(35) W. J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971).
(36) R. J. Angelici, "Synthesis and Techniques in Inorganic Chemistry," W. B. Saunders Co., Philadelphia, Pa., 1969, pp 99–104.
(37) W. Beck, W. P. Fehlhammer, D. Pollman, E. Schuieuer, and K. Feldl, *Chem. Ber.*, **100**, 3335 (1967).
(38) K. Bowman and Z. Dori, *Inorg. Chem.*, **9**, 395 (1970).
(39) These statements could also be extended to octahedral complexes but there are known exceptions, *viz.*, complexes of Cr(0), Mo(0), W(0), and Mn(I); see *e.g.*, J. F. Nixon and A. Pidcock, *Annu. Rev. NMR (Nucl. Magn. Resonance) Spectrosc.*, **2**, 345 (1969); F. B. Oglivie, J. M. Jenkins, and J. G. Verkade, *J. Amer. Chem. Soc.*, **92**, 1916 (1970); P. K. Maples and C. S. Kraihanzel, *ibid.*, **90**, 6645 (1968).
(40) R. J. Goodfellow, M. J. Hardy, and B. F. Taylor, *J. Chem. Soc., Dalton Trans.*, 2450 (1973).

(41) R. K. Harris, *Can. J. Chem.*, **42**, 2275 (1964).
(42) A Ault, *J. Chem. Educ.*, **47**, 812 (1970).
(43) D. A. Redfield, J. H. Nelson, and L. W. Cary, *Inorg. Nucl. Chem. Lett.*, **10**, 727 (1974).
(44) P. Diehl, R. K. Harris, and R. G. Jones, *Progr. Nucl. Magn. Resonance Spectrosc.*, **3**, 37 (1967).
(45) J. P. Fackler, Jr., J. A. Fetchin, J. Mayhew, W. C. Seidel, T. J. Swift, and M. Weeks, *J. Amer. Chem. Soc.*, **91**, 1941 (1969); C. G. Grimes and R. G. Pearson, *Inorg. Chem.*, **13**, 970 (1974).
(46) W. J. Louw, *J. Chem. Soc., Chem. Commun.*, 353 (1974).
(47) C. H. Langford and H. B. Gray, "Ligand Substitution Processes," Benjamin, New York, N. Y., 1965, pp 18–51.
(48) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1968, pp 351–435.

Alkoxalyl Complexes of Palladium(II) and Platinum(II)

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Alkoxalyl complexes of the general formula *trans*-MCl(COCO$_2$R)L$_2$, where M = Pt or Pd, R = CH$_3$ or C$_2$H$_5$, and L = P(C$_6$H$_5$)$_3$, P(CH$_3$)(C$_6$H$_5$)$_2$ or P(C$_2$H$_5$)$_3$, were prepared by oxidative-addition reactions of ML$_4$ with ClCOCO$_2$R. The C=O groups of the planar alkoxalyl ligand have an s-trans conformation in the solid state, but in solution PtCl(COCO$_2$CH$_3$)L$_2$ exists as two conformers as indicated by infrared studies. With Cl$_2$, PtCl(COCO$_2$CH$_3$)[P(C$_6$H$_5$)$_3$]$_2$ rapidly yields ClCOCO$_2$CH$_3$ and PtCl$_2$[P(C$_6$H$_5$)$_3$]$_2$. With C$_2$H$_5$OH and a trace of C$_2$H$_5$O$^-$, PtCl(COCO$_2$CH$_3$)[P(C$_6$H$_5$)$_3$]$_2$ is transesterified to give PtCl(COCO$_2$C$_2$H$_5$)[P(C$_6$H$_5$)$_3$]$_2$. While the platinum–alkoxalyl complexes are stable in solution, the palladium analogs readily undergo decarbonylation in solution to give the corresponding alkoxycarbonyl complexes (PdCl(CO$_2$R)L$_2$). This decarbonylation is greatly inhibited by adding phosphines (L) to the solutions. Attempts to prepare alkoxalyl complexes by CO insertion into alkoxycarbonyl complexes are also briefly described.

Palladium(II) chloride promotes the reaction of ethanol with CO and base to give diethyl carbonate[1]

$$2EtOH + CO + PdCl_2 + 2Na_2CO_3 \rightarrow (EtO)_2CO + Pd + 2NaCl + 2NaHCO_3 \tag{1}$$
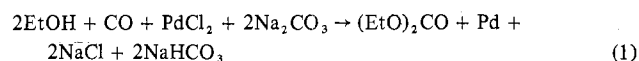
The reaction has been postulated to proceed through an ethoxycarbonyl intermediate

$$PdC\underset{OEt}{\overset{O}{\diagdown}}$$
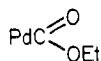
which is subsequently converted to the carbonate by ethoxide attack at the carbonyl carbon atom. The preparation and isolation[2-4] of related alkoxycarbonyl complexes, PdCl(CO$_2$R)L$_2$, stabilized by phosphine (L) ligands support this idea.

Under more vigorous conditions, PdCl$_2$ together with a cocatalyst such as CuCl$_2$ or FeCl$_3$ and a dehydrating agent catalyzes the reaction of ethyl alcohol, CO, and O$_2$ to give diethyl oxalate and smaller amounts of (EtO)$_2$CO[5]

$$2EtOH + 2CO + \tfrac{1}{2}O_2 \rightarrow EtO_2C\text{-}CO_2Et + H_2O \tag{2}$$
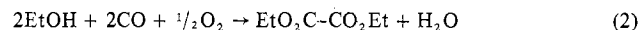
This reaction is also postulated to involve the formation of an ethoxycarbonyl complex (PdCO$_2$Et), which is then converted to the oxalate ester. At the high CO pressures, this latter step could proceed *via* CO insertion into the Pd–C bond to give an ethoxalyl complex

$$PdCO_2Et + CO \rightleftarrows Pd\overset{OO}{\overset{||\;||}{C}}COEt \tag{3}$$

which would undergo OEt$^-$ attack giving the product. The purpose of our investigation was to determine whether or not stable Pd(II) and Pt(II) complexes bearing the novel alkoxalyl ligand could be synthesized according to eq 3 as well as by other routes and, if so, to examine some of their reactions.

