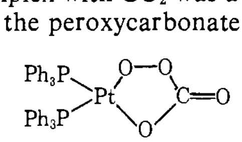
Some Reactions of Peroxobis(triphenylphosphine)platinum(II) and Analogs with Carbon Dioxide, Carbon Disulfide, and Other Unsaturated Molecules

P. J. Hayward, D. M. Blake, G. Wilkinson, and C. J. Nyman[1]

Contribution from the Departments of Chemistry, Washington State University, Pullman, Washington 99163, and the Imperial College of Science and Technology, London, S. W. 7, England. *Received March 11, 1970*

Abstract: Adducts of CO_2, CS_2, CO, aldehydes, ketones, acetone oxime, and thiourea with peroxobis(triphenylphosphine)platinum(II) and analogs (or the corresponding tetrakisphosphineplatinum(0) complex in the presence of oxygen) have been prepared. Most of the adducts are thought to have a five-membered ring structure involving a peroxo group, and the reactions of these adducts, particularly with reducing agents, have been studied. It has been shown that in many cases, the *five*-membered peroxo-containing ring can be reduced to a *four*- or *three*-membered ring without a peroxo group. The original adducts are characterized by the disappearance of the unsaturated infrared stretching frequency [ν(C=O), ν(C=S), or ν(C=N)], and for most of the compounds, the infrared vibrations of the ring are assigned.

The reactions of peroxobis(triphenylphosphine)platinum(II) with SO_2, NO_2, NO, and CO_2 to give the sulfato-, nitrato-, nitrito, and carbonato complexes have already been described.[2-4] In a preliminary note[5] we reported that the initial product of the reaction of the platinum complex with CO_2 was a peroxycarbonate. The structure of the peroxycarbonate, *viz.*



is thought to involve a five-membered ring containing a peroxy linkage, and here we describe this addition and those of other unsaturated compounds to [$(Ph_3P)_2PtO_2$], [$(Ph_3As)_4Pt$], [$(Ph_3P)_2PdO_2$], and [(diphos)$_2$Pt] (diphos = 1,2-bis(diphenylphosphino)ethane) to give adducts of similar structure. Reactions have been studied with CS_2, aldehydes, ketones, oximes, and thio compounds such as thiourea. Similar experiments have been attempted with [$(Ph_3P)_2IrCl(CO)O_2$] and [$(Ph_3P)_3RhCl(O_2)$]. Concurrent with this work, a molecular structure of the adduct of [$Ph_3P)_2PtO_2$] with acetone[6] has been reported, and this result parallels our findings.

Discussion

Reactions with CO_2. When CO_2 is bubbled into a benzene solution of [$(Ph_3P)_2PtO_2$] (or [$(Ph_3P)_4Pt$] in the presence of oxygen), greenish white crystals form which we believe to be the peroxycarbonate [$(Ph_3P)_2PtOCO_3$]·C_6H_6, based on its physical and chemical properties. The complex is unchanged by recrystallizing from benzene–methylene chloride solution in the presence of oxygen, but repeated recrystallization from a solution containing excess triphenylphosphine under nitrogen yields the carbonato complex, [$(Ph_3P)_2PtCO_3$]·C_6H_6, identical with that previously reported[4] and with a sample prepared from [$(Ph_3P)_2PtCl_2$] and silver carbonate.

Analogous peroxycarbonato and carbonato compounds could be prepared from [$(Ph_3As)_4Pt$], [(diphos)$_2$Pt], and [$(Ph_3P)_4Pd$] or [$(Ph_3P)_2PdO_2$]. As with the platinum analog, the initial product from the reaction of [$(Ph_3P)_4Pd$] with CO_2 and oxygen has been shown to be a peroxycarbonate rather than the carbonate as previously reported,[4] but owing to its instability in solution, reduction in the presence of excess triphenylphosphine was not possible. Reduction of the diphos peroxycarbonate was accompanied by partial decomposition. Direct reaction of [$(Ph_3P)_2PdCl_2$] or [(diphos)$PtCl_2$] with silver carbonate gave impure samples of the carbonates, but the decomposition products, mainly Pd or Pt metal, do not invalidate the infrared results, which show clearly the distinction between the peroxycarbonato and carbonato complexes.

Reaction with CO. When carbon monoxide (CO_2 free) was passed through a benzene solution of [$(Ph_3P)_2PtO_2$] for about 2 hr, a reddish solution was obtained from which, on partial evaporation, white or colorless crystals could be recovered. These were shown to be identical with the carbonato complex obtained by other means. On further evaporation of the red filtrate, a red-brown solid was obtained which had carbonyl absorption peaks in the infrared at 1800, 1860, and 1990 cm^{-1}. Molecular weight determinations ($CHCl_3$) indicated that the compound was polymeric and it was not studied further.

Reactions with CS_2. When CS_2 is added to a cold solution of [$(Ph_3P)_2PtO_2$] in benzene or ether, an immediate reaction occurs and bright orange crystals separate, which analyze as [$(Ph_3P)_2PtO_2 \cdot CS_2$]. Partial decomposition to a dithiocarbonate (see below) occurs unless the precipitate is filtered rapidly and kept cool, but when dry, the complex is quite stable. The exact structure of this compound is uncertain (see discussion

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[1] Address correspondence to this author at Washington State University.

