[(PPh_3)_2PtCl(CNO)]$. Platinum(II) complexes containing the cyanate group are known to occur predominantly in the form of isocyanato-[6] (Pt–N–C–O), rather than

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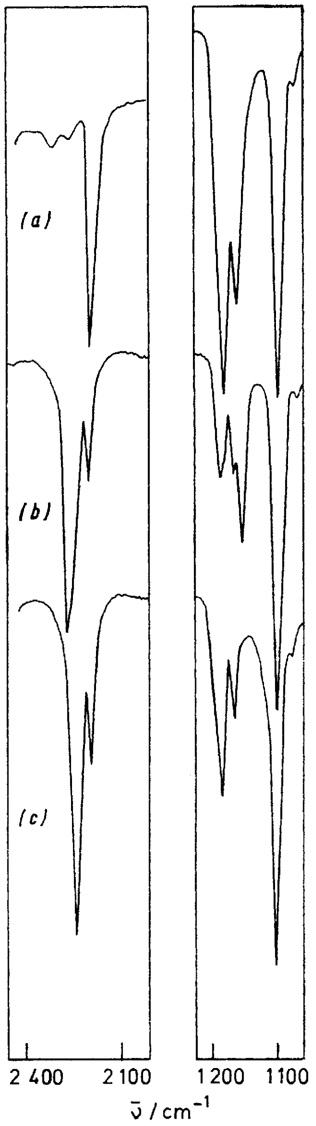
[5] W. Beck and E. Schuierer, *Chem. Ber.*, 1965, **98**, 298; W. Beck, P. Swoboda, K. Feldl, and E. Schuierer, *ibid.*, 1970, **103**, 3591.

[6] A. H. Norbury and A. I. P. Sinha, *J. Chem. Soc.* (*A*), 1968, 1598.

cyanato-complexes (Pt–O–C–N). Now, for isocyanato-co-ordination to Pt^{II} in complexes $[L_2'Pt(NCO)_2]$ (L′ = neutral N-, P-, As-, or Sb-donor), ν(C–N) is located in the region 2 300—2 150 cm^{-1}. Consequently, it seems reasonable to assign the 2 250 cm^{-1} band of $[(PPh_3)_2PtCl(CNO)]$ as ν(C–N) in Pt–N–C–O bonds. This can be explained by assuming that $[(PPh_3)_2PtCl(CNO)]$, initially obtained almost exclusively as a fulminato-complex, undergoes isomerization to the corresponding isocyanate, *i.e.* $[(PPh_3)_2PtCl(CNO)] \longrightarrow [(PPh_3)_2PtCl(NCO)]$. The isomorphism displayed by forms (*a*) and (*c*) (Figure) of the complex $[(PPh_3)_2PtCl(CNO)]$ indicates that such isomerization does not result in a significant change of the molecular packing in the crystal lattice.



I.r. spectra of the complex $[(PPh_3)_2PtCl(CNO)]$ (*a*) and (*c*) and of its chloroform adduct (*b*)

The above discussion of the i.r. spectra of $[(PPh_3)_2PtCl(CNO)]$, used to establish the presence and mode of co-ordination of the CNO group to Pt^{II}, can be taken as valid in its main features for all the complexes containing the CNO group reported in the Table. In all cases i.r. spectra show absorptions involving the CNO group occurring at *ca.* 2 300 [2ν(N–O)], 2 200 [ν(C–N)], and *ca.* 1 180—1 160 cm^{-1} [ν(N–O)] for Pt–CNO bonds, and at *ca.* 2 250 cm^{-1} [ν(C–N)] for Pt–NCO bonds. The isomerization of fulminato- to isocyanato-groups, occurring to a variable extent for all the complexes containing the CNO group, normally takes place in solution during preparation, purification, and successive handling of the complexes and depends on the nature of the solvent used, time, temperature, *etc.*