Experimental Section

Materials. The compounds PtL$_4$ (L = P(C$_6$H$_5$)$_3$ or P(CH$_3$)-(C$_6$H$_5$)$_2$) were prepared as described in the literature.[6] The analogous PdL$_4$ complexes were prepared by adding L to a pentane solution of

(π-C$_5$H$_5$)Pd(π-C$_3$H$_5$).[7] Solutions of Pd[P(C$_2$H$_5$)$_3$]$_4$ were prepared by slowly adding P(C$_2$H$_5$)$_3$ to a pentane solution of (π-C$_5$H$_5$)Pd-(π-C$_3$H$_5$) until the color turned from red to yellow. This solution was used directly for subsequent oxidative-addition reactions. The (π-C$_5$H$_5$)Pd(π-C$_3$H$_5$) was prepared either by the literature method[8] or by a more convenient modification using TlC$_5$H$_5$ instead of NaC$_5$H$_5$. This was done by stirring a solution of 1.94 g (5.3 mmol) of [(π-C$_3$H$_5$)PdCl]$_2$ and 2.87 g (10.7 mmol) of TlC$_5$H$_5$ in 25 ml of tetrahydrofuran (THF) under a nitrogen atmosphere at 25° for 5 min. After evaporating the solvent under vacuum, the residue was extracted with 50 ml of pentane. After filtering, the pentane was removed under vacuum leaving 1.89 g (85%) of the red crystalline product.

Alkoxycarbonyl Complexes by Oxidative-Addition Reactions. a. PdCl(CO$_2$CH$_3$)[P(C$_6$H$_5$)$_3$]$_2$. To a solution of 0.67 g (0.58 mmol) of Pd[P(C$_6$H$_5$)$_3$]$_4$ in 20 ml of benzene under N$_2$ was added 0.054 g (0.58 mmol) of ClCO$_2$CH$_3$. After stirring for 5 hr at 25°, the solvent was removed under vacuum and the remaining residue was washed with diethyl ether. Recrystallization from CH$_2$Cl$_2$–hexane gave the pale yellow crystalline product (0.34 g, 80% yield).

Anal. Calcd for PdCl(CO$_2$CH$_3$)[P(C$_6$H$_5$)$_3$]$_2$: C, 63.0; H, 4.56; Cl, 4.84. Found: C, 63.4; H, 4.83; Cl, 5.01.

b. PtCl(CO$_2$CH$_3$)[P(C$_6$H$_5$)$_3$]$_2$. Methyl chloroformate (ClCO$_2$-CH$_3$) was added to a refluxing solution of 1.16 g (0.94 mmol) of Pt[P(C$_6$H$_5$)$_3$]$_4$ in 50 ml of benzene under an N$_2$ atmosphere until the yellow solution became pale yellow. Removal of benzene under vacuum yielded a white solid which was washed with ether and recrystallized from CH$_2$Cl$_2$–hexane to give 0.57 g (75%) of the product. Its ir and proton nmr spectra (Table I) were virtually identical with those reported for this compound prepared by a different method.[9] The analogous Pt(Cl)(CO$_2$C$_2$H$_5$)[P(C$_6$H$_5$)$_3$]$_2$ was prepared by refluxing a 20-ml toluene solution of 0.91 g (8.4 mmol) of ClCO$_2$C$_2$H$_5$ and 0.46 g (0.47 mmol) of Pt[P(C$_6$H$_5$)$_3$]$_3$[10] for 12 hr. Isolation as described above gave 0.21 g (54%) of the white product.[9]

Alkoxycarbonyl Complexes by Carbonylation of MCl$_2$L$_2$ Complexes. a. PdCl(CO$_2$CH$_3$)[P(C$_6$H$_5$)$_3$]$_2$. A suspension of 0.74 g (1.0 mmol) of *trans*-PdCl$_2$[P(C$_6$H$_5$)$_3$]$_2$ and 0.057 g (1.0 mmol) of NaOCH$_3$ in 50 ml of CH$_3$OH was stirred under CO (1 atm) for 5 hr at 25°. The resulting pale pink solid was collected by filtration and washed with H$_2$O, C$_2$H$_5$OH, and finally ether to give 0.67 g (88%) of PdCl(C-O$_2$CH$_3$)[P(C$_6$H$_5$)$_3$]$_2$, whose spectra (Table I) were identical with those of this complex prepared by the oxidative-addition route. The platinum analog was prepared similarly from *cis*-PtCl$_2$[P(C$_6$H$_5$)$_3$]$_2$.

Table I. Infrared and Proton Nmr Data

	$\nu(CO),^a$ cm^{-1}	τ^b for –OR group
PtCl(CO$_2$Me)(PPh$_3$)$_2$,^{c}	1644	7.65 (s with satellites)^d
PtCl(CO$_2$Et)(PPh$_3$)$_2$,^{c}	1636	7.35 (m), 9.55 (t)
PtCl(COCO$_2$Me)(PPh$_3$)$_2$	1735 m, sh, 1715 s	6.98 (s)
	1665 m, sh, 1645 s	
PtCl(COCO$_2$Et)(PPh$_3$)$_2$	1650, 1710^h	6.55 (q), 9.12 (t)
PtCl(COCO$_2$Me)(PMePh$_2$)$_2$	1645, 1720	6.90 (s)^e
PdCl(CO$_2$Me)(PPh$_3$)$_2$,^{f}	1655	7.60 (s)
PdCl(CO$_2$Et)(PPh$_3$)$_2$,^{f}	1650	7.30 (q), 9.53 (t)
PdCl(COCO$_2$Me)(PPh$_3$)$_2$	1674, 1722	6.93 (s)
PdCl(COCO$_2$Et)(PPh$_3$)$_2$	1670, 1720	6.55 (q), 9.12 (t)
PdCl(COCO$_2$Me)(PMePh$_2$)$_2$	1665, 1720	6.92 (s)^g
PdCl(CO$_2$Me)(PEt$_3$)$_2$	1650	6.51 (s)
PdCl(COCO$_2$Me)(PEt$_3$)$_2$	1660, 1720	6.26 (s)
ClCOCO$_2$Me	1761 b	6.01 (s)
ClCOCO$_2$Et	1754, 1786	5.60 (q), 8.60 (t)