[2] (a) J. J. Levison and S. D. Robinson, *Inorg. Nucl. Chem. Lett.*, 4, 407 (1968); (b) J. P. Collman, M. Kubota, and J. W. Hocking, *J. Amer. Chem. Soc.*, 89, 4809 (1967).

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[4] C. J. Nyman, C. E. Wymore, and G. Wilkinson, *J. Chem. Soc. A*, 561 (1968).

[5] P. J. Hayward, D. M. Blake, C. J. Nyman, and G. Wilkinson, *Chem. Commun.*, 987 (1969).

[6] R. Ugo, F. Conti, S. Cenini, R. Mason, and G. B. Robertson, *ibid.*, 1498 (1968).

Table I. Proton Nmr Spectra of the Aldehyde and Ketone Adducts (in $CDCl_3$)[a]

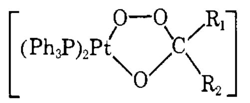
Compound	Chemical shifts (τ) from TMS: Phenyl	Aldehydic H	Methylene H	Methyl H	J, cps
Acetone				7.83	
$P_2PtO_2\cdot(CH_3)_2CO$	2.79 (30)			8.40 (6)	
$P_2PtO\cdot(CH_3)_2CO$	2.77 (30)			8.70 (6)	
$P_2PdO\cdot(CH_3)_2CO$[b]	2.50 (30)			8.79 (∼4)	
Acetaldehyde		0.20 (q) (1)		7.80 (d) (3)	
$P_2PtO_2\cdot CH_3CHO$	2.80 (30)	4.76 (q) (1)		8.63 (d) (3)	5.0
$P_2Pt(OAc)_2$	2.75 (30)			8.63 (6)	
Propionaldehyde		0.48 (t) (1)	8.11 (q) (2)	9.21 (t) (3)	8.0
$P_2PtO_2\cdot CH_3CH_2CHO$	2.77 (30)	5.02 (t) (1)	8.34 (q) (2)	9.27 (t) (3)	7.5
Cyclohexanone			7.70 (4) 8.20 (6)		
$P_2PtO_2(C_6H_{10}O)_2$	2.78 (30)		7.70 (5) 8.20 (10) 8.76 (5)		
$P_2PtO_2\cdot C_6H_{10}O$	2.75 (30)		8.13 (4) 8.72 (6)		
Chloroacetone			5.88 (2)	7.73 (3)	
$P_2PtO_2\cdot ClCH_2COCH_3$	2.71 (30)		6.08 (2)	8.43 (3)	

[a] Relative intensities, in parentheses, for the complexes are compared with the phenyl protons, standard taken as 30. P = triphenylphosphine. [b] See discussion in text.

on ir results). The complex may be reduced, by recrystallizing from benzene–methylene chloride containing excess triphenylphosphine, to the corresponding dithiocarbonate, $[(Ph_3P)_2PtS_2CO]$, identical with that prepared by the method of Fackler[7,8] by decomposition of xanthates.

When CS_2 is added to a cold solution of the palladium peroxo complex in benzene, immediate effervescence occurs and the color changes to a reddish brown. A red-brown solid is obtained which has been shown to be the dithiocarbonate $[(Ph_3P)_2PdS_2CO]$.

Reactions with Aldehydes and Ketones. Peroxobis(triphenylphosphine)platinum(II) will add 1 mol of an aldehyde or ketone to give a complex



which contains a five-membered ring system similar to the peroxycarbonates.[6] Adducts of ketones may also by prepared by stirring a solution of the ketone and $[(Ph_3P)_4Pt]$ in benzene in an atmosphere of oxygen, but a similar procedure with aldehydes gives a dicarboxylate complex rather than the aldehyde adduct. For example, with acetaldehyde, $[(Ph_3P)_2Pt(OAc)_2]$ is obtained.[9] With cyclohexanone, the initial product contains 2 mol of ketone, one of which is probably solvated to the complex since the ir shows a C=O stretch which is absent in all other adducts. In chloroform solution, dissociation occurs (nmr evidence) and recrystallization gives a product, $[(Ph_3P)_2PtO_2(\text{cyclohexanone})]\cdot {}^1/_2CHCl_3$, which shows no C=O stretch. The nmr results for the complexes prepared are given in Table I.

The aldehyde or ketone is fairly readily displaced from these compounds. Treatment of a chloroform solution of the acetone adduct with SO_2, NO_2, and CO_2 gave, respectively, the sulfato, nitrato, and *carbonato* (not peroxycarbonato) complexes. The acetone is also displaced by acetylenes to give complexes such as $[(Ph_3P)_2Pt\cdot C_2Ph_2]$ but olefins appear not to react. On prolonged standing in $CHCl_3$ solution the complex reacts with the solvent to give [*cis*-$(Ph_3P)_2PtCl_2$].