I.r. absorptions associated with the CO_2 group in the carboxylato-complexes are given in the Table. The intense absorption at 1 650—1 620 cm^{-1}, accompanied by lower-intensity bands, is assigned as $\nu_{asym}(CO_2)$. Assignment of $\nu_{sym}(CO_2)$ is sure for the benzoato-complexes (band at *ca.* 1 340 cm^{-1}), but not for the acetato- and propionato-complexes, because of the presence in the 1 375—1 250 cm^{-1} region of absorptions due to $\rho(CH_3)$ modes. Assuming in all cases that the higher energy band at *ca.* 1 375—1 345 cm^{-1} is $\nu_{sym}(CO_2)$, it is found that the energy separation, $\nu_{asym}(CO_2) - \nu_{sym}(CO_2)$ (Δ), is always within 260—290 cm^{-1} (Table). Such Δ values are large enough to suggest that the CO_2 group is acting as a unidentate ligand,[7] rather than as a bidentate chelate or bridge. Taking the unidentate nature of the other ligands bound to Pt^{II} into account, it is concluded that all the carboxylato-complexes are monomeric four-co-ordinate species. In keeping with this, a molecular weight corresponding to that of the monomeric form has been found for the complex $[(PPh_3)_2Pt(OCOPh)(CNO)]$ in $CHCl_3$ (see Experimental section), in which solvent it shows an i.r. spectrum identical to that of the solid.

The occurrence of the fulminato-group in the present complexes indicates that in the reaction between the complex $[(PPh_3)_2PtCl_2]$ and Tl α-nitroketonates the α-nitroketonic group undergoes cleavage of the C(1)–C(2) bond (Ia). Of the resulting two fragments, that carrying the NO_2 group is transformed into a CNO group co-ordinated to Pt^{II}. The first step of the reaction probably involves formation of an unstable intermediate containing the α-nitroketonic group *C*-bonded to Pt^{II} through C(2), $[(PPh_3)_2PtCl(\underset{NO_2}{\underset{|}{C}}HCOPh)]$, which is then displaced, perhaps *via* an intra-ligand oxidation-reduction reaction, to give $[(PPh_3)_2PtCl(CNO)]$ and the carboxylic acid. This is supported by formation of the complexes $[(PPh_3)_2PtCl(OCOR)]$ and $[(PPh_3)_2Pt(OCOR)(CNO)]$ containing the carboxylato-group.

Of the complexes described, only for $[(PPh_3)_2PtCl(OCOR)]$ can any suggestion be made as to the *cis*-

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[7] 'Spectroscopic Properties of Inorganic and Organometallic Compounds,' vol. 1, Chem. Soc. Spec. Period. Rep., p. 201, and references therein.

or *trans*-structure probably present. These complexes are isomorphous with those prepared directly from *cis*-[$(PPh_3)_2PtCl_2$] and [Tl(OCOR)] or [Na(OCOR)] (see Experimental section). For a *cis*-structure it would be difficult to understand why the second chloride ligand is not substituted, given that it is in a *trans*-position with respect to PPh_3, which has a strong *trans*-effect. For a *trans*-structure, however, the chloride ligand would be stabilised by the OCOR group, having only a weak *trans*-effect, *trans* to it.

Reaction of [$Pt(PPh_3)_4$] *with 2-Nitroacetophenone*.—Reaction of the complex [$Pt(PPh_3)_4$] with 2-nitroacetophenone also occurs with breaking of the C(1)–C(2) bond internal to the α-nitroketonic group with formation of the complexes [$(PPh_3)_2$]Pt(OCOPh)(CNO)] and [$(PPh_3)_2Pt(CNO)_2$]. Similar reactions with nitroacetone and 1-nitrobutan-2-one could not be attempted because of the instability of these α-nitroketones under the experimental conditions in which the reaction with 2-nitroacetophenone proceeds.

The bis(fulminate) [$(PPh_3)_2Pt(CNO)_2$] has been re-prepared by us from [$Pt(PPh_3)_4$] and $MeNO_2$ using the literature procedure,[8] and the reaction product, as a chloroform adduct, compared to the complex [$(PPh_3)_2$-$Pt(CNO)_2$], given by the reaction in benzene–ethanol–water (4 : 1 : 1) of [$Pt(PPh_3)_4$] and 2-nitroacetophenone, also obtained as a chloroform adduct. *X*-Ray powder spectra show the two species to be isomorphous.

