Conclusions. This study has produced several molecular palladium(II) complexes that contain both N- and S-bonded thiocyanate ions. With the ligands PAs, PC_2N, and PC_3N, it is impossible to ascertain definitively whether the mixed mode of thiocyanate coordination is due to steric hindrance or to the *trans* electronic influences of the donor atom, since the predicted results are the same, and in agreement with the observations. With the ligands PP, SP, FSP, and SeP, steric considerations alone favor *two* S-bonded thiocyanate ions. Isolation of the stable, mixed complex $[Pd(C_{26}H_{24}P_2)(SCN)(NCS)]$ and the reversible isomerization of $[Pd(C_{26}H_{24}As_2)(SCN)_2]$ in solution illustrate the delicate balance of electronic, steric, and solvent forces that influence the nature of thiocyanate coordination in a given complex.

Acknowledgments. The authors are grateful to Professor John Burmeister for several helpful suggestions on the original version of this paper, and to Professor G. J. Palenik for determining the structures of [Pd(PP)(NCS)(SCN)] and $[Pd(PC_3N)(SCN)(NCS)]$ by X-ray three-dimensional crystallography.

Photochemical Reactions of Oxalatobis(triphenylphosphine)platinum(II) and Related Complexes[1]

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Abstract: The oxalato complexes $ML_2C_2O_4$ (M = Pt or Pd, L = $P(C_6H_5)_3$ or $As(C_6H_5)_3$) and $Pt(diphos)C_2O_4$ (diphos = 1,2-bis(diphenylphosphino)ethane) have been prepared and characterized. Irradiation of these complexes with ultraviolet light gives carbon dioxide and reduced metal-containing species. Photochemical reactions of oxalatobis(triphenylphosphine)platinum(II) have been studied in detail. Photolysis of this complex in ethanol solution, under an inert atmosphere, yields a dimeric complex of formula $Pt_2[P(C_6H_5)_3]_4$; in the presence of triphenylphosphine the known compound $Pt[P(C_6H_5)_3]_4$ is obtained; with a disubstituted acetylene, compounds of the known type $Pt[P(C_6H_5)_3]_2$(acetylene) are obtained, whereas with phenylacetylene a diacetylide complex, $Pt[P(C_6H_5)_3]_2(C_2C_6H_5)_2$, is formed; reaction in a hydrogen atmosphere leads to partial reduction of the oxalate ion and formation of a new cluster compound of platinum, $Pt_4[P(C_6H_5)_3]_5(CO)_3$; and reaction with disubstituted acetylenes in an atmosphere of carbon monoxide gives new cluster compounds containing acetylenes, $Pt_3[P(C_6H_5)_3]_4(CO)_2$(acetylene). Physical properties, structures, and reactions of these products are discussed. Mechanisms for the photochemical reactions are discussed and the results are interpreted in terms of the formation of the coordinatively unsaturated species $Pt[P(C_6H_5)_3]_2$ in the initial decomposition of the oxalate complex. The reaction in the presence of hydrogen gas appears to be a special case in which $Pt[P(C_6H_5)_3]_2CO$ is the initial product.

Since their discovery in 1957 and 1958, tertiary phosphine complexes of palladium(0)[2] and platinum(0)[3] have proven to be versatile reagents for the synthesis of a wide variety of compounds.[4] Interest has been spurred by the reactivity of these compounds toward unsaturated molecules, reactivity in oxidative addition reactions, and use as homogeneous catalysts for oxidations by molecular oxygen. Reactions of the triphenylphosphine complexes of platinum have been the most extensively studied.[4] In many of these reactions there is evidence that a coordinatively unsaturated species having the formula $Pt[P(C_6H_5)_3]_2$ is a reactive intermediate.[4-6] A compound of this formula has been isolated.[7] More commonly, reactions are used which produce this species *in situ*. Some of these are: dissociation of $Pt[P(C_6H_5)_3]_3$;[5] dissociation of the ethylene adduct, $Pt[P(C_6H_5)_3]_2C_2H_4$;[5,8] reduction of $Pt[P(C_6H_5)_3]_2O_2$ with sodium borohydride;[8] reduction of *cis*-$Pt[P(C_6H_5)_3]_2Cl_2$ with hydrazine;[9] and deprotonation of platinum(II) hydride complexes with strong bases.[7,10] The use of $Pt[P(C_6H_5)_3]_2$ as a reactant would be advantageous because of the absence of free triphenylphosphine or other reagents that may compete for coordination sites on the platinum.

Another aspect of platinum(0) chemistry which has recently attracted interest is the synthesis and characterization of cluster compounds of platinum containing phosphines and carbon monoxide as ligands. While the number of such compounds of transition metals is rapidly growing, only a few compounds of this type are known that contain platinum.[11-13] Preliminary

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(1) D. M. Blake and C. J. Nyman, *Chem. Commun.*, 483 (1969).

(2) L. Malatesta and M. Angoletta, *J. Chem. Soc.*, 1186 (1957).

(3) L. Malatesta and C. Cariello, *ibid.*, 2323 (1958).

(4) R. Ugo, *Coord. Chem. Rev.*, **3**, 319 (1968).

(5) (a) J. P. Birk, J. Halpern, and A. L. Pickard, *Inorg. Chem.*, **7**, 2672 (1968); (b) J. P. Birk, J. Halpern, and A. L. Pickard, *J. Amer. Chem. Soc.*, **90**, 4491 (1968).