When a steady stream of hydrogen or nitrogen is passed through a solution of the acetone complex in methylene chloride, a shift to higher field is observed in the methyl nmr frequency, and a rather unstable solid may be obtained which analyzes as $[(Ph_3P)_2PtO\cdot \text{acetone}]$, which probably has a four-membered ring structure similar to the carbonato complexes. There was no evidence of an adduct, $[(Ph_3P)_2Pt\cdot \text{acetone}]$, with a three-membered ring structure such as reported for the hexafluoroacetone compound, $[(Ph_3P)_2Pt\cdot HFA]$.[10]

The reaction of acetone with $[(Ph_3P)_2PdO_2]$ gives a reddish brown solution, the nmr of which suggests the presence of $[(Ph_3P)_2PdO\cdot \text{acetone}]$ by comparison with the platinum system, but considerable decomposition occurred and no solid complex was recovered. No adducts of other aldehydes or ketones could be obtained with palladium owing to rapid decomposition in solution.

Reactions with Other Unsaturated Molecules. Other unsaturated molecules will also add to $[(Ph_3P)_2PtO_2]$ to give 1:1 adducts. With acetone oxime, a compound $[(Ph_3P)_2PtO_2\cdot \text{acetone oxime}]$ is obtained which shows bands in the ir at 3400 and 1620 cm^{-1} due to O–H modes, a strong band at 1190 cm^{-1} which is probably a ring vibration, and a weak band at 830 cm^{-1} which may be ν(O–O). Thiourea will also add to give a complex, $[(Ph_3P)_2PtO_2\cdot tu]$, which shows ir bands due to N–H modes and a strong band at 1180 cm^{-1} but no additional band near 800 cm^{-1} assignable to ν(O–O). A feature of these spectra (and also those of the aldehyde and ketone adducts) is the complete disappearance of the band due to the double-bond stretch, ν(C=O), ν(C=N), or ν(C=S), supporting the proposed ring structure.

With thioacetamide, however, a reddish brown binuclear compound is obtained of uncertain structure.

With Iridium and Rhodium. Attempts were made to prepare CO_2, CS_2, aldehyde, and ketone adducts

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(7) J. P. Fackler, W. C. Seidel, and J. A. Fetchin, *J. Amer. Chem. Soc.*, **90**, 2707 (1968).

(8) J. P. Fackler and W. C. Seidel, *Inorg. Chem.*, **8**, 1631 (1969).

(9) A recent publication [I. Harvie and R. D. W. Kemmitt, *Chem. Commun.*, 198 (1970)] reports the addition of aldehydes to $[(Ph_3P)_4Pt]$ to give acyl complexes, $[(Ph_3P)_2Pt(COR)_2]$, but the limited data reported are identical with those obtained by us for the dicarboxylate complexes, $[(Ph_3P)_2Pt(CO_2R)_2]$, prepared by the above procedure in the presence of oxygen. The identity of our complexes was confirmed by comparison with samples prepared by the action of the appropriate acid on $[(Ph_3P)_2PtCO_3]$.[4]

(10) M. Green, R. B. L. Osborn, A. J. Rest, and F. G. A. Stone, *ibid.*, 502 (1966).

of $[(Ph_3P)_2Ir(CO)Cl(O_2)]$[11] and $[(Ph_3P)_3RhCl(O_2)]$, but in every case the reactants were recovered unchanged. This difference in reactivity between these compounds and the oxygen adducts of platinum and palladium may be correlated with the known oxygen–oxygen bond lengths in the adducts[12,13]—a longer bond in the platinum adduct is indicative of stronger metal–oxygen bonding[14]—and the contrasting reversible nature of the former. In addition, if the reaction with CO_2, aldehydes, etc, involves a five-coordinate intermediate in the platinum and palladium examples, a similar mechanism would suggest rather unlikely seven-coordinate intermediates in the rhodium and iridium compounds.

Estimation of Peroxide. While elemental analyses for most of the compounds prepared were satisfactory, it was considered desirable to find some way of estimating the peroxide or oxidizing power directly. Unfortunately, no completely satisfactory method was found. No reduction was achieved with titanous chloride even in boiling solutions of dilute acid, and chromous salts were unsatisfactory since they are catalytically oxidized to Cr(III) by H^+ in the presence of platinum (always present in trace amounts as impurity). Addition of acidified iodide solutions to a solution of a peroxy compound in a small amount of ethanol gave an immediate coloration due to iodine liberated, but in time, the color faded. This was thought to be due to the oxidation of triphenylphosphine formed by partial decomposition of the complexes according to the equation

$$Ph_3P + H_2O + I_2 \longrightarrow Ph_3PO + 2H^+ + 2I^-$$

This effect was minimized by immediately filtering off the residue, washing it with ether to remove any adhered iodine, and titrating the resultant solution against standard thiosulfate. The results were always compared with a blank, run concurrently. The results, shown in Table II in terms of moles of peroxide/moles of complex were always low, ranging from 30 to 60% of the theoretical, but qualitatively, the results agree well with predictions in that only the peroxy species liberated any iodine at all. (The trace produced by $[(diphos)PtCO_3]$ is almost certainly due to some peroxy impurity, as the compound could not be obtained pure.) The results give some measure of the stability of the compounds; the lower the result, the greater the decomposition in solution. Thus the palladium carbonato and peroxycarbonato complexes decomposed very rapidly and no liberated iodine was detected at all.