The i.r. spectrum of the chloroform adduct obtained from 2-nitroacetophenone shows a very intense absorption at 2 260 cm^{-1} indicative of the presence of the CNO group preponderantly bound as an isocyanato-group. The *fulminato*-group is also present, however, as established by relatively less-intense absorptions at 2 190 and 1 160 cm^{-1}. The i.r. spectrum of the chloroform adduct prepared by us from $MeNO_2$ does not show significant differences from that given by Beck *et al.*,[8] apart from a band of weak intensity at 2 260 cm^{-1} ascribed to the presence of a small amount of the isocyanato-group. This band was apparently not present in the i.r. spectrum of the same product prepared by Beck *et al.*[8] It has been observed, however, that isomerization of the fulminate ⟶ isocyanate type also occurs for this complex when it is heated under reflux in benzene–ethanol–water (4 : 1 : 1). Therefore, the formation of larger amounts of the isocyanato-group in the complex [$(PPh_3)_2Pt(CNO)_2$] obtained from 2-nitroacetophenone is in keeping with the observed possibility of the isomerization occurring for the bis(fulminate) under the above specified conditions.

The reaction between the complex [$Pt(PPh_3)_4$] and 2-nitroacetophenone probably takes place by a mechanism somewhat different from that postulated for the reaction between [$(PPh_3)_2PtCl_2$] and Tl α-nitroketonates. As also suggested by Beck *et al.*[8] for the reaction of [$Pt(PPh_3)_4$] and $MeNO_2$, the formation of the complex [$(PPh_3)_2Pt(CNO)_2$] may reasonably be thought to occur through an unstable hydride intermediate formed by attachment to the metal atom of the α-nitroketonato-groups through C(2), followed by elimination of benzoic acid and molecular hydrogen. Isomerization of the fulminato- to the isocyanato-group presumably takes place in a second step in a similar manner to that proposed for isomerization of [$(PPh_3)_2PtCl(CNO)$] and [$(PPh_3)_2Pt(OCOR)(CNO)$].

EXPERIMENTAL

2-Nitroacetophenone was prepared as described elsewhere.[9] Nitroacetone and 1-nitrobutan-2-one were prepared following the procedure given by Hurd and Nilson.[10] The Tl^I salts of 2-nitroacetophenone and nitroacetone have already been reported,[3] that of 1-nitrobutan-2-one was prepared by adding the α-nitroketone (234 mg, 0·002 mol) to a warm (40 °C) solution of [Tl(OCOMe)] (526 mg, 0·002 mol) in absolute ethanol (10 cm^3). A yellow crystalline precipitate of [Tl(nbo)] immediately formed (yield 60%) Found: C, 15·05; H, 1·9; N, 4·25. Calc. for $C_4H_6NO_3Tl$: C, 15·0; H, 1·85; N, 4·35%). The complex is unstable in air. In the dark it is stable for *ca.* 20 h at room temperature and for 2—3 days at *ca.* 0 °C. *cis*-Dichlorobis(triphenylphosphine)platinum(II) and tetrakis(triphenylphosphine)platinum(0) were prepared following the literature procedure.[11,12]

Reactions.—[$(PPh_3)_2PtCl_2$] *with* [Tl(nap)]. The reaction was carried out using molar ratios of the complexes [$(PPh_3)_2PtCl_2$] and [Tl(nap)] between 1 : 1 and 1 : 2. The following was a typical procedure (molar ratio 1 : 1·5).

A suspension of finely ground [$(PPh_3)_2PtCl_2$] (500 mg, 0·00063 mol) and [Tl(nap)] (350 mg, 0·00095 mol) in benzene (100 cm^3) was stirred for 48 h at room temperature. TlCl which formed, and excess of [Tl(nap)], were separated by filtration and the solution was concentrated to half-volume. Addition of hexane caused formation of a crystalline precipitate, which was separated from solution, washed with a few drops of acetone, and then added to chloroform. The insoluble solid residue was separated from the chloroform solution (A), and dissolved in boiling benzene. On cooling and subsequent evaporation of the solvent, the solid crystalline material was heated (100 °C) *in vacuo* to give pure [$(PPh_3)_2PtCl(CNO)$]. After addition of the appropriate amount of hexane to solution (A), white crystals of [$(PPh_3)_2Pt(OCOPh)(CNO)$] were formed and purified by crystallization from benzene. A molecular-weight measurement in $CHCl_3$ yielded a value of 890 (calc. 882). When the molar ratio of reactants was closer to 1 : 1, the complex [$(PPh_3)_2PtCl(OCOPh)$] was isolated as an additional product. When a few drops of water were added to the initial suspension of [$(PPh_3)_2$-$PtCl_2$] and [Tl(nap)] in benzene, the complex [$(PPh_3)_2$-Pt(OCOPh)(CNO)] was mainly formed, together with almost undetectable amounts of [$(PPh_3)_2PtCl(CNO)$].