(6) A. D. Allen and C. P. Cook, *Can. J. Chem.*, **42**, 1063 (1964).

(7) R. Ugo, F. Cariati, and G. La Monica, *Chem. Commun.*, 868 (1966).

(8) C. D. Cook, and G. S. Jauhal, *J. Amer. Chem. Soc.*, **90**, 1464 (1968).

(9) G. D. Dobinson, R. Mason, G. B. Robertson, R. Ugo, F. Conti, D. Morelli, S. Cenini, and F. Bonati, *Chem. Commun.*, 739 (1967).

(10) F. Cariati, R. Ugo, and F. Bonati, *Inorg. Chem.*, **5**, 1128 (1966).

(11) (a) G. Booth, J. Chatt, and P. Chini, *Chem. Commun.*, 639 (1965); (b) G. Booth and J. Chatt, *J. Chem. Soc. A*, 2131 (1969).

(12) F. Cariati, and R. Ugo, *Chim. Ind.* (*Milan*), **48**, 1288 (1966); *Chem. Abstr.*, **66**, 65618*q* (1967).

results of X-ray diffraction studies of two of these, $Pt_4[P(C_6H_5)(CH_3)_2]_4(CO)_5$ and $Pt_3[P(C_6H_5)_3]_4(CO)_3$, have shown the former to have a distorted tetrahedral arrangement of platinum atoms and the latter a triangular array.[14] No platinum cluster compounds containing coordinated acetylenes have been reported, though they exist for most other transition metals.[15] Monomeric complexes of disubstituted acetylenes of the type $Pt[P(C_6H_5)_3]_2$(acetylene) are quite stable.[6,16] The existence of low coordination number platinum species and the synthesis of platinum cluster compounds may be related since it has been suggested that the formation of platinum–phosphine–carbonyl clusters involves the condensation of monomeric, coordinatively unsaturated species.[17] Present methods of preparing platinum cluster compounds give low yields of products which are difficult to purify. This has hindered the study of reactions of these unusual compounds.[11b]

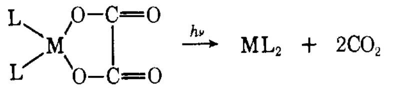
The known thermal and photochemical instability of some transition metal oxalato complexes[18] suggested another potentially useful method of preparing species of the type ML_2 (M = Pt or Pd, and L a tertiary phosphine or arsine ligand) *in situ*. Many examples of the photochemical decomposition of oxalato complexes of trivalent transition metal ions have been studied and the stoichiometry has been found to be (M′ = Fe, Co, or Mn)

$$2M'(C_2O_4)_3{}^{3-} \xrightarrow{h\nu} 2M'^{2+} + 5C_2O_4{}^{2-} + 2CO_2$$

This reaction is believed to occur *via* an initial one-electron photochemical reduction of one metal ion followed by a dark reaction in which an oxalate radical reduces a second metal ion.[18] No similar reaction has been reported for oxalate ion coordinated to a potential two-electron oxidizing agent. Nevertheless, it seemed that the reaction

$$M'(C_2O_4)^{3-} \xrightarrow{h\nu} M'^{2+} + \cdot C_2O_4{}^{-} + 2C_2O_4{}^{2-}$$

$$M'(C_2O_4)_2{}^{3-} + \cdot C_2O_4{}^{-} \longrightarrow M'^{2+} + 3C_2O_4{}^{2-} + 2CO_2$$



might be a reasonable method for the production of coordinatively unsaturated platinum(0) or palladium(0) species. Since carbon dioxide does not react with these zerovalent platinum or palladium complexes in the absence of oxygen,[19] the system would be free of competing ligands. To test this hypothesis the photochemical reactions of platinum and palladium oxalato complexes in solutions of the complexes alone and with added reagents were studied.

Results and Discussion

The oxalato complexes, having the general formula $[ML_2C_2O_4]$, were prepared by the reactions of excess of oxalic acid with the corresponding carbonato complex.

$$L_2MCO_3 + H_2C_2O_4 \cdot 2H_2O \longrightarrow L_2MC_2O_4 + CO_2 + 3H_2O$$

1, M = Pt; L = $P(C_6H_5)_3$
2, M = Pt; L = $As(C_6H_5)_3$
3, M = Pt; L_2 = $(C_6H_5)_2PC_2H_4P(C_6H_5)_2$ (diphos)
4, M = Pd; L = $P(C_6H_5)_3$

The oxalato complexes are monomeric in chloroform and the infrared bands attributable to the oxalato group are consistent with the oxalate ion acting as a bidentate ligand.[20] The electronic spectra of these complexes in the near-ultraviolet region are rather featureless, showing only the tail of a strong charge-transfer band. The spectra of compounds **2** and **4** show shoulders near 300 mμ which may be due to the lowest energy d–d bands. The oxalato complexes are stable indefinitely, as solids and in solution, in the absence of light. Exposure to light causes the solid compounds to darken in color and their solutions to decompose, giving metallic palladium in the case of compound **4** and dark orange to brown solutions in the case of the platinum complexes. The complexes are soluble in hot alcohols, acetonitrile, and chloroform but have limited solubility in organic solvents at room temperature. Ethanol was the solvent of choice for the photochemical reactions. Halogenated solvents were found to interfere in the photoreactions and were avoided in the preparation of the oxalato complexes to preclude their presence as contaminants.