^{a} In CHCl$_3$ solution. ^{b} In CDCl$_3$ solution with tetramethylsilane (τ 10.0) as an internal standard. Abbreviations: s, singlet; t, triplet; q, quartet; m, multiplet. ^{c} See ref 9. ^{d} J(PtCOCH) = 7 Hz. ^{e} For P-CH$_3$ protons, τ 7.85 (t) with satellites and J(PCH) = 4 Hz and J(PtPCH) = 33 Hz. ^{f} See ref 2. ^{g} For P-CH$_3$ protons, τ 7.93 (t) with J(PCH) = 3.5 Hz. ^{h} 1725 (s, sh), 1710 (s), 1665 (m, sh), 1652 (s) cm^{-1} in CH$_2$Cl$_2$.

b. PdCl(CO$_2$CH$_3$)[P(C$_2$H$_5$)$_3$]$_2$. A suspension of 0.39 g (0.95 mmol) of *trans*-PdCl$_2$[P(C$_2$H$_5$)$_3$]$_2$ and 0.20 g (1.90 mmol) of Na$_2$CO$_3$ in 25 ml of CH$_3$OH was stirred under CO (1 atm) for 15 min. After vacuum removal of the CH$_3$OH, the orange-brown residue was extracted with 40 ml of pentane. After treatment with activated charcoal and filtration, the pale yellow solution was concentrated under vacuum to about 15 ml. Cooling to –20° gave white needles of the product (0.13 g, 32%), which was identified by its spectra (Table I).

Preparation of Alkoxalyl Complexes. a. PtCl(COCO$_2$R)L$_2$ (R = CH$_3$, C$_2$H$_5$; L = P(C$_6$H$_5$)$_3$, P(CH$_3$)(C$_6$H$_5$)$_2$). These complexes were all prepared similarly. As an example, 0.23 g (1.92 mmol) of methyl oxalyl chloride (ClCOCO$_2$CH$_3$) was added to a solution of 2.39 g (1.93 mmol) of Pt[P(C$_6$H$_5$)$_3$]$_4$ in 50 ml of benzene under an N$_2$ atmosphere. Stirring for 5 min at 25° gave a pale yellow solution. Benzene was removed under vacuum leaving a yellow solid. The solid was triturated with ether and recrystallized from CH$_2$Cl$_2$–hexane to give yellow crystals of PtCl(COCO$_2$CH$_3$)[P(C$_6$H$_5$)$_3$]$_2$ (1.30 g, 81%; mp 215–220° with loss of CO).

Anal. Calcd for PtCl(COCO$_2$CH$_3$)[P(C$_6$H$_5$)$_3$]$_2$: C, 55.6; H, 3.95. Found: C, 55.7; H, 4.04.

The alkoxalyl complexes in the platinum series are all bright yellow crystalline solids which are stable both in solution and in the solid state at room temperature and are not decomposed by air or water.

b. PdCl(COCO$_2$R)L$_2$ (R = CH$_3$, C$_2$H$_5$; L = P(C$_6$H$_5$)$_3$, P-(CH$_3$)(C$_6$H$_5$)$_2$). Like their platinum analogs, the palladium alkoxalyl complexes were also prepared by the oxidative-addition method. As a typical example, 0.313 g (2.30 mmol) of ClCOCO$_2$C$_2$H$_5$ was added to a solution of 2.66 g (2.30 mmol) of Pd[P(C$_6$H$_5$)$_3$]$_4$ in 40 ml of toluene at 0°. After stirring the solution for 15 min at 0°, 80 ml of ether was added to precipitate the yellow solid product. After filtration, the solid was washed several times with ether and then dried under vacuum to give PdCl(COCO$_2$C$_2$H$_5$)[P(C$_6$H$_5$)$_3$]$_2$ (1.47 g, 84%) as a bright yellow powder.

Anal. Calcd for PdCl(COCO$_2$C$_2$H$_5$)[P(C$_6$H$_5$)$_3$]$_2$: C, 62.5; H, 4.61; Cl, 4.62. Found: C, 62.0; H, 4.54; Cl, 4.54.

The PdCl(COCO$_2$CH$_3$)[P(C$_2$H$_5$)$_3$]$_2$ complex was prepared by allowing equimolar (1.97 mmol) Pd[P(C$_2$H$_5$)$_3$]$_4$ and ClCOCO$_2$CH$_3$ to react in 10 ml of pentane at 25°. After filtering, the solution was concentrated under vacuum and cooled to –20° giving yellow crystals (~15%) of the product.

The complexes in this series are all bright yellow solids which are stable in the solid state and do not react with air or water. Unlike their platinum analogs, however, they do undergo noticeable decomposition when stored at room temperature for several months. In CH$_2$Cl$_2$, CHCl$_3$, or benzene solution, they are not stable and readily lose CO to give the corresponding alkoxycarbonyl complexes. Addition of P(C$_6$H$_5$)$_3$ to these solutions greatly retards this decarbonylation thus allowing the complexes to be recrystallized from CH$_2$Cl$_2$–hexane.

Transesterification of PtCl(COCO$_2$CH$_3$)[P(C$_6$H$_5$)$_3$]$_2$. To a solution of 0.22 g (0.26 mmol) of PtCl(COCO$_2$CH$_3$)[P(C$_6$H$_5$)$_3$]$_2$ in 15 ml

of dry THF was added 5 ml of C$_2$H$_5$OH containing a trace of NaOC$_2$H$_5$. After stirring for 2 hr at 25°, an additional 10 ml of C$_2$H$_5$OH was added causing the precipitation of a light yellow solid (0.20 g), which was washed with C$_2$H$_5$OH and dried under a stream of N$_2$. A proton nmr spectrum of the precipitate in CDCl$_3$ indicated by comparison with spectra of authentic samples (Table I) that 88% of it was PtCl(COCO$_2$C$_2$H$_5$)[P(C$_6$H$_5$)$_3$]$_2$ while the remaining 12% was unreacted starting material.