The complex [$(PPh_3)_2PtCl(OCOPh)$] could also be prepared by direct synthesis from [$(PPh_3)_2PtCl_2$] and [Tl(OCOPh)] (molar ratio 1 : 1 to 1 : 2 with invariable results). The reactants were heated under reflux in

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[8] W. Beck, K. Schorpp, and F. Kern, *Angew. Chem.*, 1971, **83**, 43.

[9] C. Ercolani, I. Collamati, and G. Sartori, *Atti Accad. naz. Lincei, Rend. Classe Sci. fis. mat. nat.*, 1966, **40**, 558.

[10] C. D. Hurd and M. E. Nilson, *J. Org. Chem.*, 1955, **20**, 927.

[11] K. A. Jensen, *Z. anorg. Chem.*, 1936, **229**, 225.

[12] L. Malatesta and C. Cariello, *J. Chem. Soc.*, 1958, 2323.

$CHCl_3$–MeOH (1 : 1) for 30 min. The solution was filtered to separate TlCl, then evaporated to dryness and the solid residue crystallized from benzene. Isomorphism was established for the complex [$(PPh_3)_2$PtCl(OCOPh)] prepared as above and that obtained from [$(PPh_3)_2PtCl_2$] and [Tl(nap)].

The complex [$(PPh_3)_2$PtCl(CNO)] can be converted into [$(PPh_3)_2$Pt(OCOPh)(CNO)] as follows. A suspension of [$(PPh_3)_2$PtCl(CNO)] and [Tl(OCOPh)] (molar ratio 1 : 1) in $CHCl_3$–MeOH (1 : 1) was heated under reflux, with stirring, for *ca.* 2 h. After cooling, the solid material, consisting mainly of TlCl, was separated by filtration, washed with chloroform, and the washings added to the solution. This was evaporated to dryness and the solid residue recrystallized from chloroform–hexane. White crystals of [$(PPh_3)_2$Pt(OCOPh)(CNO)] were obtained.

The complex [$(PPh_3)_2$Pt(OCOPh)(CNO)] can be converted into [$(PPh_3)_2$PtCl(CNO)] as follows. The complex [$(PPh_3)_2$Pt(OCOPh)(CNO)] (*ca.* 100 mg) was added to a mixture of CH_2Cl_2 (5 cm^3), acetone (3 cm^3), and 6N-HCl (5—6 drops). The crystalline precipitate which slowly formed was recrystallized from benzene and identified as [$(PPh_3)_2$PtCl(CNO)]. The reaction mixture was evaporated and the presence of $PhCO_2H$ established in the solid residue.

[$(PPh_3)_2PtCl_2$] *with* [Tl(na)]. A suspension of the complex [$(PPh_3)_2PtCl_2$] (395 mg, 0·0005 mol) and [Tl(na)] (230 mg, 0·00075 mol) (molar ratio 1 : 1·5) in benzene (100 cm^3) was stirred for 48 h at room temperature. The solid material, separated by filtration from the solution (A), was treated with $CHCl_3$ which dissolves [$(PPh_3)_2$PtCl(OCOMe)] and leaves TlCl as a solid residue. The chloroform solution was evaporated to dryness, and the complex [$(PPh_3)_2$PtCl(OCOMe)] washed with cold benzene and then crystallized from hot benzene. The benzene solution (A) was evaporated to 1/3rd of its initial volume and then added to hexane [solution (B)]. The solid crystalline precipitate, which consists of [$(PPh_3)_2$Pt(OCOMe)(CNO)], was separated by filtration, washed with a small amount of cold benzene, and then crystallized from dichloromethane–acetone. Solution (B) was evaporated to dryness, and the solid residue washed with a small amount of ethanol. The undissolved material, recrystallized from chloroform–light petroleum, and then dried *in vacuo*, was found to be [$(PPh_3)_2$PtCl(CNO)]. With the above molar ratio of reactants the amounts of [$(PPh_3)_2$PtCl(OCOMe)] and [$(PPh_3)_2$Pt(OCOMe)(CNO)] formed were approximately the same. If the molar ratio was 1 : 1, the former complex is the major product. The reverse occurred with a 1 : 2 molar ratio.