Photolysis of ethanol solutions of the oxalato complexes caused the evolution of approximately 2 mol of carbon dioxide per mole of complex, as is shown in Table I. Blank determinations showed that no carbon dioxide was produced under identical conditions but in the absence of light. The production of carbon dioxide was accompanied by formation of a palladium mirror on the walls of the reaction vessel in the case of compound **4**. The platinum compounds **2** and **3** gave brown and yellow precipitates, respectively, which showed infrared bands characteristic of the coordinated arsine and phosphine ligands but these reactions were not investigated further. Only the photochemical

Table I. Yields of Carbon Dioxide and Benzene from Photochemical Reactions of the Oxalato Complexes

Reactants	Mol of CO_2/mol of complex[a,b]	Mol of C_6H_6/mol of complex
$Pt(PPh_3)_2C_2O_4$	1.98	0.3 ± 0.1
$Pt(AsPh_3)_2C_2O_4$	1.76	
$Pt(diphos)C_2O_4$	1.87	
$Pd(PPh_3)_2C_2O_4$	1.89	
$Pt(PPh_3)_2C_2O_4 + H_2$	0.87[c]	<0.05
$Pt(PPh_3)_2C_2O_4 + CO$		<0.05
$Pt(PPh_3)_2C_2O_4 + PPh_3$		2.0 ± 0.2

[a] The error in these values is ±2%. Traces of unreacted starting material could be detected after each of these reactions. [b] In the absence of light no CO_2 was evolved. [c] Under the same conditions, using an identical sample of the oxalate, except in a nitrogen atmosphere, 1.78 mol of CO_2 was obtained.

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(13) G. Booth and J. Chatt, *J. Chem. Soc. A*, 634 (1966).

(14) R. G. Vranka, L. F. Dahl, P. Chini, and J. Chatt, *J. Amer. Chem. Soc.*, **91**, 1574 (1969).

(15) F. L. Bowden, and A. B. P. Lever, *Organometal. Chem. Rev.*, **3**, 227 (1968).

(16) E. O. Greaves, C. J. L. Lock, and P. M. Maitlis, *Can. J. Chem.*, **46**, 3879 (1968).

(17) P. Chini, *Inorg. Chim. Acta Rev.*, **2**, 31 (1968).

(18) A. W. Adamson, W. L. Waltz, E. Zinato, D. W. Watts, P. Fleischauer, and D. Lindholm, *Chem. Rev.*, **68**, 541 (1968).

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

(20) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley, New York, N. Y., 1963, p 211.

reactions of **1** were studied in detail. Oxygen was rigorously excluded from the reaction mixtures during photolysis since its presence resulted in the formation of dark brown intractable product mixtures.

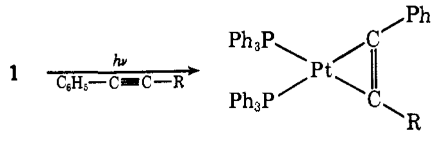
The photolysis of **1** in ethanol gave a bright yellow product (**5**) which is stable in air, in the solid state, and

$$\underset{\mathbf{1}}{Pt[P(C_6H_5)_3]_2C_2O_4} \xrightarrow{h\nu} \underset{\mathbf{5}}{Pt_2[P(C_6H_5)_3]_4}$$

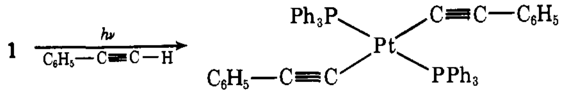
can be recrystallized from benzene. A compound of the same formula has been reported to be a product of the thermal decomposition of $Pt[P(C_6H_5)_3]_2SO_2$ but no details were given.[21] Molecular weight determination in benzene indicated the complex **5** to be dinuclear. The infrared, mass, and proton nmr spectra of **5** had only features which are characteristic of coordinated triphenylphosphine. Notably, there was no infrared band or nmr signal which would indicate the presence of a hydride bonded to platinum. Decomposition of **5** by aqueous potassium cyanide yields triphenylphosphine and, in some samples, traces of diphenylphosphine (about 2% by weight). Benzene solutions of **5** do not react with oxygen and carbon dioxide to give a carbonato complex as do monomeric platinum(0) complexes of phosphines and arsines,[18] and prolonged heating of **5** with triphenylphosphine in ethanol does not cause its decomposition. Because triphenylphosphine has not been found to act as a bridging ligand,[22] it is most reasonable to formulate **5** as a dimer with a platinum–platinum bond. Failure to isolate the monomer PtL_2 very likely reflects the instability of this species under the conditions of reaction.[7]