Reaction of PtCl(COCO$_2$CH$_3$)[P(C$_6$H$_5$)$_3$]$_2$ with Cl$_2$. An excess of Cl$_2$ was condensed onto a solution of 0.12 g (0.14 mmol) of PtCl(COCO$_2$CH$_3$)[P(C$_6$H$_5$)$_3$]$_2$ in CDCl$_3$ at –196° under vacuum. On warming to room temperature, a yellow solid precipitated and was separated by filtration. The proton nmr spectrum of the CDCl$_3$ solution showed only the characteristic singlet (τ 6.01) of ClCO-CO$_2$CH$_3$; the infrared spectrum of this solution indicated the presence of ClCOCO$_2$CH$_3$ by the ν(C=O) band at 1760 cm^{-1}. The yellow solid was identified as *trans*-PtCl$_2$[P(C$_6$H$_5$)$_3$]$_2$ (0.11 g, 96%) by its strong ν(Pt–Cl) band at 343 cm^{-1}.[11]

When the reaction was carried out with equimolar amounts (0.23 mmol) of complex and Cl$_2$ under the same conditions as above, ClCOCO$_2$CH$_3$ was again observed but the tan solid precipitate was identified as *cis*-PtCl$_2$[P(C$_6$H$_5$)$_3$]$_2$ by characteristic ν(Pt–Cl) bands at 295 and 320 cm^{-1}.[11]

Results and Discussion

Syntheses and Structures. Prior to examining the forward and reverse reactions expressed in eq 3, we prepared several alkoxycarbonyl complexes *via* either one of two methods. The first was by oxidative-addition of alkyl chloroformates to Pd(0) and Pt(0) complexes

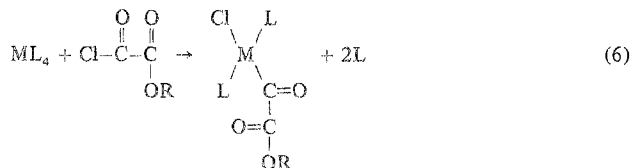$$ML_4 + Cl\text{-}CO_2R \rightarrow MCl(CO_2R)L_2 + 2L \qquad (4)$$
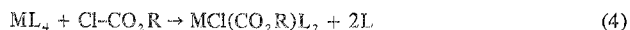
where M = Pd or Pt, R = CH$_3$ or C$_2$H$_5$, and L = a phosphine. This route had previously[2] been used to generate PdCl(C-O$_2$C$_2$H$_5$)[P(C$_6$H$_5$)$_3$]$_2$ at room temperature, but we find that refluxing benzene or toluene solutions are required to accomplish the same reactions of Pt, thus demonstrating the greater reactivity of Pd(0) as compared to Pt(0).

The second method involved alkoxycarbonylation with CO and an alcohol in the presence of a base (B)

$$MCl_2L_2 + CO + ROH + B \rightarrow MCl(CO_2R)L_2 + BH^+Cl^- \qquad (5)$$
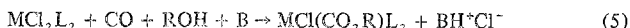
where M = Pd or Pt, L = a phosphine, and B = OR$^-$ or Na$_2$CO$_3$. The syntheses of several other related complexes from MX$_2$L$_2$ derivatives have been accomplished by this method; these include Pd(NCO)(CO$_2$R)L$_2$,[3] PdCl(CO$_2$R)L$_2$,[4] Pt(NCO)(CO$_2$R)L$_2$,[3,12] and Pt(O$_2$CCF$_3$)(CO$_2$R)L$_2$.[13] All of these reactions presumably proceed by alcohol or alkoxide attack on a cationic carbonyl intermediate[9] MX(CO)L$_2^+$ resulting from CO displacement of an X$^-$ ligand.

The most convenient route for the preparation of alkoxalyl complexes of Pd(II) and Pt(II) involves oxidative-addition of alkyl oxalyl chlorides to zerovalent metal–phosphine complexes

$$ML_4 + Cl\text{-}C(=O)\text{-}C(=O)\text{-}OR \rightarrow \begin{array}{c} Cl \\ | \\ M \\ | \\ L \end{array} \begin{array}{c} L \\ \diagup \\ \diagdown \\ C=O \\ | \\ O=C \\ | \\ OR \end{array} + 2L \qquad (6)$$

where M = Pd or Pt, R = CH$_3$ or C$_2$H$_5$, and L = a phosphine. These reactions proceed readily at room temperature or below to give the yellow products in high yield. The concomitant formation of a small amount of *trans*-PtCl(H)L$_2$[14] in the reaction of ClCOCO$_2$C$_2$H$_5$ with PtL$_4$ is suspected to arise from the reaction of PtL$_4$ with HCl present in ClCOCO$_2$C$_2$H$_5$ as a hydrolysis product.

Previously this laboratory reported[15] a preliminary X-ray structural investigation of *trans*-PdCl(COCO$_2$CH$_3$)[P-(C$_6$H$_5$)$_3$]$_2$ which showed the molecule to have the basic geometry given in eq 6 with the plane of the planar methoxalyl

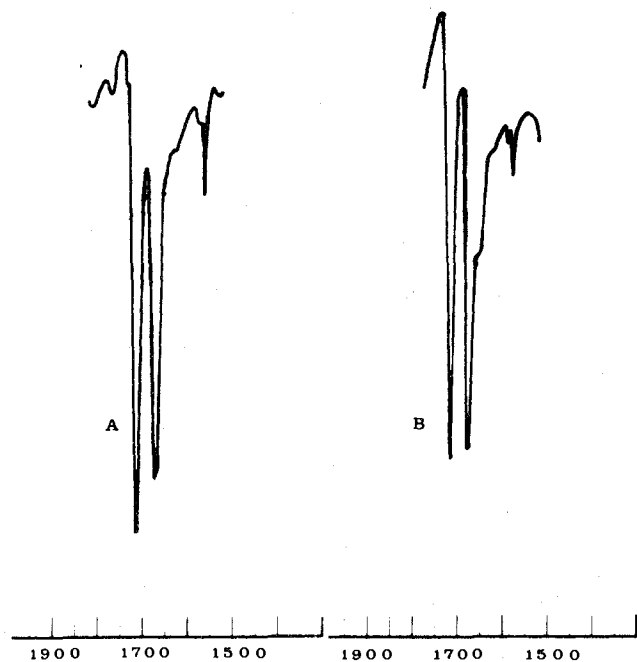**Figure 1.** Infrared spectra of PdCl(COCO$_2$CH$_3$)[P(C$_6$H$_5$)$_3$]$_2$ (A) and PtCl(COCO$_2$CH$_3$)[P(C$_6$H$_5$)$_3$]$_2$ (B) in Nujol mulls.