The complex [$(PPh_3)_2$Pt(OCOMe)(CNO)] could also be obtained from [$(PPh_3)_2$PtCl(CNO)] in a way similar to that used for [$(PPh_3)_2$(OCOPh)(CNO)]. Crystallization was from benzene.

[$(PPh_3)_2PtCl_2$] *with* [Tl(nbo)]. The stability of [Tl(nbo)] in benzene was assessed as follows. The salt (160 mg, 0·0005 mol) was suspended in benzene (50 cm^3) and kept at room temperature, with stirring, for 48 h; the solvent was then evaporated and the solid residue recovered unchanged.

The complexes [$(PPh_3)_2PtCl_2$] (395 mg, 0·0005 mol) and [Tl(nbo)] (240 mg, 0·00075 mol) were suspended in benzene (100 cm^3), with stirring, in the dark for 48 h. TlCl which formed was separated by filtration and the solution evaporated to 1/3rd of its initial volume and then added to hexane. The precipitate which formed was isolated and added to a small amount of benzene {such as to dissolve most of the complex [$(PPh_3)_2$Pt($OCOCH_2Me$)(CNO)] and leave behind [$(PPh_3)_2$PtCl(CNO)]}. The complex [$(PPh_3)_2$Pt($OCOCH_2Me$)(CNO)] was crystallized from $CHCl_3$–EtOH yielding the corresponding solvated derivative containing one molecule of $CHCl_3$,which can be eliminated by heating at 130 °C *in vacuo* for 1 h. With a 1 : 1 molar ratio of the reactants in the above order, the major products were [$(PPh_3)_2$PtCl(CNO)] and [$(PPh_3)_2$PtCl($OCOCH_2Me$)]. With a molar ratio of 1 : 2, [$(PPh_3)_2$Pt($OCOCH_2Me$)(CNO)] was mainly formed.

The complex [$(PPh_3)_2$PtCl($OCOCH_2Me$)] could also be obtained by the reaction of [$(PPh_3)_2PtCl_2$] with [Na($OCOCH_2Me$)] (molar ratio 1 : 2), as for the synthesis of [$(PPh_3)_2$PtCl(OCOPh)]. The impure material obtained, crystallized from benzene, was shown to be isomorphous to that obtained from [$(PPh_3)_2PtCl_2$] and [Tl(nbo)].

[$Pt(PPh_3)_4$] *with* 2-*nitroacetophenone*. The complex [$Pt(PPh_3)_4$] (625 mg, 0·0005 mol) and 2-nitroacetophenone (330 mg, 0·002 mol) were added to benzene–ethanol–water (4 : 1 : 1) (60 cm^3) and the reaction mixture heated under reflux under an atmosphere of nitrogen for 3 days in the dark. The benzene phase was then separated, evaporated to dryness, and the solid residue obtained converted into a white crystalline material by addition of acetone (B). The white crystals were dissolved in $CHCl_3$ and fractionated by precipitation with light petroleum. The adduct [$(PPh_3)_2Pt(CNO)_2$],$CHCl_3$ was isolated first and desolvated *in vacuo* at 100 °C for 0·5 h to give [$(PPh_3)_2Pt(CNO)_2$] (210 mg), then crystalline [$(PPh_3)_2$Pt(OCOPh)(CNO)] was also obtained (95 mg). Evaporation of the acetone solution (B), followed by extraction of the residue with light petroleum and concentration of of this latter solution by exposure to air, gave $PhCO_2H$.

Physical Measurements.—I.r. spectra in the region 4 000—250 cm^{-1} were recorded on a Beckmann IR 20 spectrometer. A Beckmann IR 7 instrument was used to check the frequency of the more interesting absorptions. *X*-Ray powder spectra were obtained with a Debye powder camera, 114·6 mm in diameter, using Cu-K_α (Ni-filtered) radiation (λ 1·5418 Å). Molecular-weight measurements were carried out with a Mechrolab Inc. model 301-A vapour-pressure osmometer in benzene solution at 25 °C.

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