$$\mathbf{1} \xrightarrow[CHCl_3]{h\nu} cis\text{-}Pt[P(C_6H_5)_3]_2Cl_2$$

$$\mathbf{1} \xrightarrow[P(C_6H_5)_3]{h\nu} Pt[P(C_6H_5)_3]_4$$



6a, R = Ph
6b, R = Et



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Photochemical reactions of **1** in the presence of chloroform, triphenylphosphine, diphenylacetylene, and phenylethylacetylene gave known compounds which were identified by comparison of their physical and chemical properties with those of authentic samples. The oxalato complex, **1**, does not react with these reagents in the absence of light. In contrast to the reaction of **1** with disubstituted acetylenes to give products containing one acetylene molecule per platinum (**6a**, **6b**), the reaction with phenylacetylene gave a product incorporating two acetylenic moieties per platinum (**7**). This complex is monomeric in chloroform and shows an infrared band at 2130 cm^{-1} which is assigned to ν(C≡C) of the coordinated acetylide ligands. The proton nmr spectrum does not show resonances due to an acetylenic proton or a hydride ion. The *trans* configuration for the complex shown was assigned by analogy with the structures of other known platinum acetylide complexes.[23,24] The *cis* and *trans* forms of this compound have been prepared by reaction of the corresponding chloro complex with the sodium salt of the acetylene.[24a] These were found to be catalysts for the linear polymerization of phenylacetylene.[24b] Under the conditions of the photochemical preparation, compound **7** probably arises from an oxidative addition–reductive elimination sequence wherein two molecules of the acetylene add to give a platinum(IV) dihydride–diacetylide complex which then eliminates H_2 to give the observed product. Formation of a stable platinum(IV) dihydride by oxidative addition of terminal acetylenes to platinum(0) complexes has been reported.[25]

The most unusual reactions of compound **1** are those which give cluster compounds of platinum. When **1** is photolyzed either with hydrogen gas bubbling through the mixture or under an atmosphere of hydrogen, the reaction mixture becomes orange and a golden yellow product (**8**) can be isolated from the solution in high yield (75%). During the reaction only about 1 mol of

$$\mathbf{1} \xrightarrow[H_2]{h\nu} \underset{\mathbf{8}}{Pt_4[P(C_6H_5)_3]_5(CO)_3} + 4CO_2$$

carbon dioxide per mole of the oxalato complex is evolved (Table I). Compound **8** is stable indefinitely both in solution and as a solid in the absence of oxygen. The infrared spectrum of **8** shows a sharp band of medium intensity at 1780 cm^{-1} which is assigned to ν(C≡O) for bridging carbonyl groups. The presence of only one band suggests that the carbonyl groups may be equivalent. There is no change in the infrared spectrum of **8** when it is prepared in a deuterium atmosphere nor is there evidence of a Pt–H bond in the proton nmr spectrum. Molecular weights determined in chloroform support the formulation of **8** as a tetrameric cluster and show that the compound does not dissociate to an appreciable extent. The source of the carbon monoxide in **8** is apparently the oxalate ion. An alternate source, the solvent ethanol,[26] is not considered to be likely because of the relatively mild reaction conditions, the observed reduction in the yield of carbon dioxide, and the necessity of hydrogen in the reaction. The presence of 1-hexene or cyclohexene did not alter the course of the reaction; however, very low yields of hexane and cyclohexane, respectively, were detected in the product mixture.

Compound **8** is quite robust. It can be refluxed in ethanol for at least 30 hr with no detectable effect. The compound undergoes a reversible reaction with triphenylphosphine. Thus, when an orange solution of **8** in ethanol was treated with an excess of this ligand there was an immediate change to dark green. Dilution or heating gave the original color, and addition of a saturated solution of triphenylphosphine in hexane to

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(21) R. S. Nyholm, A. J. Layton, G. A. Pneumaticakis, and M. L. Tobe, *Chem. Ind.* (*London*), 465 (1967).

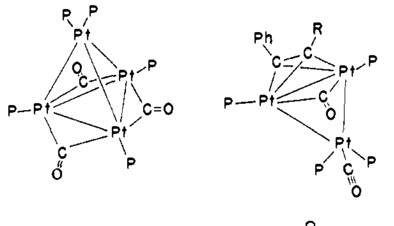
(22) B. R. Penfold in "Perspectives in Structural Chemistry," Vol. II, Wiley, New York, N. Y., 1968, p 71.

(23) M. I. Bruce, D. A. Harbourne, F. Waugh, and F. G. A. Stone, *J. Chem. Soc. A*, 356 (1968).

(24) (a) I. Collomati and A. Furlani, *J. Organometal. Chem.*, **17**, 457 (1969); (b) I. Collomati, A. Furlani, and G. Sartori, *ibid.*, **17**, 463 (1969).

(25) J. H. Nelson, H. Jonassen, and D. M. Roundhill, *Inorg. Chem.*, **8**, 2591 (1969).

(26) L. Vaska, *J. Amer. Chem. Soc.*, **86**, 1943 (1964).



8 9

Figure 1. Provisional structures for the new platinum cluster compounds, **8**, $Pt_4[P(C_6H_5)_3]_5(CO)_3$, and **9**, $Pt_3[P(C_6H_5)_3]_4(CO)_2(C_6H_5{-}C{\equiv}C{-}R)$ ($R = C_6H_5$ or C_2H_5). Phenyl groups on triphenylphosphine are omitted for clarity.

the green solution resulted only in the nearly quantitative precipitation of **8**. Refluxing of **8** with triphenylphosphine in ethanol for up to 12 hr caused no noticeable decomposition. Treatment of solutions of **8** in chloroform with carbon monoxide results in an immediate formation of a dark red solution. This color change is accompanied by the appearance of infrared bands at 2040 (m) and 2070 (w) cm^{-1} attributable to the presence of a terminal carbonyl group in the complex. A new band at 1810(w) cm^{-1} due to bridging carbonyl groups also appears. Unlike the reaction of **8** with triphenylphosphine, the carbon monoxide reaction is not reversible. Attempts to isolate the product of this reaction gave materials showing a variable number of carbonyl bands. These reactions of **8** with additional ligands may indicate the presence of coordinatively unsaturated metal atoms in the cluster. The structure proposed for **8** in Figure 1 is consistent with its properties.

