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Reactions of Carbonato and Oxalato Complexes of Platinum(II). Formation of Cationic Clusters of Platinum

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Oxalatobis(triphenylphosphine)platinum(II) reacts with carbon monoxide and acetylenes in ethanol to produce cluster cations with the formula $[Pt_3[P(C_6H_5)_3]_4CO(C_6H_5C{=}C(H)R)]^+$ ($R = C_6H_5$ or CH_3). An analog containing methyldiphenylphosphine is also reported. A second type of cluster cation with the apparent formula $[Pt_3[P(C_6H_5)_3]_4]^+$ is obtained by reaction of the oxalato complex with hydrogen. Nitrate, fluoroborate, and fluorophosphate salts of these cations have been isolated. In order to characterize these compounds and elucidate the path of their formation, some reactions of carbonatobis(triphenylphosphine)platinum(II) with carbon monoxide and acetylenes and reactions of platinum(0)–acetylene complexes with carbon monoxide and acids have been investigated.

Investigation of the chemistry of the tertiary phosphine–carbon monoxide–platinum system has produced a number of cluster compounds containing two, three or four platinum atoms per molecule.[2,3] More recently, mixed clusters containing platinum and the iron group metals have been reported.[4] These reports foretell a rich area for further study. A general feature of these compounds is the nonadherence to the 18-electron rule.[2a,3,4] A second trend, in the case of the clusters containing only platinum, is lability with respect to dissociation into monomers in the presence of added ligands and facile equilibria between cluster types.[2a] Two clusters formulated as $[Pt_3(PPh_3)_4(CO)_2(PhC{\equiv}CPh)]$ and $[Pt_4(PPh_3)_5(CO)_3]$ obtained *via* photochemical reactions of oxalatobis(triphenylphosphine)platinum(II) did not show this lability.[3] The latter compound can be recovered after refluxing overnight with triphenylphosphine and the nature of the former is not altered by the same treatment. The synthesis of these compounds in high yield is not critically sensitive to concentration, reaction time, temperature, and other variables as are most of the other known platinum(0) clusters.[2a] These intriguing differences have prompted us to investigate the nature of these compounds further. This has led to the reformulation of the clusters reported by Blake and Nyman as the first cationic clusters in the Pt–CO–PR$_3$ system. As part of this study some reactions of other carboxylato–platinum(II) complexes in alcohols have been investigated in order to elucidate the steps in the formation of the cluster compounds. This has made possible generalizations which help to clarify the chemistry of these complexes in alcoholic solvents.[5,6]

Results

Reactions of Carbonato–Platinum(II) Complexes.—Carbonato–platinum(II) complexes containing tertiary phosphines or arsines are reduced to platinum(0) species in alcoholic solvents.[6] Disubstituted acetylenes, carbon monoxide, and ethylene react with the carbonato complex in ethanol to give known platinum(0) adducts (reactions 1, 2, and 3; $L = P(C_6H_5)_3$). In

$$L_2PtCO_3 + PhC{\equiv}CPh \longrightarrow L_2Pt(PhC{\equiv}CPh) \qquad (1)$$

$$L_2PtCO_3 + CO \longrightarrow L_2Pt(CO)_2 + \underset{1}{PtL_2[C(O)OEt]_2} \qquad (2)$$

$$L_2PtCO_3 + C_2H_4 \longrightarrow L_2Pt(C_2H_4) \qquad (3)$$

contrast to oxalato complexes, the carbonato complex reacts in the dark with diphenylacetylene in a carbon monoxide atmosphere to give a mixture of products (reaction 4) whose composition depends on the relative amounts of added ligands that are present. The un-

$$L_2PtCO_3 + PhC{\equiv}CPh + CO \xrightarrow{EtOH} L_2Pt(CO)_2 + L_2Pt(PhC{\equiv}CPh) + L_2Pt[C(O)OEt]_2 \qquad (4)$$

usual diethoxycarbonyl complex (1) is obtained in low yield from all the reactions of the carbonato complex in which carbon monoxide is a reactant. This shows the characteristic $\nu(C{=}O)$ at 1630 cm^{-1} and C–O–C bending mode at 1015 cm^{-1} of the alkoxycarbonyl group.[5] Molecular weight and nmr data also support this formulation of **1**. In reaction 2 the yield of carbon dioxide is 1.8 mol/mol complex compared to 1.0 mol/mol complex under nitrogen indicating that the carbon monoxide functions in part as the reducing agent. In other reactions acetaldehyde can be detected by isolation of its 2,4-dinitrophenylhydrazone indicating the ethanol is being oxidized. As is expected[7] there is a rapid equilibrium between the dicarbonyl and acetylene adducts.