Figure 2. Infrared spectra of PtCl(COCO$_2$CH$_3$)[P(C$_6$H$_5$)$_3$]$_2$ in CH$_2$Cl$_2$ solution (A) and in C$_6$H$_6$ solution (B).

ligand nearly perpendicular to the square plane formed by the Pd, Cl, and two P atoms. The observed 1:2:1 triplet for the phosphine CH$_3$ groups in the proton nmr spectra (Table I) of the MCl(COCO$_2$CH$_3$)[P(CH$_3$)(C$_6$H$_5$)$_2$]$_2$ complexes indicates[16] a trans geometry for the complexes of both Pd(II) and Pt(II).

The chemical shift of the methyl protons in the methoxycarbonyl and methoxalyl ligands is at higher field (Table I) than in the starting chlorides, ClCO$_2$CH$_3$ and ClCOC-O$_2$CH$_3$. This is most likely due in part to the lower electron-withdrawing ability of the metal as compared to Cl, but it also appears that the phenyl groups in the phosphine ligand cause a significant upfield shift. This is particularly noticeable for the methoxycarbonyl complexes, PdCl(CO$_2$-CH$_3$)L$_2$, where L is P(C$_2$H$_5$)$_3$ (τ 6.51) or P(C$_6$H$_5$)$_3$ (τ 7.60). A similar trend may be noted (Table I) in the methoxalyl complexes as well, but the effect is smaller because of the increased distance between the methyl group and the phosphines. A similar shielding effect by phosphine phenyl groups was previously[17] observed in the related dialkylcarbamoyl complexes. The methoxycarbonyl complexes of Pt typically show splitting of the methyl protons by [195]Pt (33% abundant) to give a 1:4:1 pattern with J(PtCOCH) equal to 7 Hz. Due to the increased distance from the Pt atom, the methyl group in the methoxalyl complexes shows no measurable splitting by the [195]Pt.

The infrared spectra (Table I) of all of the alkoxalyl complexes show two strong, well-separated ν(C=O) carbonyl bands. (As discussed below, each of these may occur as two absorptions due to the presence of conformational isomers.) The lower frequency absorption occurs in the 1640–1670-cm^{-1} region and may be assigned to the carbonyl group adjacent to the metal. This assignment is based on the low carbonyl frequencies observed for alkoxycarbonyl complexes of both Pd(II) and Pt(II), Table I. The higher frequency ν(C=O) band occurs in the region 1710–1725 cm^{-1}. This region is common for organic esters and supports assignment of the ester carbonyl ν(C=O) mode to this band.

The methoxalyl ligand in PdCl(COCO$_2$CH$_3$)[P(C$_6$H$_5$)$_3$]$_2$ in the solid state[15] has an s-trans geometry with the carbonyl oxygen atoms in the ligand trans to each other. A Nujol mull infrared spectrum of this complex shows only two carbonyl
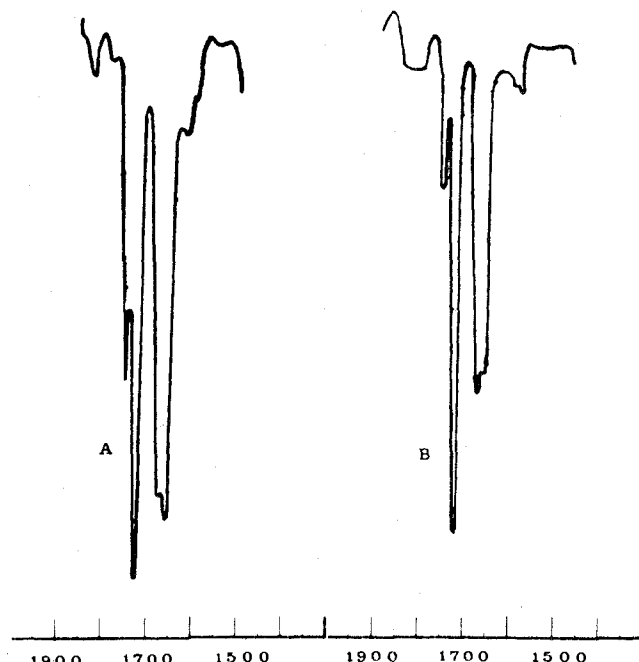
bands (Figure 1) at 1675 and 1720 cm^{-1}. In CHCl$_3$, again only these two bands appear slightly shifted to 1674 and 1722 cm^{-1}. Thus it appears that only one isomer, the s-trans, is present in solutions of this complex.

