Oxidative Addition Reactions of Aldehydes and Related Molecules with Tetrakis(triphenylphosphine)platinum(0)

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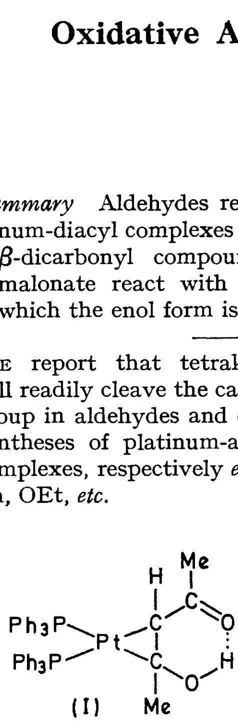
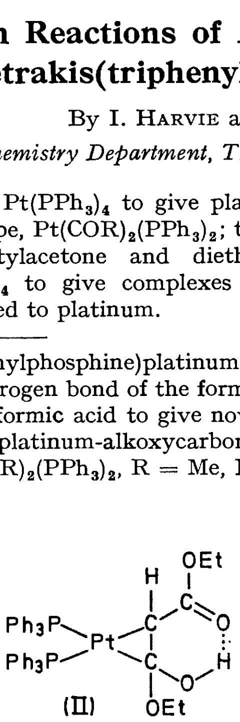
Summary Aldehydes react with $Pt(PPh_3)_4$ to give platinum-diacyl complexes of the type, $Pt(COR)_2(PPh_3)_2$; the β-dicarbonyl compounds, acetylacetone and diethyl malonate react with $Pt(PPh_3)_4$ to give complexes in which the enol form is complexed to platinum.

WE report that tetrakis(triphenylphosphine)platinum(0) will readily cleave the carbon–hydrogen bond of the formyl group in aldehydes and esters of formic acid to give novel syntheses of platinum-acyl and platinum-alkoxycarbonyl complexes, respectively *e.g.* $Pt(COR)_2(PPh_3)_2$, R = Me, Et, Ph, OEt, *etc.*



(I)



(II)

Treatment of tetrakis(triphenylphosphine)platinum(0) with benzaldehyde gives a high yield of the complex, $Pt(COPh)_2(PPh_3)_2$. The complex is monomeric in benzene solution and exhibits two strong bands in the i.r. spectrum due to the C=O stretching frequencies of the acyl groups (Table). There is no band in the i.r. spectrum which can be assigned to a metal–hydrogen stretching frequency and there is no peak in the ^1H n.m.r. spectrum characteristic of a platinum hydride species. We therefore formulate the complex as a square-planar four-co-ordinate complex of platinum(II). Other aldehydes behave similarly, as does the formyl group in esters of formic acid (Table). These reactions are quite different to those of certain mono-substituted acetylenes[1] and secondary amines[2] which give platinum hydride complexes with $Pt(PPh_3)_4$.

I.r. data of complexes (*Nujol mulls*)

	ν_{CO}(cm^{-1})	ν_{OH}(cm^{-1})
$Pt(COPh)_2(PPh_3)_2$ ..	1637, 1623	—
$Pt(CO{\cdot}Et)_2(PPh_3)_2$ ..	1639, 1608	—
$Pt(CO{\cdot}OEt)_2(PPh_3)_2$ ..	1682, 1626	—
(I)	1682	3350[a]
(II)	1681	[b]

[a] Very broad band. [b] Very broad band from 3300—3400 cm^{-1}

Kinetic studies[3] on the decarbonylation of aldehydes by chlorotris(triphenylphosphine)rhodium(I) suggest that metal-acyl complexes are involved in these reactions, but no rhodium acyl complexes could be detected.

In view of the reactivity of the formyl group with $Pt(PPh_3)_4$ we are currently investigating the reactivity of other molecules which contain activated carbon hydrogen bonds. Preliminary studies with acetylacetone and diethyl malonate show that with $Pt(PPh_3)_4$ in refluxing benzene carbon–hydrogen bond cleavage does not occur. Instead, formally zerovalent platinum–olefin complexes are obtained which contain acetylacetone and diethyl malonate co-ordinated in their enol forms.

These we formulate as (I) and (II), respectively, on the bases of analysis, molecular weight, i.r., and n.m.r. data. Acetylacetone has previously been shown[4] to co-ordinate in its enol form in the platinum(II) complex, PtCl(acac)-$[CH_3CO{\cdot}CH{=}C(OH)CH_3]$.

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[4] D. Gibson, J. Lewis, and C. Oldham, *J. Chem. Soc.* (*A*), 1967, 72.