Reactions of Oxalato–Platinum(II) Complexes in Ethanol.—The complex oxalatobis(triphenylphosphine)platinum(II) (**2**) undergoes no reaction alone or in the presence of acetylenes in ethanol in the dark.[3] It does react with carbon monoxide in the dark (reaction 5,

$$PtL_2C_2O_4 + CO \xrightarrow[50^\circ]{EtOH} PtL_2(CO)_2 \qquad (5)$$

$L = P(C_6H_5)_3$) to give the dicarbonyl complex. In mixtures of disubstituted acetylenes and carbon monoxide bright yellow cluster compounds are obtained (reaction 6). Cluster compound **3** was previously ob-

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[1] Undergraduate research participant supported by the University Organized Research Fund.

[2] (a) J. Chatt and P. Chini, *J. Chem. Soc. A*, 1538 (1970); (b) R. D. Gillard, R. Ugo, F. Cariati, S. Cenini, and F. Bonati, *Chem. Commun.*, 869 (1969).

[3] D. M. Blake and C. J. Nyman, *J. Amer. Chem. Soc.*, **92**, 5359 (1970).

[4] M. I. Bruce, G. Shaw, and F. G. A. Stone, *Chem. Commun.*, 1268 (1971).

[5] D. M. Barlex, R. D. W. Kemmitt, and G. W. Littlecott, *ibid.*, 613 (1969).

[6] D. M. Blake and R. Mersecchi, *ibid.*, 1045 (1971).

[7] A. D. Allen and C. D. Cook, *Can. J. Chem.*, **42**, 1063 (1964).

$$2 + \mathrm{PhC{\equiv}CR} + \mathrm{CO} \xrightarrow[90^\circ]{\mathrm{EtOH}} [\mathrm{Pt_3L_4(CO)(RC{=}C(H)Ph)}]^+,\mathrm{C_2O_4Et^-} +$$

$$\mathbf{3},\ \mathrm{L} = \mathrm{P(C_6H_5)_3};\ \mathrm{R} = \mathrm{C_6H_5}$$

$$\mathbf{4},\ \mathrm{L} = \mathrm{P(C_6H_5)_3};\ \mathrm{R} = \mathrm{CH_3}$$

$$\mathit{trans}\text{-}\mathrm{Ph(H)C{=}C(Ph)CO_2Et} \quad (6)$$

tained *via* a photochemical reaction and formulated as $[Pt_3L_4(CO)_2(PhC{\equiv}CPh)]$.[3] In the earlier report a strong, sharp ir band at 2040 cm^{-1} was assigned to a terminal carbonyl group and weaker band at 1780 cm^{-1} to a bridging carbonyl group. It has now been found that compounds **3** and **4** are in fact ionic and may be converted to nitrate, tetrafluoroborate, or hexafluorophosphate salts (reaction 7). Upon conversion to

$$[\mathrm{Pt_3L_4(CO)(RC{=}C(H)Ph)}]^+,\mathrm{C_2O_4Et^-} + \mathrm{NaY} \xrightarrow{\mathrm{MeOH}} [\mathrm{Pt_3L_4(CO)(RC{=}C(H)Ph)}]^+,\mathrm{Y^-} \quad (7)$$

$$\mathbf{3},\ \mathrm{L} = \mathrm{P(C_6H_5)_3};\ \mathrm{R} = \mathrm{C_6H_5}$$

$$\mathbf{4},\ \mathrm{L} = \mathrm{P(C_6H_5)_3};\ \mathrm{R} = \mathrm{CH_3}$$

$$\mathbf{a},\ \mathrm{Y} = \mathrm{BF_4};\ \mathbf{b},\ \mathrm{Y} = \mathrm{NO_3};\ \mathbf{c},\ \mathrm{Y} = \mathrm{PF_6}$$

these salts the band at 2040 cm^{-1} is not altered but the band at 1780 cm^{-1} no longer appears; however bands are present which are characteristic of the new anions (NO_3^-, 1350; BF_4^-, 1060; and PF_6^-, 840 cm^{-1}). The 1780-cm^{-1} band in the initial product is attributable to the presence of an anionic oxalato species[8] that acts as the counterion for the yellow cluster cation. Salts of the yellow cation can also be obtained by starting with other carboxylato complexes of platinum or by the reaction of acids of weakly coordinating anions with platinum(0) acetylene or carbonyl compounds (reaction 8). Acids such as acetic, fluoroboric, or fluorophosphoric acid can be used.

$$\mathrm{PtL_2(CO)_2} + \mathrm{PhC{\equiv}CPh} + \mathrm{CO} + \mathrm{HX} \xrightarrow{\mathrm{EtOH}} [\mathrm{Pt_3L_4(CO)(PhC{=}C(H)Ph)}]^+,\mathrm{X^-} \quad (8)$$

Hydrochloric acid gives only *cis*-dichlorobis(triphenylphosphine)platinum(II). In glacial acetic acid reaction 9 ($L = P(C_6H_5)_3$) is rapid

$$\mathrm{PtL_2(PhC{\equiv}CPh)} + \mathrm{CO} + \mathrm{PhC{\equiv}CPh} \xrightarrow{\mathrm{HC_2H_3O_2},\ 25^\circ} \mathbf{3}\ \text{(as the acetate salt)} + \mathrm{PtL_2(C_2H_3O_2)_2} \quad (9)$$

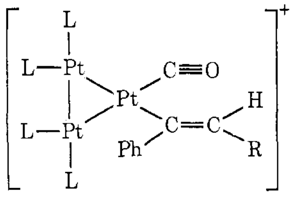
but the product is contaminated with the diacetato complex.