Photolysis of **1** in the presence of diphenylacetylene or phenylethylacetylene under an atmosphere of carbon monoxide gives results quite different from the reaction of **1** with those reagents separately.[27] Reaction of **1** with these acetylenes in the presence of carbon monoxide gives pale yellow solutions from which new compounds (**9a** and **9b**, respectively) can be isolated. These lemon yellow, microcrystalline products are stable

$$\mathbf{1} \xrightarrow[C_6H_5C\equiv C-R,\ CO]{h\nu} Pt_3[P(C_6H_5)_3]_4(CO)_2(C_6H_5{-}C{\equiv}C{-}R)$$

$$\mathbf{9a},\ R = C_6H_5 \qquad \mathbf{b},\ R = C_2H_5$$

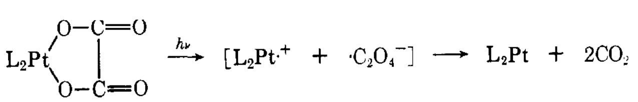
indefinitely under nitrogen as solids and in solution. They are very soluble in ethanol or chloroform. Conclusive evidence for the presence of the acetylenic ligand in these clusters is provided by the analyses as well as mass spectral studies. The mass spectra of **9a** and **9b** showed very intense peaks at *m/e* 178 and 130, respectively, corresponding to the parent ions of diphenylacetylene and phenylethylacetylene, in addition to other peaks characteristic of the fragmentation patterns of the acetylenes and triphenylphosphine. The observed peaks are similar to those of complexes **6a** and **6b** of the type $Pt[P(C_6H_5)_3]_2$(acetylene).

The infrared spectra of both **9a** and **9b** show a very strong, sharp band at 2060 cm^{-1} and another of medium intensity at 1780 cm^{-1}. The similarity in profile and frequency of the 1780-cm^{-1} band to the frequencies due to the bridging carbonyl groups in compound **8** lends support to a similar assignment for **9a** and **9b**. The 2060-cm^{-1} band is assigned to a terminal carbonyl group. A "weakly" bound acetylenic ligand, which would show $\nu(C{\equiv}C)$ in this region, is not expected to exhibit such an intense band.[28] Furthermore, reaction of **9b** with an excess of triphenylphosphine causes the 1780-cm^{-1} band to slowly disappear, but does not affect the 2060-cm^{-1} band. A "weakly" bound acetylene would be expected to be displaced under these conditions. The band is in the same region as that due to the terminal carbonyl group in a product obtained in the reaction of **8** with carbon monoxide. There is no infrared band in the spectrum of **9a** or **9b** which can be assigned to $\nu(C{\equiv}C)$ of the coordinated acetylene. The proton nmr spectrum of **9b** shows, in addition to the resonance of the phenyl groups, a series of weak, poorly resolved peaks in the regions τ 8–10.[29] These are believed to be due to the ethyl group. The difficulty in detecting the ethyl resonances is compounded by the expected coupling of the ethyl protons with ^{195}Pt (34% abundance, $I = ^1/_2$) and ^{31}P (100% abundance, $I = ^1/_2$), similar to that observed in the complex $Pt[P(C_6H_5)_3]_2(C_6H_5C{\equiv}CCH_3)$.[30]

In the absence of a complete structural determination, only a tentative assignment for the structure of this new type of platinum cluster compound is possible. One structure that is consistent with the data available for **9a** and **9b** is shown in Figure 1. In this structure the platinum atoms form a triangle and the acetylene molecule acts as a bridge between two metal atoms, similar to that in $Co_2(CO)_6(C_2H_5C{\equiv}CC_2H_5)$.[31]

The presence of small amounts of diphenylphosphine in some of the products of the photochemical reactions of **1** prompted us to check some of the reaction mixtures for the presence of benzene and other possible products from the decomposition of the triphenylphosphine such as biphenyl. The results are shown in Table I. No biphenyl was detected. It is not known whether the benzene and diphenylphosphine originate from reaction of the free[32] or coordinated ligand.

A mechanism for the photoreactions of $Pt[P(C_6H_5)_3]_2C_2O_4$ consistent with the observed results is shown below



$$L_2Pt(O_2C_2O_2) \xrightarrow{h\nu} [L_2Pt^{\cdot +} + \cdot C_2O_4^{\,-}] \longrightarrow L_2Pt + 2CO_2$$

Analogous to mechanisms proposed earlier,[18] the reaction may proceed by a photoinduced one-electron reduction, giving an unstable platinum(I) complex which is then reduced by the oxalate radical in a thermal reaction. The coordinatively unsaturated species, L_2Pt, then reacts with added reagents or with itself if other reagents are not present. The products observed are the same as those found in other systems in which this species is postulated.[4] The different course in the photolysis when molecular hydrogen is present in the reaction mixture may be explained in terms of the re-

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[27] The photochemical reaction of **1** with carbon monoxide gives a brown product, which shows a strong infrared band at 1785 cm^{-1}, indicating the presence of bridging carbonyl groups. Attempts to recrystallize this product resulted in the appearance of new infrared bands in the carbonyl region, indicating that decomposition was occurring.

(28) J. Chatt, R. G. Guy, L. A. Duncanson, and D. T. Thompson, *J. Chem. Soc.*, 5170 (1963).

(29) It was not possible to integrate the spectrum because of the limited solubility of the complex.