In the Nujol mull spectrum (Figure 1) of PtCl(COCO$_2$-CH$_3$)[P(C$_6$H$_5$)$_3$]$_2$, two strong bands at 1670 and 1710 cm^{-1} suggest the presence of the s-trans isomer by comparison with the spectrum of the analogous Pd(II) complex. A shoulder on the lower frequency band suggests the possible presence of another isomer. In solution (Figure 2), the complex shows two pairs of carbonyl bands, the lower frequency pair being only partially resolved. This also indicates the presence of two isomers of the complex, presumably resulting from different conformations of the alkoxalyl ligand. The planarity of the methoxalyl ligand and short C–C bond distance (1.41 Å)[15] in PdCl(COCO$_2$CH$_3$)[P(C$_6$H$_5$)$_3$]$_2$ suggest that some partial double bonding occurs in the C–C bond. This planar geometry could be maintained but rotation around the C–C bond could give either the s-trans or s-cis isomer. These conformers appear to be the most likely structures for the detected isomers.

s-trans   s-cis
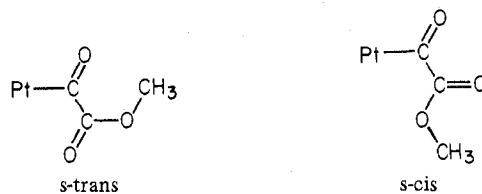
The 1660- and 1715-cm^{-1} bands are assigned to the s-trans isomer, based on the similarity of their positions both with the spectrum of PdCl(COCO$_2$CH$_3$)[P(C$_6$H$_5$)$_3$]$_2$ and with the solid-state spectrum of PtCl(COCO$_2$CH$_3$)[P(C$_6$H$_5$)$_3$]$_2$. The other two absorptions at 1735 and 1640 cm^{-1} may then be assigned to the s-cis conformation.

The approximate relative ratios of the s-cis to s-trans isomers in different solvents at room temperature are indicated by the ratio of the 1735- to 1715-cm^{-1} band intensities. These ratios, which are shown in Table II, increase in general as the dielectric constant of the solvent increases. This trend is consistent with polar solvents stabilizing the more polar s-cis isomer over the s-trans form. The same general trend was observed for PtCl(COCO$_2$CH$_3$)[P(CH$_3$)(C$_6$H$_5$)$_2$] for which the band

Table II. Effect of Solvent Polarity on the s-cis:s-trans Isomer Ratio of $PtCl(COCO_2CH_3)[P(C_6H_5)_3]_2$

Solvent	Dielectric constant	Ratio[a]	Solvent	Dielectric constant	Ratio[a]
C_6H_6	2.27	0.16	CH_2Cl_2	8.93	0.41
CS_2	2.63	0.17	CH_3NO_2	35.9	0.59
$CHCl_3$	4.73	0.27	CH_3CN	38.8	0.48

[a] Ratio of absorbances of the 1735- to 1715-cm^{-1} bands.

intensity ratios (in parentheses) increased with the solvent as follows: C_6H_6 (0.19) < $CHCl_3$ (0.34) < CH_2Cl_2 (0.45). The slightly higher ratios for the $P(CH_3)(C_6H_5)_2$-containing complex in all solvents suggest that this less bulky ligand (as compared to $P(C_6H_5)_3$) favors the formation of more of the sterically crowded s-cis isomer.

The relative s-cis:s-trans ratio of isomers also increases as the temperature of the solution increases. The solvents, the temperatures of the solutions of $PtCl(COCO_2CH_3)[P(C_6H_5)_3]_2$, and the 1735 cm^{-1}:1715 cm^{-1} intensity ratios (in parentheses) are as follows: C_6H_6, 25° (0.16), 40° (0.17), 60° (0.18); $CHCl_3$, 25° (0.23), 40° (0.26); CH_2Cl_2, -75° (0.32), 25° (0.41). These data suggest that the s-trans to s-cis isomerization is endothermic.

In contrast to the alkoxalyl complexes, nonmetal oxalyl derivatives such as the oxalyl halides (XOCCOX)[18] and dimethyl oxalate $(CH_3O_2CCO_2CH_3)$[19] exist in nonplanar as well as planar forms. Their existence in nonplanar forms indicates that there is relatively free rotation around the C–C bond and little double bonding between the two carbon atoms. The low barrier to rotation is also consistent with the normal single-bond distances ($\sim$1.53 Å)[18,19] observed in these compounds.

Reactions of Alkoxalyl Complexes. Unlike alkoxycarbonyl complexes which react with acids to form carbonyl complexes and alcohols,[20] the alkoxalyl complexes $MCl(COCO_2CH_3)[P(C_6H_5)_3]_2$, M = Pt or Pd, are stable to treatment with aqueous HBF_4 or Cl_3CCO_2H in $CHCl_3$.

Transesterification of the methoxalyl ligand occurs under mild conditions

$$PtCl(COCO_2CH_3)[P(C_6H_5)_3]_2 + C_2H_5OH \xrightarrow[\text{2 hr, } C_2H_5O^-]{\text{THF, 25°}}$$

$$PtCl(COCO_2C_2H_5)[P(C_6H_5)_3]_2 \qquad (7)$$
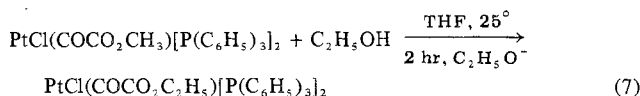
Since the starting complex is not soluble in ethanol, ester exchange does not occur in that solvent either with or without added $C_2H_5O^-$.

When Cl_2 is bubbled into a $CHCl_3$ solution of *trans*-$PtCl(COCO_2CH_3)[P(C_6H_5)_3]_2$, cleavage of the Pt–C bond occurs with formation of $ClCOCO_2CH_3$ as the only carbonyl-containing product

$$PtCl(COCO_2CH_3)[P(C_6H_5)_3]_2 + Cl_2 \xrightarrow[25°]{CHCl_3} PtCl_2[P(C_6H_5)_3]_2 +$$
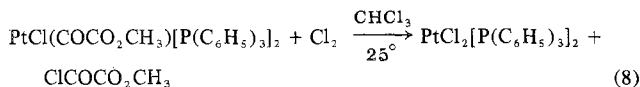
$$ClCOCO_2CH_3 \qquad (8)$$

Bright yellow *trans*-$PtCl_2[P(C_6H_5)_3]_2$ precipitates from solution and was identified by its far-infrared spectrum.[11] When the reaction is carried out using equimolar Cl_2 and $PtCl(COCO_2CH_3)[P(C_6H_5)_3]_2$, again $ClCOCO_2CH_3$ forms, but the complex precipitates as the *cis*-$PtCl_2[P(C_6H_5)_3]_2$. It is not clear why different isomers of $PtCl_2[P(C_6H_5)_3]_2$ are produced depending upon the amount of Cl_2 present.