Table II. Results of Peroxide Titrations

Compound	Mol of peroxide/mol of complex[a]
$(Ph_3P)_2PtOCO_3$	0.4
$(Ph_3P)_2PtCO_3$	0
$(diphos)PtOCO_3$	0.3
$(diphos)PtCO_3$	Trace (<0.05)
$(Ph_3P)_2PdOCO_3$	d
$(Ph_3P)_2PdCO_3$	d
$(Ph_3P)_2PtO_2CS_2$	0.4
$(Ph_3P)_2PtS_2CO$	0
$(Ph_3P)_2PdS_2CO$	0
$(Ph_3P)_2PtO_2 \cdot CH_3COCH_3$	0.6
$(Ph_3P)_2PtO_2$	0.45
$(Ph_3P)_2PdO_2$	0.3

[a] d = decomposed rapidly; see text.

Infrared Spectra. The infrared spectra of the carbonates and peroxycarbonates in the range 2000–300 cm^{-1} are given in Table IIIA. (Since publication of our note,[5] we have had access to a more accurate and wider ranged infrared instrument, which has permitted more accurate determination of band positions. In a few cases, we have changed our assignments in view of additional evidence.) The assignments are based on those of Nakamoto[15] for bidentate carbonates, and the bands were identified here by comparison with the spectra of $[cis\text{-}(Ph_3P)_2PtCl_2]$ and corresponding complexes of triphenylarsine and diphos.

All the complexes show a band above 1600 cm^{-1} which may readily be assigned to $\nu(C{=}O)$ (ν_1); in some of the compounds, the band is split into two components. The energy of this band is generally greater in the carbonato complexes, but the converse is true of $\nu_{as}(C\text{–}O)$ (ν_5), which is observed near 1180 cm^{-1} in the carbonates but rises to near 1250 cm^{-1} in the peroxycarbonates. Greatest shift of both bands was noted in the diphos compounds. In contrast to these bands, $\nu_s(C\text{–}O)$ (ν_2) shows very little variation between the compounds, but the π deformation (ν_8) is usually higher in the peroxycarbonates. Reduced ring strain permitting stronger bonding within the five-membered ring of the peroxycarbonates compared with the four-membered ring of carbonates may account for these variations.

An additional band near 780 cm^{-1} is observed only in the peroxy species and may be assigned to essentially an O–O stretch.

Assignment of ν_3 is uncertain owing to the multitude of strong phosphine bands in this region (750–700 cm^{-1}), and the band assigned to ν_3 by Nyman, *et al.*,[4] is almost certainly a phosphine band. In the carbonate complexes, ν_6 is usually observed as a shoulder on the side of the phosphine bands so the exact position is uncertain, but in the peroxycarbonates, two bands are observed at about 580 and 550 cm^{-1} which may be assigned to this mode. Two bands assignable to metal anion stretches (ν_7 and ν_4) are observed in most of the complexes, and these are both higher in energy in the carbonates than in the peroxycarbonates. Assignments (of ν_7, ν_4) for the diphos complexes are uncertain because of ligand vibrations in the region. Metal–phosphorus stretches could usually be identified around 420 cm^{-1}, but most of the complexes also also gave one or two bands in the range 440–465 cm^{-1}, which, though probably internal phosphine modes,[16] may also have a metal–phosphorus component or be due to phosphine oxide impurity.[16]

The infrared spectra of the dithiocarbonates (Table IIIB) have been interpreted on the same basis as those of the carbonates, but identification of all the bands

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(11) L. Vaska, *Science*, 140, 809 (1963).

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(13) T. Kashiwagi, N. Yasuoka, N. Kasai, M. Kakudo, S. Takahashi, and N. Hagihana, *Chem. Commun.*, 743 (1969).

(14) J. A. McGinnety, N. C. Payne, and J. A. Ibers, *J. Amer. Chem. Soc.*, 91, 6301 (1969).

(15) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley, New York, N. Y., 1963, p 163.

(16) G. B. Deacon and J. H. S. Green, *Spectrochim. Acta, Part A*, 24, 845 (1968).

Table III. Infrared Spectra (cm^{-1}) (Excluding Phosphine Bands)

A

Compound	ν_1 $\nu(C{=}O)$	ν_5 $\nu_{as}(C{-}O)$	ν_2 $\nu_s(C{-}O)$	ν_8 π	$\nu(O{-}O)$	ν_3 Ring def	ν_6 $\delta(C{=}O) + \nu(C{-}O)$	ν_7 $\nu(M{-}O)$	ν_4 $\nu(M{-}O)$	$\nu(M{-}P)$	Other
$(Ph_3P)_2PtCO_3$	1685 (vs)	1185 (s)	980 (s)	815 (s)		*a*	675 (sh)	409 (m)	363 (vs)	409 (m)	
$(Ph_3P)_2PtOCO_3$	1678 (vs)	1243 (vs)	978 (s)	836 (sh)	780 (m)	*a*	585 (m) 555 (s)	387 (s)	305 (vs)	429 (w)	
$(Ph_3As)_2PtCO_3$	1693 (vs)	1187 (s)	975 (s)	810 (s)		*a*	678 (s)	427 (m)	344 (vs)	$\nu(M{-}As)$[b]	
$(Ph_3As)_2PtOCO_3$	1685 (vs)	1240 (s)	973 (s)	829 (sh)	773 (s)	*a*	582 (s) 565 (s)	390 (m)	318 (vs)	$\nu(M{-}As)$[b]	
$(Ph_3P)_2PdCO_3$	1655 (vs) 1630 (vs)	1200 (vs)	989 (s)	817 (s)		*a*	667 (sh)	402 (s)	370 (vs)	418 (sh)	1272 (w)
$(Ph_3P)_2PdOCO_3$	1661 (vs) 1604 (m)	1256 (vs)	978 (vs)	833 (sh)	780 (s)	*a*	569 (m) 552 (m)	384 (s)	317 (s)	423 (m)	
(diphos)$PtCO_3$	1665 (vs)	1175 (s)	972 (sh)	815 (s)		*a*	*a*	*a*	352 (m)[a]	*a*	
(diphos)$PtOCO_3$	1620 (vs)	1368 (s) 1265 (s-br)	983 (m)	836 (m)	780 (sh)	*a*	583 (w) 557 (w)	352 (m)[a]	*b, c*	*a*	643 (sh)