The salts of **3** and **4** are soluble in polar organic solvents but insoluble in benzene or ether. The conductivity of **3a** is consistent with its being a 1:1 electrolyte.[9] Degradation of **3a** by fusion with an excess of bis(diphenylphosphino)ethane (diphos) produces 1.3 mol of gas that will pass a 77°K trap, *trans*-stilbene, and bibenzyl (reaction 10). The gas in excess of the

$$\mathbf{3a} + \text{diphos} \xrightarrow{200^\circ} 1.3\ \text{mol gas} + \mathit{trans}\text{-}\mathrm{PhHC{=}CHPh} + \mathrm{PhH_2CCH_2Ph} \quad (10)$$

predicted 1 mol may be hydrogen. The presence of labile hydrogen in the reaction is consistent with the formation of alkane and alkene rather than diphenylacetylene. Reaction of **3b** with hydrogen chloride in methylene chloride also produces *trans*-stilbene and some bibenzyl. The residue of this reaction shows a strong $\nu(C{\equiv}O)$ absorption at 2105 cm^{-1}.

The proton nmr spectra for compound **4a** show the presence of phenyl, vinyl, and methyl protons in the correct ratio. The appearance of the two resonances in the methyl region indicates that the isomers with the vinyl methyl α or β to the platinum may both be present, or that cis and trans isomers may be present. The predominant form has not been established. The spectrum of compound **3a** shows only the phenyl resonance, which obscures the region in which the vinyl peak should appear. The results of this study lead us to propose a triangle of platinum atoms for the yellow cluster cation.



3, $L = P(C_6H_5)$; $R = C_6H_5$
4, $L = P(C_6H_5)$; $R = CH_3$

The vinyl group is assumed to be cis as in other known platinum(II)–vinyl complexes.[10] In accord with the position of $\nu(C{\equiv}O)$ in the ir, the carbonyl group is attached to a formally cationic platinum center. Due to the inherent dangers in assigning structures to cluster compounds in the absence of an X-ray study those proposed here must be considered tentative.

In an attempt to obtain more structural information the analog of **3c** containing methyldiphenylphosphine was synthesized *via* reaction 11. The bright yellow

$$\mathrm{PtL'_2C_2O_4} + \mathrm{CO} + \mathrm{PhC{\equiv}CPh} \xrightarrow[60^\circ]{\mathrm{EtOH}} [\mathrm{Pt_3L'_5(CO)(PhC{=}CHPh)}]^+,\mathrm{C_2O_4Et^-} \quad (11)$$

$$\big\downarrow \mathrm{PF_6^-},\ \mathrm{MeOH}$$

$$[\mathrm{Pt_3L'_5(CO)(PhC{=}CHPh)}]^+,\mathrm{PF_6^-}$$

$$\mathbf{5},\ \mathrm{L'} = \mathrm{PCH_3(C_6H_5)_2}$$

compound, **5**, was shown to be pure by thin layer chromatography. It has a strong band at 2030 cm^{-1}. The shift to lower energy is consistent with the reduced electronegativity of the methyl substituted phosphine. Elemental analysis showed an L′:Pt ratio of 5:1 in contrast to 4:1 for compounds **3** and **4**. In marked contrast to the nmr spectra of other platinum clusters containing this ligand there appears a series of sharp resonances in the methyl region. The spectrum at 100 MHz can be resolved into four overlapping triplets of doublets and a singlet. The triplets of doublets are clearly due to the coupling of methyl protons to one phosphorus and one platinum. These five resonances each correspond to three protons. The reason that one methyl resonance appears as a singlet is not clear. Addition of methyldiphenylphosphine to the nmr sample obscures part of the spectrum; however, the multiplets that are not overlapped remain unchanged. Notably, the free ligand resonance appears at τ 8.27 $J(P\text{–}H) = 4$ Hz. This nmr spectrum is consistent with the lack of symmetry in the structure proposed for clusters **3**, **4**, and **5**. The fifth phosphine in

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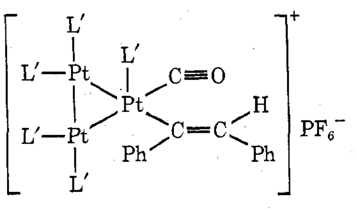
[8] In reaction 6 this is shown as monoethyl oxalate but we have not sought to establish the nature of the anion in the crude products.

[9] W. J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971).

[10] B. E. Mann, B. L. Shaw, and N. I. Tucker, *Chem. Commun.*, 1333 (1970).

compound **5** is postulated to be at the carbonyl-substituted platinum atom.