(30) E. O. Greaves, R. Bruce, and P. M. Maitlis, *Chem. Commun.*, 860 (1967).

(31) W. G. Sly, *J. Amer. Chem. Soc.*, **81**, 18 (1959).

(32) M. L. Kaufman and C. E. Griffin, *Tetrahedron Lett.*, 769 (1965).

action of hydrogen with the d^9 platinum(I) species, leading to formation of $Pt[P(C_6H_5)_3]_2CO$, which could react with other monomers to give the observed product.[17] Reaction of hydrogen with a d^9 platinum(I) species is analogous to the behavior of other d^9 systems in the homogeneous activation of molecular hydrogen.[33] The photodecomposition products obtained from the oxalate ion are known to be pH dependent, with carbon dioxide, carbon monoxide, and formic acid being possible products.[18] This suggests that the interaction with hydrogen may lead to a protonated oxalato species which undergoes subsequent decomposition[34] to give $Pt[P(C_6H_5)_3]_2CO$.

The work which has been described shows that the photolysis of oxalato complexes is a useful method of generating reactive species in the synthesis of new compounds and a potential method for producing catalytically active species *in situ*.

Experimental Section

Potassium tetrachloroplatinite and sodium tetrachloropalladite were purchased from J. Bishop and Co. Triphenylphosphine from Carlisle Chemical Co. was recrystallized from ethanol under nitrogen. Other phosphines and arsines were from Strem Chemical Co. and were used without further purification. The acetylenic compounds were from Farchan Chemical Co. Nitrogen was Matheson Prepurified grade. Hydrogen gas was used after passage through a "Deoxo" catalytic purifier. Other reagents were commercial samples and used without further purification. The complexes $Pt(PPh_3)_2CO_3 \cdot C_6H_6$, $Pd(PPh_3)_2CO_3$,[19] $Pt(diphos)_2$,[35] and $Pt(AsPh_3)_4$[3] were prepared by standard methods. Infrared spectra were recorded on Beckman IR-8 or Perkin-Elmer 700 spectrometers with an accuracy of ±5 cm^{-1} and were calibrated against polystyrene film. Ultraviolet and visible spectra were obtained using a Cary Model 14 spectrophotometer. ^1H nmr spectra of chloroform-*d* solutions were recorded using Varian A-60 or DP-60 spectrometers. Chemical shifts are given in parts per million relative to tetramethylsilane. Molecular weights were determined using a Perkin-Elmer Hitachi 115 osmometer. Melting points were determined on a micro-hot-stage apparatus and are uncorrected. Mass spectra were obtained on a Varian M-66 mass spectrometer with a nonvolatile sample probe.[36] Photochemical reactions were carried out using a Hanovia G54A10, 200-W, medium-pressure mercury arc lamp placed approximately 5 cm from the reaction mixture. Benzene, hexane, and cyclohexane yields were determined using a HI-FI Model 600-D gas chromatograph with a $^1/_8$-in. × 10-ft column packed with 20% UCON 2000 on 70–80 acid-washed DMCS Chromosorb W. Triphenylphosphine and diphenylphosphine produced by the decomposition of the platinum complexes with potassium cyanide were determined using an Aerograph Model A-90-P gas chromatograph with a 0.25-in. × 5-ft column packed with 20% SF-96 on 60–80 Firebrick operating at 250°. Carbon dioxide was determined using the method of Patchornik and Shalitin.[37] Microanalyses were carried out by Chemalytics, Inc., Tempe, Ariz., and Galbraith Laboratories, Inc., Knoxville, Tenn. Oxygen analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.[38]

Carbonatobis(triphenylarsine)platinum(II). A suspension of 10 g of tetrakis(triphenylarsine)platinum(0) in 300 ml of benzene was treated with a vigorous flow of oxygen and carbon dioxide for 3 hr. The resulting gray solid was recovered and recrystallized from boiling benzene–methylene chloride containing 3 g of triphenylarsine. The yield was 3.2 g (50%) of the colorless crystalline product, $Pt(AsPh_3)_2CO_3 \cdot C_6H_6$: mp 186–193° dec; ir (Nujol) 1690 (s), 1030 (w), 810 (m), 755 (m), and 685 (m) cm^{-1}.

Anal. Calcd for $PtC_{43}H_{36}As_2O_3$: C, 54.61; H, 3.84; mol wt, 945.7. Found: C, 54.36; H, 3.86; mol wt (in $CHCl_3$), 946.

Oxalatobis(triphenylphosphine)platinum(II) (1). To 12.0 g of carbonatobis(triphenylphosphine)platinum(II) suspended in 100 ml of ethanol was added 2.1 g of oxalic acid dihydrate. The mixture was stirred for 20 hr in a flask wrapped with aluminum foil. The crude product was recovered by filtration and dissolved in 900 ml of boiling ethanol. Upon cooling, a fine, colorless, crystalline precipitate of the complex formed. The yield was 10 g (90%); mp 290–295° dec; ir (Nujol) 1710 (s), 1675 (s), 1350 (s), 885 (w), and 790 (s) cm^{-1}; uv (CH_3CN) 305 mμ (shoulder, ε 913).

Anal. Calcd for $PtC_{38}H_{30}O_4P_2$: C, 56.51; H, 3.74; P, 7.67; mol wt, 807.7. Found: C, 56.25; H, 3.79; P, 7.86; mol wt (in $CHCl_3$), 839.