B

	$\nu(C{=}O)$	$\nu_{as}(C{-}S)$	$\nu_s(C{-}S)$	π	$\nu(O{-}O)$	Ring def	$\delta(C{=}O) + \nu(C{-}O)$	$\nu(M{-}S)$	$\nu(M{-}S)$	$\nu(M{-}P)$
$(Ph_3P)_2PtS_2CO$	1695 (vs) 1615 (vs)	*b*	982 (m)	835 (vs)		*a*	576 (m) 556 (w)	*b, c*	*b, c*	421 (m)
$(Ph_3P)_2PtO_2{\cdot}CS_2$[a]	1560 (vs)	*b*	921 (m)	835 (w)	800 (m)	*a*	550 (s)	*b, c*	*b, c*	422 (w)
$(Ph_3P)_2PdS_2CO$	1685 (vs) 1610 (vs)	*b*	976 (sh)	831 (m)		*a*	638 (sh)[a]	385 (vw)[a]	335 (vw)[a]	422 (m)

C

	$\nu(C{=}S)$	$\nu(C{-}S)$	$\nu(M{-}C)$	$\nu(M{-}S)$	$\nu(O{-}O)$	$\nu(M{-}O)$	$\nu(M{-}P)$
$(Ph_3P)_2PtCS_2$	1146 (vs)	651 (s)	536 (s)	316 (m)			420 (m)
$(Ph_3P)_2PtO_2$					825 (vs)	475 (s) 496 (sh)[a]	422 (m)
$(Ph_3P)_2PdO_2$					877 (vs)	487 (s) 496 (sh)[a]	420 (m)

D

	$\nu_{as}(C{-}O)$ + lig vib	ν_2 $\nu_s(C{-}O)$	ν_5	$\nu(O{-}O)$	ν_3 Ring def	ν_6 $\delta(C{-}C)$ + $\nu(C{-}O)$	ν_7 $\nu(M{-}O)$	ν_4 $\nu(M{-}O)$	$\nu(M{-}P)$	
$(Ph_3P)_2PtO_2{\cdot}(CH_3)_2CO$	1214 (m) 1180 (vs) 1140 (m)	965 (vs)	845 (m)	808 (w)	*a*	656 (s) 579 (s)	378 (s)	*b, c*	428 (s), 421 (s)	
$(Ph_3P)_2PtO{\cdot}(CH_3)_2CO$	1268 (m) 1215 (w) 1140 (w, br) 1117 (w, br)	968 (m)	*a*		*a*	663 (sh) 574 (s)	378 (m)	*b, c*	421 (s)	
$(Ph_3P)_2PtO_2{\cdot}C_6H_{10}O$	1260 (m) 1245 (m)	970 (m)	840 (vw)	*b*	*a*	644 (m) 572 (s)	386 (m)	*b, c*	420 (m)	
$(Ph_3P)_2PtO_2{\cdot}CH_3CHO$	*a*	*b*	845 (sh)	780 (w)	*a*	661 (sh) 598 (s)	368 (w-br)	*b, c*	423 (s)	900 (m)[d] 560 (sh)
$(Ph_3P)_2PtO_2{\cdot}CH_3CH_2CHO$	1260 (sh) 1187 (s)	976 (s)	848 (w)[a]	*b*	*a*	664 (s) 565 (s)	348 (m)	*b, c*	422 (s)	2800 (s)[e] 930 (d)[d] 488 (s)
$(Ph_3P)_2PtO_2{\cdot}ClCH_2COCH_3$	1234 (w) 1202 (w) 1133 (w)	949 (w)	824 (w)	774 (sh)	*a*	664 (sh) 575 (s)	*a*	*b, c*	418 (s)	
$(Ph_3P)_2PtO_2{\cdot}C_6H_5COCH_3$	1268 (m) 1236 (m) 1145 (m)	938 (m)	840 (w)	800 (m)	*a*	667 (sh) 568 (sh)	*a*	*b, c*	423 (m)	590 (w-sh)

[a] Assignment uncertain (usually owing to ligand bands in region). [b] Band not observed. [c] Band probably below range of instrument. [d] Aldehydic C–H bend. [e] Aldehydic C–H stretch.

was rather more difficult, and several predicted bands were apparently not observed. The spectrum of [$(Ph_3P)_2PtO_2CS_2$] is reported, but assignments are in doubt, as the exact structure of the complex is still under investigation. The strong band at 1560 cm^{-1} is at too high an energy to be assigned to $\nu(C{=}S)$ and assignment to $\nu(C{=}O)$ would preclude a peroxy linkage in the structure. However, an additional band of medium intensity at 800 cm^{-1} (compared with the dithiocarbonate) could satisfactorily be assigned to ν(O–O). The positions of S–O single-bond stretching frequencies do not appear to be well documented, but it would be expected to be below the usual ν(O–O) region. No evidence of M–O or M–S stretches was observed in this compound. On balance, we prefer a structure involving a C=O bond, possibly formed by rearrangement of an initial adduct.