5, $L' = PCH_3(C_6H_5)_2$

The addition of methyldiphenylphosphine to a solution of **3a** in methylene chloride causes the color to change from yellow to orange but does not detectably alter the ir spectrum over the period of 2 days. An nmr spectrum of **3a** plus methyldiphenylphosphine in dimethyl sulfoxide-d_6 shows only a broad unresolved hump in the methyl region. The spectrum of the sample was constant for 3 days at room temperature.

The observation of the hydrocarboxylation of the excess diphenylacetylene in reaction 6 suggested that the cation in compound **3** might be a catalyst for this process.[11] Reaction of diphenylacetylene with carbon monoxide at 80° for 4 days in the presence of salt **3a** gave about 10% conversion to the α-phenylcinnamate ester.

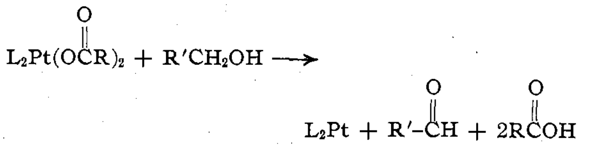
The photochemical reaction[12] of oxalato complex **2** with hydrogen in ethanol (reaction 12, $L = P(C_6H_5)_3$) produces a cluster previously formulated as $[Pt_4L_5(CO)_3]$.[3] This was based on the assignment of an ir band at 1780 cm⁻¹ to the presence of bridging carbonyl groups. As in the case of compounds **3** and **4** this band disappears when **6** is converted to the fluoroborate or nitrate salt. Salts **6a** and **6b** can be crystallized as golden yellow needles from acetone or acetonitrile. The compounds show no ir bands other than those attributable to triphenylphosphine. The nmr spectrum of **6a** (τ 2–32) shows only a resonance due to the phenyl groups. Treatment of **6a** with carbon monoxide in methylene chloride gives rise to carbonyl bands at 2070 (m), 2040 (s), and 1820 (s) cm⁻¹ in the ir. Conductivity measurements are consistent with the salt being a 1:1 electrolyte; treatment of the solution with carbon monoxide does not alter the conductivity. Fusion with diphos at 240° produces only a trace of gas. Reaction with carbon tetrachloride did not result in the formation of chloroform. The significance of this result is questionable since the compound is not soluble in carbon tetrachloride. Attempts to prepare the methyldiphenylphosphine analog of **6** gave a mixture of products that could not be satisfactorily separated. This mixture showed a number of discrete peaks in the methyl region of the nmr spectrum.

$$\mathrm{PtL_2C_2O_4} + \mathrm{H_2} \xrightarrow[45^\circ]{h\nu} [\mathrm{Pt_3L_4}]^+,\mathrm{C_2O_4Et}^- \xrightarrow{\mathrm{NaY}} [\mathrm{Pt_3L_4}]^+,\mathrm{Y}^- \qquad (12)$$

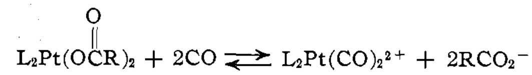
2 **6** **6a**, $Y = BF_4$
6b, $Y = NO_3$

Discussion

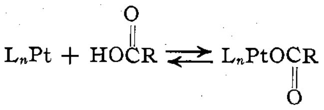
Cationic cluster compounds represent only a small fraction of transition metal clusters that have been prepared, anionic ones being much more numerous.[13] The new members of this small group of compounds that are reported here arise only when a proton acid is available in the preparative medium. The reactions of the carbonato and oxalato complexes and of other carboxylato complexes[5,6] in ethanol can be considered as examples of base induced reduction of platinum metal complexes by alcohols.[14] The carboxylate ion acts as the base in the reduction (eq 13). Reaction of the carboxylato complexes with carbon monoxide very likely involves the formation of cationic carbonyl complexes (eq 14) which may subsequently be converted to platinum(0) species and carbon dioxide.[15] This path is supported by the isolation of the diethoxycarbonyl complex, **1**, as was pointed out by the referees. Depending on the relative basicity of the resulting platinum(0) species and carboxylate ion, an equilibrium can be established[16] (eq 15). Similar equilibria have been studied for iridium(I) complexes.[17] This protonation can account for the formation of the vinyl complexes **3**, **4**, and **5** if the platinum(0) species is an acetylene complex. Similar protonations are known for monomeric platinum–acetylene complexes.[5,10,18] The difference between the reactions of the carbonato complex with carbon monoxide and acetylenes (reaction 4) and that of the oxalato complex, or other carboxylato complexes (reaction 6), is the result of the instability of the carbonic acid formed in the former case. It decomposes leaving no acid to act as a proton donor. The necessity of the protonation step in the formation of the yellow cluster cations and probable intermediacy of platinum(0) species in their formation *via* carboxylato complexes is shown by the preparative sequence involving $Pt(PPh_3)_2(PhC{\equiv}CPh)$. Reaction with carbon monoxide and excess diphenylacetylene in ethanol produces only an equilibrium mixture of the monomeric dicarbonyl and acetylene complexes. This mixture can rapidly be converted to the yellow cation by addition of an acid with a noncoordinating anion.