Oxalatobis(triphenylarsine)platinum(II) (2). A suspension of 3.2 g of the carbonato complex in 40 ml of ethanol containing 400 mg of oxalic acid dihydrate was stirred for 12 hr. The crude product was recrystallized from hot ethanol, affording 3 g (80%) of fine, colorless crystals: mp 270–275° dec; ir (Nujol) 1710 (s), 1670 (s), 1345 (s), 890 (w), and 795 (s) cm^{-1}; uv (CH_3CN) 330 mμ (shoulder, ε 345).

Anal. Calcd for $PtC_{38}H_{30}As_2O_4$: C, 50.96; H, 3.38; mol wt, 895.6. Found C, 51.04; H, 3.36; mol wt (in $CHCl_3$), 939.

Oxalato[1,2-bis(diphenylphosphino)ethane]platinum(II) (3). The crude product of the reaction of oxygen and carbon dioxide with 2 g of bis[1,2-bis(diphenylphosphino)ethane]platinum(0) in 60 ml of benzene (yield 0.9 g) was added to a solution of 300 mg of oxalic acid dihydrate in a mixture of 15 ml of benzene and 2 ml of ethanol. The mixture was stirred for 7 hr and filtered. The crude product was recrystallized from hot benzene–ethanol (1:1). The yield of colorless, crystalline $Pt(diphos)C_2O_4 \cdot C_6H_6$ was 0.8 g (85%); mp 248–249° dec; ir (Nujol) 1700 (s), 1680 (s), 1365 (m), and 795 (m) cm^{-1}.

Anal. Calcd for $PtC_{34}H_{30}O_4P_2$: C, 53.76; H, 3.98; P, 8.16. Found: C, 54.47; H, 4.10; P, 7.4.

Oxalatobis(triphenylphosphine)palladium(II) (4). The carbonato complex, 5.5 g, was stirred with 1.3 g of oxalic acid dihydrate in 100 ml of benzene–ethanol (12:1) for 20 hr in a foil-wrapped flask. The crude product was recrystallized from 400 ml of ethanol. This gave 4.0 g (70%) of pale yellow, crystalline product, mp 176–181° dec; ir (Nujol) 1695 (s), 1680 (s), 1660 (s), 1360 (s), 900 (w), and 785 (s) cm^{-1}; uv (CH_3CN) λ_{max} 285 mμ (ε 21,590).

Anal. Calcd for $PdC_{38}H_{30}O_4P_2$: C, 63.48; H, 4.21; P, 8.62; mol wt, 719.0. Found: C, 63.39; H, 4.28; P, 8.47; mol wt (in $CHCl_3$), 695.

Tetrakis(triphenylphosphine)diplatinum (5). Compound **1** (500 mg) was added to 30 ml of ethanol in a Vycor reaction tube. The mixture was then bubbled with nitrogen for 20 min. The reaction mixture was then degassed by alternately freezing and thawing it while under vacuum to ensure removal of oxygen. After the third thawing the system was filled with nitrogen to 20 cm above atmospheric pressure. The reaction vessel was then placed in a Pyrex jacket cooled by a rapid flow of air, and irradiation was begun. Vigorous stirring was provided by a magnetic stirrer. The mixture rapidly became orange and a bright yellow precipitate began to form within a few hours. After irradiation for 26 hr the mixture was filtered, yielding 300 mg of yellow powder (67%). This was recrystallized from hot benzene, under nitrogen, by slow addition of *n*-hexane to produce cloudiness and then allowing the mixture to cool to room temperature, to give small lemon yellow crystals, mp 248–250° dec.

Anal. Calcd for $Pt_2C_{72}H_{60}P_4$: C, 60.08; H, 4.20; P, 8.61; mol wt, 1439.4. Found: C, 59.00; H, 3.72; P, 8.93; mol wt (in C_6H_6), 1419.

Photochemical Reaction of Compound 1 with Triphenylphosphine. The procedure used in the preparation of compound **5** was followed except 340 mg of triphenylphosphine was added to the reaction mixture. Filtration after irradiation for 26 hr gave 510 mg (65%) of tetrakis(triphenylphosphine)platinum(0). This was identified by comparison of its melting point, infrared spectrum, and chemical reactions with those of an authentic sample.

Bis(triphenylphosphine)(diphenylacetylene)platinum (6a). The procedure for compound **5** was followed except 220 mg of diphenylacetylene was added to the mixture. After irradiation for 24 hr the mixture was filtered, yielding 450 mg (80%) of pale cream-colored crystals. This was identified as **6a** by its infrared spectrum, melting point, and elemental analysis: mp 160–165° dec; mass spectrum *m/e* (70 eV) 178 (vs); ir (Nujol) 1740 (s) cm^{-1}.

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(33) J. Halpern, *Annu. Rev. Phys. Chem.*, **16**, 103 (1965).

(34) The formate complex, $Pt[P(C_6H_5)_3]_2(HCO_2)_2$, was found by us to yield 2 mol of CO_2 upon photolysis, suggesting that a formate species is not the source of coordinated carbon monoxide.

(35) J. Chatt, F. A. Hart, and H. R. Watson, *J. Chem. Soc.*, 2537 (1962).

(36) Only major peaks other than those due to triphenylphosphine are listed for the infrared and mass spectra of the compounds.

(37) A. Patchornik and Y. Shalitin, *Anal. Chem.*, **33**, 1887 (1961).