When Cl_2 is bubbled into a solution of $PtCl(CO_2CH_3)[P(C_6H_5)_3]_2$ in $CHCl_3$, the colorless solution turns yellow but no precipitate forms. The infrared spectrum of this solution shows in addition to the $\nu(C=O)$ band for $ClCO_2CH_3$ at 1776 cm^{-1} bands at 1680 and 1720 cm^{-1}. This reaction is more complex than that of the methoxalyl compound, and the other products have not been identified.

The palladium(II)–alkoxalyl complexes rapidly undergo

decarbonylation to give the corresponding alkoxycarbonyl complexes when dissolved in either $CHCl_3$, CH_2Cl_2, or benzene at room temperature

$$PdCl(COCO_2R)L_2 \xrightarrow[\text{in soln}]{25°} PdCl(CO_2R)L_2 + CO \qquad (9)$$
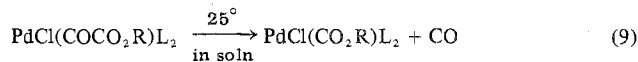
Bubbles of CO are released from the solutions, and infrared and proton nmr spectra indicate the formation of the alkoxycarbonyl complex as the only other product.

For $PdCl(COCO_2CH_3)[P(C_6H_5)_3]_2$ dissolved in $CHCl_3$ at 25°, the decarbonylation was approximately half complete after 10 min and complete after 20 min. When the original solution was cooled to -20°, virtually no decarbonylation occurred even after 2 days. The decarbonylation could also be greatly retarded by adding $P(C_6H_5)_3$ to the solutions. When 0.2 mol of $P(C_6H_5)_3$/mol of $PdCl(COCO_2CH_3)[P(C_6H_5)_3]_2$ was added to the $CHCl_3$ solution, only a small amount of decarbonylation had occurred after 10 hr, but it was complete after 2 days. However, when 2.0 mol of $P(C_6H_5)_3$/mol of complex were used, no decarbonylation was observed even after 2 days.

One might consider the decarbonylation to proceed *via* $-CO_2R$ migration from the oxalyl ligand to the Pd, followed by loss of the resulting CO ligand. Added $P(C_6H_5)_3$ could retard the decarbonylation by coordinating to the Pd of the starting complex, thereby preventing the $-CO_2R$ migration. This $P(C_6H_5)_3$ coordination appears, however, not to occur since the solution infrared spectrum of $PdCl(COCO_2CH_3)[P(C_6H_5)_3]_2$ was the same in the presence and absence of added $P(C_6H_5)_3$. An alternative decarbonylation mechanism is one that proceeds by initial $P(C_6H_5)_3$ dissociation from the complex, followed by $-CO_2R$ migration and CO evolution. In this case, added $P(C_6H_5)_3$ would suppress the initial phosphine dissociation and thereby retard the overall rate of decarbonylation. This appears to be the more likely mechanism.

In contrast to the palladium complexes, their platinum analogs were stable in solution at 25°. For $PtCl(COCO_2CH_3)[P(C_6H_5)_3]_2$ in $CHCl_3$ at 25°, no decarbonylation was observed after several weeks. At 50°, no decarbonylation occurred after several hours. However, in refluxing benzene (80°), decarbonylation was complete in 2 hr. When the solid was heated under vacuum to 175°, about 75% of the starting material decarbonylated to give $PtCl(CO_2CH_3)[P(C_6H_5)_3]_2$ after 30 hr. At temperatures above 200°, the complexes melted to give clear yellow liquids with evolution of a gas (presumably CO).

Several attempts were made to prepare the alkoxalyl complexes *via* the insertion of CO into the M–C bond of alkoxycarbonyl complexes (eq 3). While there was no evidence for such a reaction with $PdCl(COCO_2CH_3)[P(C_6H_5)_3]_2$ under a variety of conditions, the analogous $P(C_2H_5)_3$ complex did appear to undergo the reaction

$$PdCl(CO_2CH_3)[P(C_2H_5)_3]_2 + CO \rightarrow$$

$$PdCl(COCO_2CH_3)[P(C_2H_5)_3]_2 \qquad (10)$$
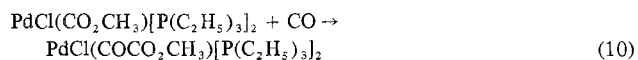
In one run, the occurrence of an absorption at 1720 cm^{-1} in the spectrum of the reaction mixture of $PdCl(CO_2CH_3)[P(C_2H_5)_3]_2$ with CO (17 atm) in pentane solvent at 25° for 21 hr indicated the formation of the alkoxalyl complex. Decarbonylation (eq 9) of the methoxalyl product was prevented by adding $P(C_2H_5)_3$ to the completed reaction solution while it was still under CO pressure. Unfortunately formation of the alkoxalyl complex under these conditions was not reproducible. It appears that trace quantities of an unknown catalyst in the starting alkoxycarbonyl complex may have promoted the reaction.

Registry No. $PtCl(COCO_2Me)(PPh_3)_2$, 50589-30-5; $PtCl(COCO_2Et)(PPh_3)_2$, 50589-31-6; $PtCl(COCO_2Me)(PMePh_2)_2$,

53042-43-6; PdCl(CO2Me)(PPh3)2, 50763-37-6; PdCl-(COCO2Me)(PPh3)2, 50589-28-1; PdCl(COCO2Et)(PPh3)2, 50589-29-2; PdCl(COCO2Me)(PMePh2)2, 53042-37-8; PdCl-(CO2Me)(PEt3)2, 53042-41-4; PdCl(COCO2Me)(PEt3)2, 53042-42-5; PtCl(CO2Me)(PPh3)2, 20524-02-1; Pd(PPh3)4, 14221-01-3; Pt-(PPh3)4, 14221-02-4; *trans*-PdCl2(PPh3)2, 28966-81-6; *trans*-PdCl2(PEt3)2, 15642-19-0; Pt(PMePh2)4, 27121-53-5; Pd(PMePh2)4, 24981-80-4; Pd(PEt3)4, 52230-29-2; ClCO2Me, 79-22-1; ClCOCO2Me, 5781-53-3; ClCOCO2Et, 4755-77-5.