$$\mathrm{L_2Pt(O\overset{O}{\overset{\|}{C}}R)_2 + R'CH_2OH \longrightarrow L_2Pt + R'\text{-}\overset{O}{\overset{\|}{C}}H + 2R\overset{O}{\overset{\|}{C}}OH} \qquad (13)$$



$$\mathrm{L_2Pt(O\overset{O}{\overset{\|}{C}}R)_2 + 2CO \rightleftharpoons L_2Pt(CO)_2{}^{2+} + 2RCO_2{}^-} \qquad (14)$$



$$\mathrm{L_nPt + HO\overset{O}{\overset{\|}{C}}R \rightleftharpoons L_nPtO\underset{\underset{O}{\|}}{C}R} \qquad (15)$$

A platinocyclobutenone complex, $[(PPh_3)_2PtC(O)C(Ph){=}CPh]$, has been found to arise by insertion of platinum(0) into the diphenylcyclopropenone ring.[19]

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[11] C. W. Bird, "Transition Metal Intermediates in Organic Synthesis," Academic Press, New York, N. Y., 1967.

[12] Complex **2** will react with hydrogen in ethanol at 90° but the reaction mixture proved less tractable in our hands than that obtained *via* photolysis.

[13] R. D. Johnston, *Advan. Inorg. Chem. Radiochem.*, **13**, 471 (1970).

[14] J. Chatt, B. L. Shaw, and A. E. Field, *J. Chem. Soc.*, 3466 (1964).

[15] H. C. Clark, K. R. Dixon, and W. J. Jacobs, *J. Amer. Chem. Soc.*, **91**, 1346 (1969).

[16] K. Thomas, J. T. Dumler, B. W. Renoe, C. J. Nyman, and D. M. Roundhill, *Inorg. Chem.*, **11**, 1795 (1972).

[17] A. J. Deeming and B. L. Shaw, *J. Chem. Soc. A*, 1802 (1969).

[18] P. B. Tripathy, B. W. Renoe, K. Adzamli, and D. M. Roundhill, *J. Amer. Chem. Soc.*, **93**, 4406 (1971).

[19] W. Wong, S. J. Singer, W. D. Pitts, S. F. Watkins, and W. H. Baddley, *J. Chem. Soc., Chem. Commun.*, 672 (1972).

Notably it was not detected in reactions of the diphenylacetylene complex with carbon monoxide where it might be expected to arise by insertion of carbon monoxide into the platinum–carbon bond.

The nature of the orange cation in **6a** and **6b** is not yet known. Analytical and other data are in accord with the formula given. The necessity for hydrogen in the formation of **6** and the deficiency of ligands in the formula suggest that the orange ion may be a hydride. This would also account for the apparent diamagnetism of the compound. In the absence of direct evidence for a hydride or for the presence of other ligands it is most prudent to leave the question of a structure for **6** open.

The path by which the diphenylacetylene is hydrocarboxylated in reaction 6 is not yet known. The vinyl–carbonyl cluster, **3**, is an attractive intermediate[11] and this is supported by formation of ethyl *trans*-α-phenylcinnamate in its reaction with the acetylene, carbon monoxide, and oxalic acid in ethanol. However conditions where the clusters **3**, **4**, or **5** will act as effective catalysts for this reaction have not yet been found. The possibility that platinum(II) carboxylates will oxidize substrates other than carbon monoxide and alcohols is also under investigation.

Experimental Section

The complexes $Pt[P(C_6H_5)_3]_2CO_3$,[20] $Pt[P(C_6H_5)_3]_2C_2O_4$,[3] $Pt[PCH_3(C_6H_5)_2]_4$,[21] $Pt[P(C_6H_5)_3]_2(C_6H_5C{\equiv}CC_6H_5)$,[22] and $Pt[P(C_6H_5)_3]_2(CO)_2$[23] were prepared by methods previously described. The acetylenes used were checked for purity by glc analysis. Infrared spectra were recorded on a Perkin-Elmer Model 257 instrument. Proton nmr spectra were obtained on Varian T-60 and HA-100 spectrometers. Gas chromatographic analyses were performed on a Perkin-Elmer F-11 instrument. Nitrogen and carbon monoxide used in carbon dioxide analysis[3] were purified by passage through a column of Ascarite. Conductivities were measured in nitromethane in a cell with a constant of 0.84 and compared with conductivities of sodium tetraphenylborate (Λ_M = 86.2 mho cm^2 mol^{-1}) and tetraphenylarsonium chloride (Λ_M = 87.5 mho cm^2 mol^{-1}) measured in the same cell. Molecular weights were determined with a Mechrolab osmometer. The new compounds were checked for purity by chromatography on silica gel plates using ethanol or isopropyl alcohol as the liquid phase. Microanalyses were performed by Galbraith Laboratory, Knoxville, Tenn. Analytical and infrared data are presented in Table I.

