Some Novel Peroxycarbonate Complexes of Platinum(II)

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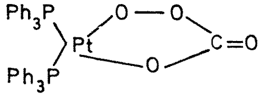
Summary Unsaturated molecules will add to peroxobis-(triphenylphosphine) platinum(II) to give new peroxy-complexes.

DURING the preparation of carbonato(bistriphenylphosphine) platinum(II),[1] an initial "impure" product was reported which differed in i.r. spectrum and m.p. from the final recrystallized sample. This "impure" product has now been shown to be a peroxycarbonato-species and has been characterized by its i.r. spectrum, chemical properties, and by elemental analysis.

When carbon dioxide and oxygen are bubbled into a benzene solution of tetrakis(triphenylphosphine)platinum(0), the initial product obtained melts at 143—145° and shows i.r. bands at 1678, 1250, 815, and 778 cm.$^{-1}$, in addition to the phosphine bands. Recrystallization from benzene–methylene chloride in an oxygen atmosphere yields the same product, but in the presence of excess triphenylphosphine under a nitrogen atmosphere, the compound is reduced to the carbonato-complex as previously reported. The i.r. spectrum of the latter shows bands at 1684, 1180, and 815 cm.$^{-1}$. The additional band in the former at 778 cm.$^{-1}$ is assigned to, essentially, ν(O–O) of a peroxy-grouping and the compound is thought to have the structure:



similar to that determined by Ugo *et al.*[2] for the compound peroxy(acetone)bis(triphenylphosphine)platinum(II), $(Ph_3P)_2PtO_2$(acetone). In this compound, the band at 855 cm.$^{-1}$ may be assigned to ν(O–O) (although Ugo tentatively assigned this to a C–O vibration) since on passing nitrogen or hydrogen through a solution of the compound the band disappears.[3]

In the corresponding bis(diphenylphosphino)ethane (diphos) complexes, the C=O stretch shifts from 1627 to 1685 cm.$^{-1}$ on reduction with triphenylphosphine, although an analytically pure sample of the carbonato-species has not yet been obtained.

TABLE

Compound	Colour	m.p.	I.r. spectrum (cm.$^{-1}$)			
			ν(C=O)	ν(C–O) + (O–C=O)	ν(O–O)	ν(M–O)
$(Ph_3P)_2Pt{\cdot}O{\cdot}CO_3$	White	143—145°	1678 vs	1250 s	778 m	558 vs 364 vs
$(Ph_3P)_2Pt{\cdot}CO_3$	White	203—205°	1685 vs	1185 s	—	[c]
$(diphos)Pt{\cdot}O{\cdot}CO_3$	White	162—164°	1627 vs	1380 vs	835 m	537 vs 357 s
$(diphos)Pt{\cdot}CO_3$	White	>200°	1685 vs	1190 s	—	[c]
$(Ph_3P)_2PtO_2{\cdot}CS_2$	Orange	155—165°	1560 vs[a]	[b]	800 m	[c]
$(Ph_3P)_2PtS_2CO$	White or pale yellow	265—267°	1680 1615 vs	[b]	—	[c]

[a] Assignment uncertain.
[b] No band observed.
[c] No spectrum obtained in this region.

When CS_2 is added to a solution of peroxobis(triphenylphosphine)platinum(II), a bright orange crystalline precipitate is obtained which analyses as $(Ph_3P)_2PtO_2{\cdot}CS_2$. The compound, monomeric in chloroform, has a strong i.r. band at 1560 cm.$^{-1}$ which cannot be satisfactorily assigned either to a C=S or C=O stretch, and another strong band at 800 cm.$^{-1}$ which may be a ν(O–O) since it disappears on reduction. Exact structural determination of this compound must await an *X*-ray analysis but it appears, chemically, to be analogous to the compound $(Ph_3P)_2PtOCO_3$. Reduction with triphenylphosphine gives a compound $(Ph_3P)_2PtS_2CO$, which has no i.r. band at 800 cm.$^{-1}$ and is identical to the compound obtained by Fackler[4] by decomposition of xanthate complexes. This compound may also be obtained by photochemical decomposition of oxalatobis(triphenylphosphine)platinum(II) in the presence of CS_2. There is evidence that both CO and CO_2 are produced by this reaction as expected.

All the peroxy-compounds liberated iodine from acid potassium iodide solution, (although the acetone complex did so only with difficulty); under the same conditions, no reaction was observed with the reduced compounds.

Physical data for the complexes are listed in the Table. Analytical results for all the compounds [except (diphos) $PtCO_3$ as mentioned above] were satisfactory.

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[4] J. P. Fackler, jun., W. C. Seidal, and J. A. Fetchin, *J. Amer. Chem. Soc.*, 1968, **90**, 2707.