References and Notes

(1) M. Graziani, P. Uguagliati, and G. Carturan, *J. Organometal. Chem.*, **27**, 275 (1971).
(2) P. Fitton, M. P. Johnson, and J. E. McKeon, *Chem. Commun.*, 6 (1968).
(3) W. Beck and K. V. Werner, *Chem. Ber.*, **104**, 2901 (1971); K. V. Werner and W. Beck, *ibid.*, **105**, 3947 (1972).
(4) M. Hidai, M. Kokura, and Y. Uchida, *J. Organometal. Chem.*, **52**, 431 (1973).
(5) D. M. Fenton and P. J. Steinwand, *J. Org. Chem.*, **39**, 701 (1974).

(6) L. Malatesta and C. Cariello, *J. Chem. Soc.*, 2323 (1958).
(7) A. J. Mukhedkar, M. Green, and F. G. A. Stone, *J. Chem. Soc. A*, 3023 (1969).
(8) B. L. Shaw, *Proc. Chem. Soc., London*, 247 (1960).
(9) H. C. Clark, K. R. Dixon, and W. J. Jacobs, *J. Amer. Chem. Soc.*, **91**, 1346 (1969).
(10) C. D. Cook and G. S. Jauhal, *Can. J. Chem.*, **45**, 301 (1967).
(11) P. Haake and S. H. Mastin, *J. Amer. Chem. Soc.*, **93**, 6823 (1971).
(12) W. Beck, M. Bauder, G. La Monnica, S. Cenini, and R. Ugo, *J. Chem. Soc. A*, 113 (1971).
(13) D. M. Barlex and R. D. W. Kemmitt, *J. Chem. Soc., Dalton Trans.*, 1436 (1972).
(14) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 5075 (1962).
(15) J. Fayos, E. Dobrzynski, R. J. Angelici, and J. Clardy, *J. Organometal. Chem.*, **59**, C33 (1973).
(16) J. M. Jenkins and B. L. Shaw, *J. Chem. Soc. A*, 770 (1966).
(17) C. R. Green and R. J. Angelici, *Inorg. Chem.*, **11**, 2095 (1972).
(18) K. Hagen and K. Hedberg, *J. Amer. Chem. Soc.*, **95**, 4796 (1973).
(19) J. K. Wilmshurst and J. F. Horwood, *J. Mol. Spectrosc.*, **21**, 48 (1966); H. J. Maria and S. P. McGlynn, *ibid.*, **42**, 177 (1972).
(20) R. J. Angelici, *Accounts Chem. Res.*, **5**, 335 (1972).

Infrared Spectra and Bonding of Metal Complexes of Platinum–Carbon Bonded Acetylacetone Complexes

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Infrared spectra of K[PtCl(acac)2] and its metal complexes M[PtCl(acac)2]$_n$ (M = (VO)^{II}, Co(II), Ni(II), Cu(II), Zn(II), Pd(II) for $n = 2$; M = Fe(III) for $n = 3$) and NiBr2(acacH)2 have been measured and assigned. The metal isotope technique has been utilized to assign the M–O(keto-acac) stretching bands. Comparisons of infrared spectra between Ni[PtCl(acac)2]2, [PtCl(acac)2]$^-$, and NiBr2(acacH)2 reveal that the C=O groups of Ni[PtCl(acac)2]2 retain the keto character even after coordination to the Ni atom and that its Ni–O(keto-acac) bonds are much weaker than those of enol-acac complexes. Similar results have been obtained for other metal complexes.

Introduction

The versatility of acetylacetone (acacH) as a coordinating ligand is well recognized.[1-3] An extensive infrared study has been made on the O-bonded enol-acac complexes (structure I) which are most common among many acetylacetonato


I
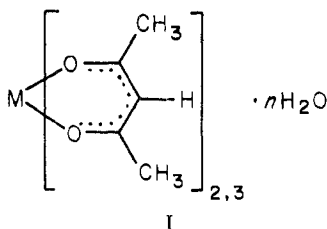
complexes.[4] The C-bonded acetylacetonato complex, K-[PtCl(acac)2], was first prepared by Werner.[5] However, its structure and bonding were not known until X-ray analysis[6] revealed the structure II which contains one O-bonded enol-

II
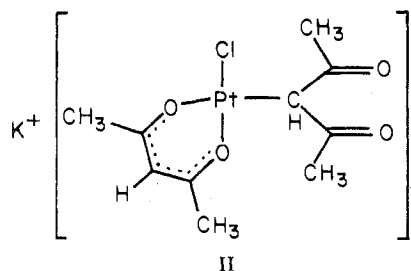
and one C-bonded keto-acac group. We have previously

studied the infrared spectra of this and other C-bonded acac complexes.[7,8]

Lewis and Oldham[9] have shown that the above complex anion (structure II) can form neutral complexes of the type (structure III) with a number of divalent metals including the

III
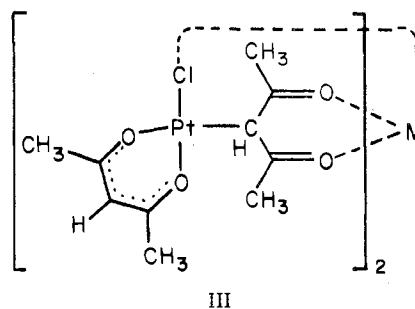
VO^{2+} and UO2^{2+} ions. They studied the infrared spectra, electronic spectra, and magnetic susceptibility of these complexes and concluded that the majority of them take a six-coordinate octahedral structure in which two chlorine atoms occupy the fifth and sixth positions of the coordination sphere of the metal (M) and that one of the acac groups in [PtCl-(acac)2]$^-$ coordinates to the metal in the keto form.

In order to obtain more information about the nature of bonding between the metal and the C-bonded acac anion (structure II), we have carried out detailed vibrational analyses on a series of metal complexes of structure III. This paper reports the infrared spectra of M[PtCl(acac)2]2 where M is Co(II), Ni(II), Cu(II), Zn(II), Pd(II), and (VO)^{II}, and Fe[PtCl(acac)2]3. We have shown previously[10] that the