Carbonatobis(methyldiphenylphosphine)platinum(II).—A solution of 13 g of tetrakis(methyldiphenylphosphine)platinum(0) in 130 ml of benzene was treated with oxygen and carbon dioxide for 3 hr. The colorlesss precipitate was recovered and washed with benzene and ether; yield 5.1 g (60%). The product was recrystallized from methylene chloride–*n*-hexane to which 0.5 ml of methyldiphenylphosphine had been added.

Oxalatobis(methyldiphenylphosphine)platinum(II).—A suspension of 2.4 g of the carbonato complex in a solution of 0.5 g of oxalic acid in 15 ml of ethanol was stirred for 36 hr. Filtration gave 2.2 g (82%) of the colorless solid. This was recrystallized from 150 ml of ethanol to give the complex as its ethanol solvate. Nmr: τ 2.64 (m, C_6H_5), 8.92 (triplet of doublet, J(P–H) = 12 Hz, J(Pt–H) = 28 Hz, P–CH_3), 7.1 (q, CH_2–CH_3), 9.55 (t, CH_2–CH_3).

Di(ethoxycarbonyl)bis(triphenylphosphine)platinum(II) (1).—A suspension of 0.63 g of carbonatobis(triphenylphosphine)platinum(II) in ethanol was stirred in a carbon monoxide atmosphere (10 psi) at 50° for 25 hr. Filtration gave 0.51 g of cream colored powder. This was shown by ir to be predominantly dicarbonylbis(triphenylphosphine)platinum(0). The presence of the ethoxycarbonyl product was indicated by a sharp band at 1630 cm^{-1}. The product mixture was extracted with *n*-hexane (40 ml) and the resulting orange solid[24] stirred with 25 ml of warm acetone. The complex is then recovered as a white powder by filtration, yield 0.1 g. This can be recrystallized from benzene–*n*-hexane. Nmr ($CDCl_3$): τ 2.64 (m, 30, $P(C_6H_5)_3$), 7.14 (q, 4, J = 7 Hz, CH_2), 9.63 (t, 6, J = 7 Hz, CH_3). Mol wt ($CHCl_3$): found, 960; calcd, 866. During the reaction with carbon monoxide about 1.8 mol of carbon dioxide is evolved in contrast to about 1.0 mol when the reaction is run under nitrogen.

Reactions of Carbonatobis(triphenylphosphine)platinum(II).—Refluxing 0.25 g of the carbonato complex with 0.25 g of diphenylacetylene in ethanol in an inert atmosphere for 4 hr yields 0.26 g of diphenylacetylenebis(triphenylphosphine)platinum(0).

Reaction of 0.4 g of the carbonato complex in ethanol at 40° in an ethylene atmosphere (1.5 atm) for 4 days gives 0.2 g (50%) of ethylenebis(triphenylphosphine)platinum(II).

General Method for Synthesis of the Vinyl–Carbonyl Cluster Compounds 3 and 4 from Oxalatobis(triphenylphosphine)platinum(II). $\{Pt_3[P(C_6H_5)_3]_4(CO)(C_6H_5C_2HC_6H_5)\}^+,Y^-$ (3a, 3b, and 3c).—The oxalato complex, 1.5 g (1.85 mol), and 0.5 g of diphenylacetylene (2.7 mmol) were placed in a 210-ml "pop" bottle fitted with a cap and Buna N liner. The bottle was thoroughly purged with carbon monoxide *via* syringe needle and 30 ml of ethanol was added. The mixture was stirred at 80° for 5 days. The resulting clear, lemon yellow solution was evaporated to a thick oil and this left to stir under 50 ml of ether overnight. The resulting yellow powder contains the product, as an oxalate salt, plus some starting material. The crude yield is 1.2 g. The ether extract was saved for glc analysis which showed that the excess diphenylacetylene had been converted to ethyl *trans*-α-phenylcinnamate, which was identified by comparison of its ir spectrum and retention time with those of an authentic sample.

The crude product can be converted to the BF_4^- (**3a**), NO_3^- (**3b**), or PF_6^- (**3c**) salt by the following procedure. The crude product, 0.6 g, was stirred in 8 ml of methanol. The suspension was filtered to remove any unreacted oxalato complex that was present. A solution of sodium fluoroborate (0.5 g in 3 ml of H_2O) was added dropwise to the clear filtrate with vigorous stirring until the yellow precipitate persisted. Filtration, after 2 hr, gave 0.4 g of product. This was washed with ether and water and then dried *in vacuo* overnight. These salts can be recrystallized from warm acetonitrile or acetone solution by the addition of *n*-hexane up to the cloud point. The compounds were found to be pure by thin layer chromatography on silica gel.