Although not strictly part of this work, the spectrum of [$(Ph_3P)_2PtCS_2$][17] is included (Table IIIC) for com-

[17] M. C. Baird and G. Wilkinson, *Chem. Commun.*, 514 (1966).

Table IV. Analyses[a]

Compound	Color	Mp, °C	% C	% H	% O	% P	% Pt (as ash)	Other
$(Ph_3P)_2PtCO_3 \cdot C_6H_6$	White	202–205 dec	59.6 (60.2)	4.1 (4.2)		6.7 (7.2)	23.0 (22.7)	
$(Ph_3P)_2PtOCO_3 \cdot C_6H_6$	White	143–145 dec	58.6 (59.1)	4.1 (4.2)	6.0 (7.3)	7.1 (7.1)	21.3 (22.3)	
$(Ph_3As)_2PtCO_3 \cdot C_6H_6$	White	186–193 dec	54.4 (54.6)	3.9 (3.8)				Mol wt 946 (946)
$(Ph_3As)_2PtOCO_3 \cdot C_6H_6$	White		53.5 (53.7)	3.8 (3.8)				
$(Ph_3P)_2PdCO_3$[b]	Brown	140 dec	60.8 (64.3)	4.2 (4.4)	7.3 (7.0)	9.0 (9.0)		
$(Ph_3P)_2PdOCO_3 \cdot C_6H_6$	Yellow	91–93 dec	65.7 (65.8)	4.6 (4.6)		8.2 (7.9)	11.9 (13.5) (Pd)	
(diphos)$PtCO_3$[b]	White	>200	46.3 (49.6)	3.6 (3.7)		8.2 (9.5)	34.1 (29.9)	
(diphos)$PtOCO_3 \cdot C_6H_6$	White	162–164 dec	51.1 (50.8)	4.1 (3.8)		8.8 (8.7)		
$(Ph_3P)_2PtO_2 \cdot CS_2$	Orange	155–165 dec	53.2 (53.7)	3.9 (3.7)		7.5 (7.5)	23.0 (23.5)	% S 7.5 (7.7)
$(Ph_3P)_2PtS_2CO \cdot C_6H_6$	White or pale yellow	265–267 dec	58.7 (58.1)	4.2 (4.1)	1.5 (1.8)	6.9 (6.9)		% S 6.6 (7.2)
$(Ph_3P)_2PdS_2CO$	Brown	140–142 dec	60.4 (61.4)	4.1 (4.2)		8.6 (8.6)		% S 8.5 (8.9)
$(Ph_3P)_2PtO_2 \cdot (CH_3)_2CO$	Pale yellow	172–174	57.9 (57.9)	4.6 (4.5)		7.5 (7.6)		
$(Ph_3P)_2PtO \cdot (CH_3)_2CO$	White	145–155 dec	59.3 (59.0)	5.0 (4.6)		7.6 (7.8)		
$(Ph_3P)_2PtO_2 \cdot CH_3CHO$	White	170–174	57.6 (57.4)	4.5 (4.3)				
$(Ph_3P)_2PtO_2 \cdot CH_3CH_2CHO$	White	175–180	58.0 (57.9)	4.4 (4.5)				
$(Ph_3P)_2PtO_2 \cdot (C_6H_{10}O)_2$	White	156–158	61.0 (60.8)	5.5 (5.3)		6.1 (6.5)		
$(Ph_3P)_2PtO_2 \cdot C_6H_{10}O \cdot {}^1/_2CHCl_3$	White	156–158	56.3 (56.1)	4.1 (4.5)		6.9 (6.8)		% Cl 5.7 (5.9)
$(Ph_3P)_2PtO_2 \cdot C_6H_5COCH_3$	White	121–125	60.2 (60.6)	4.4 (4.4)		7.4 (7.1)		
$(Ph_3P)_2PtO_2 \cdot ClCH_2COCH_3$	White	225–235 dec	55.5 (55.5)	4.1 (4.1)				

[a] When recrystallized from other solvents, many complexes contained 1 mol (usually) of solvent, and analysis reflected this. Melting points seemed unaffected by the solvent included. Calculated analyses in parentheses. [b] Analytically pure samples could not be obtained.

parison with the other sulfur complexes, and those of the starting materials, $[(Ph_3P)_2MO_2]$ (M = Pd, Pt) (Table IIID), which appear not to have been published completely before, are reported. The spectrum of $[(Ph_3P)_2PtCS_2]$ shows four bands not attributable to phosphine modes, which may be unambiguously assigned to ν(C=S), 1146;[17] ν(C—S), 651; ν(M—C), 536; and ν(M—S), 316 cm^{-1}. Three bands are expected from the peroxo group in the complexes $[(Ph_3P)_2MO_2]$, and three bands are observed. The O–O stretch has already been reported,[4] but the two further bands in each case may be assigned to ν(M–O).