(38) Oxygen analyses on the cluster compounds were not reproducible and were high by as much as a factor of three or four.

Anal. Calcd for $PtC_{50}H_{40}P_2$: C, 66.88; H, 4.47; P, 6.90. Found: C, 66.88; H, 4.47; P, 6.03.

Bis(triphenylphosphine)(phenylethylacetylene)platinum (6b). The procedure followed for compound **5** was followed except 200 mg of phenylethylacetylene was added to the mixture. Filtration after 26 hr gave 350 mg (65%) of pale cream-colored crystals: mp 130–138° dec; mass spectrum (70 eV) 129 (vs), 115 (vs); ir (Nujol) 1750 (m) cm^{-1}.

Anal. Calcd for $PtC_{46}H_{40}P_2$: C, 65.01; H, 4.74; P, 7.29. Found: C, 64.53; H, 4.67; P, 6.75.

***trans*-Di(phenylacetylide)bis(triphenylphosphine)platinum(II) (7).** The procedure followed for compound **5** was used except 130 mg of phenylacetylene was added after the initial bubbling with nitrogen. Filtration after 26 hr gave 280 mg (50%) of cream-colored powder: mp 165–169° dec; ir (Nujol) 2130 (m) and 780 (w) cm^{-1}.

Anal. Calcd for $PtC_{52}H_{40}P_2$: C, 67.75; H, 4.37; P, 6.72; mol wt, 922.0. Found: C, 68.42; H, 4.57; P, 6.20; mol wt (in $CHCl_3$), 976.

Tricarbonylpentakis(triphenylphosphine)tetraplatinum (8). The procedure for **5** was followed except the system was filled with hydrogen to a pressure of 1.5 atm. After irradiation for 28 hr, the clear, orange solution was evaporated in a stream of nitrogen to a volume of about 4 ml. Slow addition of 20 ml of *n*-hexane–ethanol (6:1) gave 200 mg (75%) of fibrous, yellow precipitate. Additional product could be obtained from the filtrate. Compound **8** is very soluble in ethanol and chloroform but only slightly soluble in benzene. Recrystallization from refluxing ethanol by slow addition of *n*-hexane afforded small golden yellow needles: mp 217–220° dec (*in vacuo*); ir ($CHCl_3$) 1780 (m) cm^{-1}; mass spectrum (70 eV) showed only the fragmentation pattern of triphenylphosphine and carbon monoxide.

Anal. Calcd for $Pt_4C_{93}H_{75}O_3P_5$: C, 51.34; H, 3.47; P, 7.12; mol wt, 2175.8. Found: C, 51.44; H, 3.57; P, 7.12; mol wt (in $CHCl_3$), 2050.

Dicarbonyltetrakis(triphenylphosphine)(diphenylacetylene)triplatinum (9a). The procedure for **6a** was followed except the system was filled with carbon monoxide to a pressure of 1.5 atm. After irradiation for 29 hr the mixture was filtered to remove a trace of colorless solid. The yellow filtrate was concentrated to about 5 ml in a stream of nitrogen and 4 ml of *n*-hexane–ethanol (6:1) was slowly added. Filtration gave 400 mg (quantitative yield) of dark yellow powder. This was dissolved in 16 ml of refluxing ethanol, under nitrogen, and *n*-hexane was added until the mixture became cloudy. Upon cooling to room temperature, fine, yellow crystals formed: mp 170–175° dec (*in vacuo*); ir ($CHCl_3$) 2060 (vs) and 1775 (m) cm^{-1}; mass spectrum (70 eV) 256 (s), 178 (vs), and 165 (vs).

Anal. Calcd for $Pt_3C_{88}H_{70}O_2P_4$: C, 56.56; H, 3.77; P, 6.63; mol wt, 1868.7. Found: C, 56.74; H, 4.18; P, 6.42; mol wt (in $CHCl_3$), 1630.

Dicarbonyltetrakis(triphenylphosphine)(phenylethylacetylene)triplatinum (9b). The procedure used for **9a** was followed except 200 mg of phenylethylacetylene was used. The mixture was filtered after 27 hr to remove a trace of colorless solid. The yellow filtrate was evaporated to about 3 ml and ether was added. The yield of crude yellow product was 330 mg (87%). This was recrystallized in the same manner as **9a** to give fine, yellow crystals: mp 173–178° dec (*in vacuo*); ir ($CHCl_3$) 2060 (vs) and 1775 (m) cm^{-1}; mass spectrum (70 eV) 208 (m), 129 (s), 116 (vs), 114 (vs), and 91 (m).

Anal. Calcd for $Pt_3C_{84}H_{70}O_2P_4$: C, 55.42; H, 3.87; P, 6.80; mol wt, 1820.6. Found: C, 55.37; H, 4.00; P, 6.49; mol wt (in $CHCl_3$), 1625.

Reaction of Compound 8 with Triphenylphosphine. To the orange solution of 100 mg of compound **8** in 5 ml of ethanol was added 50 mg of triphenylphosphine. The solution immediately turned dark green. Heating the solution to reflux caused the original orange color to return; upon cooling the mixture reverted to the dark green color. After refluxing for 20 hr complex **8** could be recovered by precipitation with *n*-hexane.

Attempts to isolate the green complex by addition of a saturated solution of triphenylphosphine in *n*-hexane to ethanol solutions of **8** resulted only in the precipitation of **8** from the green reaction mixture.

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