The same procedure using 1-phenyl-1-propyne is followed in the preparation of the methyl substituted vinyl compounds (**4a**, **4b**, and **4c**). **3a** nmr (C_2D_6SO): τ 2.84 (m, C_6H_5),[25] $\Lambda_M(CH_3NO_2)$ 118 mho cm^2 mol^{-1}; **4a** nmr (C_2D_6SO): τ 2.85 (m, 65, C_6H_5), 4.62 (m, 1, vinyl H), 8.44 (apparent broad triplet, 3, J(Pt–H) = 10 Hz, CH_3) and 8.90 (apparent triplet, 0.2, J(Pt–H) = 14 Hz, CH_3).

$\{Pt_3[P(C_6H_5)_2CH_3]_5(CO)[C_6H_5)_2C_2H]\}^+,PF_6^-$ (5).—A solution of 1.0 g of oxalatobis(methyldiphenylphosphine)platinum(II) and 0.5 g of diphenylacetylene in 30 ml of ethanol was stirred at 70° under carbon monoxide (10 psi) for 60 hr. The clear yellow solution[26] was evaporated to a thick oil and this extracted with three 30-ml portions of ether. The resulting yellow, sticky residue was dissolved in 5 ml of methanol containing 0.05 g of diphenylacetylene. After filtration to remove cloudiness, a fresh aqueous solution of ammonium fluorophosphate was added dropwise with vigorous stirring until the precipitate persisted. The mixture was then refrigerated for 2 hr. The mixture was filtered and the product washed with a cold water–methanol mixture (25:75), then with water, and dried *in vacuo*. Chromatography on silica gel plates, eluting with ethanol or isopropyl alcohol showed only one component to be present. The compound can be recrystallized from methanol. **5** nmr ($CDCl_3$): τ 2.80 (m, 60, C_6H_5), 4.0 (triplet of doublets, 1, J(P–H) = 5 Hz, J(Pt–H) = 28 Hz, vinyl H), 7.34 (triplet of doublets, 3, J(P–H) = 9.5 Hz, J(Pt-H) = 46 Hz, P–CH_3), 7.95 (triplet of doublets, 3, J(P–H) = 7.0 Hz, J(Pt–H) = 22 Hz, P–CH_3), 8.12 (s, 3, P–CH_3), 8.42 (triplet of doublets, 3, J(P–H) = 8.0 Hz, J(Pt–H) = 36 Hz, P–

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(24) This solid contains a mixture of **1** and $[Pt_3(CO)_3[P(C_6H_5)_3]_4]$.[1]

(25) The resonance of the vinyl proton was obscured by the phenyl signal.

(26) In some preparations, using longer reaction times, an orange solution was obtained. Addition of diphenylacetylene would give an immediate return to the yellow color.

TABLE I

ANALYTICAL AND INFRARED DATA

No.	Compound	Mp,[a] °C	Analytical data[b]					ν(CO)[c]
			C	H	P	N	B	
	$Pt[P(C_6H_5)_2CH_3]_2CO_3$	206–208	49.48 (49.47)	3.97 (3.97)				*d*
	$Pt[P(C_6H_5)_2CH_3]_2C_2O_4 \cdot C_2H_5OH$	276–277	49.54 (49.39)	4.42 (4.42)				*e*
1	$Pt[P(C_6H_5)_3]_2[C(O)OC_2H_5]_2$	198–202	58.78 (58.26)	4.89 (4.66)	6.44 (7.15)			*f*
3a	$\{Pt_3[P(C_6H_5)_3]_4(CO)[(C_6H_5)_2C_2H]\}^+,BF_4^-$	163–166	54.33 (54.64)	3.85 (3.74)	6.00 (6.48)		0.50 (0.57)	2040
3b	$\{Pt_3[P(C_6H_5)_3]_4(CO)[(C_6H_5)_2C_2H]\}^+,NO_3^-$	154–156	55.52 (54.89)	3.98 (3.76)	6.29 (6.51)	0.67 (0.74)		2040
3c	$\{Pt_3[P(C_6H_5)_3]_4(CO)[(C_6H_5)_2C_2H]\}^+,PF_6^-$	163–180	54.18 (52.60)	3.45 (3.60)	8.00 (7.89)			2040
4a	$\{Pt_3[P(C_6H_5)_3]_4(CO)[(C_6H_5)C_2(H)CH_3]\}^+, BF_4^-$	195–196	54.52 (53.28)	3.76 (3.76)	6.11 (6.69)		0.22 (0.59)	2040
4b	$\{Pt_3[P(C_6H_5)_3]_4(CO)[(C_6H_5)C_2(H)CH_3]\}^+, NO_3^-$	145–152	55.40 (53.48)	4.14 (3.78)	6.92 (6.73)	0.86 (0.76)		2040
4c	$\{Pt_3[P(C_6H_5)_3]_4(CO)[(C_6H_5)C_2(H)CH_3]\}^+, PF_6^-$	185–189	53.07 (51.17)	3.59 (3.61)	7.99 (8.05)			2040
5	$\{Pt_3[P(C_6H_5)_2CH_3]_5(CO)[(C_6H_5)_2C_2H]\}^+, PF_6^-$	94–101	50.11 (49.57)	3.99 (3.95)	10.01 (9.59)			2030
6a	$\{Pt_3[P(C_6H_5)_3]_4\}^+,BF_4^-$	246–248	50.96 (50.24)	3.58 (3.51)	6.45 (7.20)		0.70 (0.63)	
6b	$\{Pt_3[P(C_6H_5)_3]_4\}^+,NO_3^- \cdot CH_3C(O)CH_3$	186–187	52.08 (51.34)	3.78 (3.79)	7.84 (7.06)	0.70 (0.80)		*g*