Table IIID gives the ir spectra of adducts of $[(Ph_3P)_2PtO_2]$ with aldehydes and ketones, which have a ring structure similar to that of the peroxycarbonates. ($[(Ph_3P)_2PtO \cdot$ acetone] has a four-membered ring structure similar to the carbonates.) Many of the ligands have bands due to C–H and C–C modes in the region where ν_{as}(C–O) is expected and unambiguous assignment has not proved possible. The symmetric C–O stretch (ν_2, using the same notation as previously for ring vibrations) is observed in a position close to that in the peroxycarbonates, as is ν_8, and the peroxy stretch is observed in most of the complexes around 800 cm^{-1}. The adducts of acetaldehyde and propionaldehyde also show an additional band near 900 cm^{-1} which may be assigned to the aldehydic C–H bend. This C–H stretch was observed in the propionaldehyde complex at 2800 cm^{-1}. All the compounds showed two bands in the ranges 565–578 and 644–677 cm^{-1}, which may be attributed to a mode corresponding to ν_6 in the peroxycarbonates. Although two M–O stretches are expected, only one band is observed, at about 370 cm^{-1}; but comparison with the peroxycarbonates suggests that this is ν_7 and that ν_4 is beyond the limits of the instrument.

Previous comments on ν(M–P) are applicable here also.

Experimental Section

Preparation of the Complexes. Peroxycarbonates. The compound $[(Ph_3P)_2PtOCO_3]$ was prepared by bubbling a rapid stream of carbon dioxide and oxygen into a rapidly stirred solution of tetrakis(triphenylphosphine)platinum (1.0 g) in dry benzene (~20 ml). After about 30 min, the solution turned colorless and a pale green-white precipitate was observed. This was filtered off, washed with dry benzene, and dried *in vacuo*. The yield of $[(Ph_3P)_2PtOCO_3] \cdot C_6H_6$ was 0.6–0.65 g (86–93%). The compound could also be prepared by bubbling CO_2 through a benzene solution of peroxobis(triphenylphosphine)platinum(II). Good yields of $[(Ph_3As)_2PtOCO_3] \cdot C_6H_6$, [(diphos)$PtOCO_3] \cdot C_6H_6$, and $[(Ph_3P)_2PdOCO_3] \cdot C_6H_6$ could be prepared in an analogous manner from the corresponding tetrakis(phosphine)metal(0) complex, though the reaction time varied from 15 min to 1–2 days. In all cases carbon dioxide and oxygen were passed until no further reaction was observed.

Carbonates. The compounds $[(Ph_3P)_2PtCO_3]$ and $[(Ph_3As)_2PtCO_3]$ could be prepared from the corresponding peroxycarbonate by recrystallizing from a methylene chloride–benzene solution in the presence of an excess of ligand. Typically, about 1 g of the compound was dissolved in about 15–20 ml of methylene chloride, and about 3 g of ligand was added. The mixture was refluxed overnight, and on cooling, an equal volume of dry benzene was added and the solution allowed to evaporate. The complete procedure was carried out in an atmosphere of nitrogen. The crystals formed were filtered off, washed with dry benzene and ether to remove triphenylphosphine and triphenylphosphine oxide, and dried *in vacuo*; yield, 50–80%. The purity of the product was checked by its infrared spectrum and the above recrystallization repeated if necessary. Usually, two recrystallizations were sufficient to produce a satisfactory product. Attempted recrystallization of [(diphos)$PtOCO_3$] gave an impure product, and with $[(Ph_3P)_2PdOCO_3]$, complete decomposition occurred in solution. The carbonates could also be prepared by stirring a suspension of dichlorobis(phosphine)metal(II) (1 g) with freshly prepared silver carbonate (3.4 g) in methylene chloride (30 ml) in a darkened flask under nitrogen for 1–2 hr. The resulting suspension was filtered to separate the silver chloride formed and the unused silver carbonate from the solution. The complex was obtained by evaporation of the filtrate in a stream of nitrogen. The complex was then washed with dry benzene and dried *in vacuo*; yield about 80% with $[(Ph_3P)_2PtCl_2]$ and $[(Ph_3As)_2PtCl_2]$. The product with [(diphos)$PtCl_2$] was never obtained pure; some unchanged starting material and other impurities were always present, even after recrystallization from methylene chloride, the only solvent in which the compound was appreciably soluble. The complex $[(Ph_3P)_2PdCO_3]$ tended to decompose in solution as it was formed, so with $[(Ph_3P)_2PdCl_2]$, the suspension was stirred only for about 15 min. However, the product obtained was always impure.

Adduct of Carbon Disulfide with $[(Ph_3P)_2PtO_2]$. Carbon disulfide was added dropwise to a solution or suspension of $[(Ph_3P)_2PtO_2]$ (0.75 g) in ice-cold benzene–ether (5 ml/5 ml) until no further reaction was observed (usually 3–4 drops). The orange crystals formed were filtered off rapidly, washed with ice-cold ether, and dried *in vacuo*. The compound tended to decompose to the dithiocarbonate analog in solution but was quite stable when dry; yield, 0.75 g (about 90%). A similar procedure with $[(Ph_3P)_2PdO_2]$ gave the dithiocarbonate directly, and oxygen was evolved on addition of CS_2.