[a] In evacuated tubes. The cluster compounds all showed signs of decomposition before melting. [b] Calculated values in parentheses. The C–H analyses are generally averages of two or three determinations. [c] Methylene chloride solution. [d] Ir(Nujol) Pt–CO_3: 1670 (vs), 1630 (m), 1290 (s), 985 (m), and 820 (m) cm^{-1}. [e] Ir(Nujol) Pt–C_2O_4: 1705 (vs), 1680 (vs), 1660 (sh), 1370 (vs), and 790 (s) cm^{-1}. [f] Ir(Nujol) Pt–C(O)OEt: 1630 (vs) and 1015 (s) cm^{-1}. [g] Ir(CH_2Cl_2) ν(C=O) acetone: 1715 (vs) cm^{-1}.

CH_3), and 8.78 (triplet of doublets, 3, J(P–H) = 9.5 Hz, J(Pt–H) = 34 Hz, P–CH_3).

Reaction of Oxalatobis(triphenylphosphine)platinum(II) with Hydrogen.—The oxalato complex, 1.5 g, was suspended in 45 ml of ethanol in a hydrogen atmosphere (1.5 atm total hydrogen pressure) in a Vycor reaction tube. This was irradiated in a Rayonet RP-200 photoreactor using 3100 Å lamps for 6 days. The resulting clear, dark orange solution was evaporated to about 5 ml. Upon stirring for a few minutes under a nitrogen flow a heavy golden yellow precipitate formed. This was washed into a filter with 85:15 *n*-hexane–ethanol and the solid washed with that solvent mixture until washes were pale yellow. Yield of the golden yellow product as an oxalate salt is 0.6 g.

This can be converted to the BF_4^- (**6a**) or NO_3^- (**6b**) salt by the same procedure used for the vinyl-cluster compounds. These salts can be conveniently recrystallized from hot acetonitrile or acetone by addition of *n*-hexane, under nitrogen.[27] The salts were thus obtained as golden yellow needles. **6a** nmr (C_2D_6SO): τ 2.84 (m, C_6H_5). No other resonances were observed between τ 2 and 32, $\Lambda_M(CH_3NO_2)$ = 84.2 mho cm^2 mol^{-1}. Fusion of **6a** with diphos at 250° produces 0.07 mol of gas/mol of complex. Stirring 0.1 g of **6a** in 2 ml of carbon tetrachloride at 55° for 4 days produced no chloroform and left the complex unchanged.

Degradation of 3a.—The following experiments were performed. (1) Fusion of the BF_4^- salt, **3a**, at 200° with an excess of 1,2-bis(diphenylphosphino)ethane produced 1.2 mol of gas, not condensable at −196°. Analysis of the residue by glc showed the presence of *trans*-stilbene and bibenzyl in an approximate ratio of 5:1. (2) Reaction of 0.1 g of the NO_3^- salt, **3b**, in methylene chloride with hydrogen chloride gas gave a product with ν(C≡O) moved to 2105 cm^{-1} (vs). No band possibly due to hydride was observed. Analysis of the mixture by glc showed *trans*-stilbene and bibenzyl in an approximate ratio of 4:1. (3) A 0.03 g sample of the BF_4^- salt, **3a**, was allowed to stand with 0.05 g of triphenylphosphine in methylene chloride. The color of the solution changed from yellow to light orange but no change was observed in the ν(C≡O) region of the ir over a period of 30 hr. (4) Addition of 15 ml of methyldiphenylphosphine to a 10% solution of **3a** in DMSO-d_6 caused an immediate color change from yellow to orange. The nmr spectrum of this solution showed only a very broad hump in the methyl region.

Test of Compound 3a as a Catalyst for Hydrocarboxylation of Diphenylacetylene.—A solution of 0.05 g of **3a** (0.026 mmol), 0.05 g of diphenylacetylene (0.3 mmol), and 0.01 g of oxalic acid dihydrate (0.08 mmol) in 5 ml of ethanol was held at 85° in a carbon monoxide atmosphere (10 psi) for 4 days. Analysis showed approximately 10% conversion of the acetylene to ethyl *trans*-α-phenylcinnamate.

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[27] Recrystallization of the clusters from acetone results in inclusion of variable amounts of solvent in the product. This persists even after prolonged drying *in vacuo*.[2a]