Dithiocarbonatobis(triphenylphosphine)platinum(II). This adduct could be prepared by recrystallizing the above complex (0.5 g) from a methylene chloride–benzene solution containing triphenylphosphine (1.3–1.5 g) under nitrogen, as described above.

Aldehyde and Ketone Adducts. These were prepared by the following general method: about 1 g of $[(Ph_3P)_2PtO_2]$ was dissolved or suspended in benzene under nitrogen and an excess of ligand added with stirring. (The ligand was added in benzene solution if a solid.) With aldehydes, an immediate precipitate was noticed, and with ketones, a precipitate formed on stirring for a few minutes. The solid was then filtered off, washed with dry benzene, and dried *in vacuo*; yields, usually about 90%. Adducts with acetone oxime, thiourea, and thioacetamide were prepared in an exactly analogous manner. Ether was sometimes added to hasten precipitation.

Reduction of $[(Ph_3P)_2PtO_2 \cdot$Acetone$]$. Bubbling a stream of nitrogen or hydrogen through a solution of $[(Ph_3P)_2PtO_2 \cdot \text{acetone}]$ ($\sim$1 g) in methylene chloride (25 ml) for several days gave the complex as a white solid. Solvent was added as necessary during this time to maintain a fairly constant level. The product was recovered by evaporation, washed with dry ether, and dried *in vacuo*. It was not ascertained whether or not the hydrogen or nitrogen was oxidized during this reaction. Attempts to reduce the aldehyde and ketone adducts with triphenylphosphine in the same manner as with peroxycarbonates resulted in the re-formation of tetrakis(triphenylphosphine)platinum(0).

Physical Measurements. Infrared spectra were recorded on a Beckman IR-4 prism instrument calibrated with a polystyrene film (4000–600 cm^{-1}) and atmospheric water vapor (600–300 cm^{-1}). Microanalyses were performed by Chemalytics Inc. and by Schwarzkopf Microanalytical Laboratories. Melting points were measured on a hot stage microscope in air and are uncorrected. Nmr spectra were obtained on a Varian A60 spectrometer using solutions in $CDCl_3$. Analyses of compounds are given in Table IV.

Reactions of Labile Metal Ions with Oligopeptides. V.[1] Copper(II) with Glycylglycine and Glycylsarcosine

R. F. Pasternack, M. Angwin, and E. Gibbs

Contribution from the Department of Chemistry, Ithaca College, Ithaca, New York 14850. Received January 22, 1970

Abstract: The complexation reactions of glycylsarcosine and glycylglycine with copper(II) have been studied using the temperature-jump technique. At 25°, the rate constants for the reactions $Cu^{2+} + L^- \rightleftharpoons CuL^+$ (k_1, k_{-1}) are for glycylsarcosine, $k_1 = 4.0 \times 10^8\ M^{-1}\ \text{sec}^{-1}$, $k_{-1} = 170\ \text{sec}^{-1}$, and for glycylglycine, $k_1 = 3.5 \times 10^8\ M^{-1}\ \text{sec}^{-1}$, $k_{-1} = 960\ \text{sec}^{-1}$. In addition, for the latter ligand, a slower effect appears at pH $\sim$4, which has been ascribed to the reaction $Cu(HGG)^+ \rightleftharpoons CuGG + H^+$ (k_D, k_H). The rate constants at 25° are $k_D = 76\ \text{sec}^{-1}$ and $k_H = 8.7 \times 10^5\ M^{-1}\ \text{sec}^{-1}$. The bonding model for metal ion peptide complexes suggested by Rabin is consistent with these kinetic results. The reactions for glycylglycine were studied at other temperatures and the activation energies were determined. The activation energy for complexation is consistent with the suggestion that the rate-determining step is the removal of a water molecule from an axial position in tetragonally distorted $Cu(H_2O)_6{}^{2+}$. The activation energy for the protonation reaction is considerably larger than that usually obtained for reactions of this type and is consistent with structural rearrangement subsequent to proton attack.

Considerable interest has been shown recently in the structures of metal complexes of oligopeptides in solution. Special attention has been paid to the peptide complexes of nickel(II), cobalt(II), and especially copper(II). The emphasis on copper(II) is related quite likely to the important role this metal ion plays in certain biochemical processes and to the fact that it is unique in the extent to which it facilitates dissociation of peptide link hydrogen atoms. Most of the previous studies on the aqueous chemistry of copper–peptide complexes have involved potentiometric titration,[2–6] calorimetry,[3] optical rotary dispersion,[6] visible[6] and infrared spectroscopy,[4,5] nmr spectrometry,[7] and electron spin resonance.[8] Using the copper–glycycIglycine complex as a specific example, several workers suggest that the structure stable in the pH range in which the peptide nitrogen is protonated is one in which bonding occurs through the amine nitrogen and carbonyl oxygen[2] (*cf.* Figure 1a). However, other workers[4,5,7] have interpreted their results as indicating strong metal-to-carboxyl oxygen interaction which, in the absence of dimers,[8] leads them to suggest the structure shown in Figure 1b.

We are reporting on the kinetics of the reactions of copper(II) with glycylglycine and glycylsarcosine. The temperature-jump technique has been used to obtain

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